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CHAPTER I.

INTRODUCTION.

The Natural Sciences. Before we advance very far in the study of nature, it becomes evident that the one large study must be divided into a number of more limited ones for the convenience of the investigator as well as of the student. These more limited studies are called the Natural Sciences.

Since these divisions are made for mere convenience, and not because there is any division in nature itself, it often happens that the different sciences are very intimately related, and a thorough knowledge of any one of them involves a considerable acquaintance with several others. Thus the botanist must know something about animals as well as about plants; the student of human physiology must know something about physics, as well as about zoology and anatomy.

Mineralogy, Physics and Chemistry. Mineralogy, physics and chemistry form a group of sciences related in this close way, and it is not an easy matter to make an exact definition of any one of them. In a general way, however, it may be said that mineralogy deals with the composition and properties of the various substances which compose the earth's crust and with their distribution in nature. Chemistry and physics have for their object the study of the laws which govern the composition of all substances, the properties of substances and the changes which they can be made to undergo.

Two Kinds of Changes in Matter. An examination of these changes shows that they can all be classified under two heads: those in which no new kind of matter is formed, and those which result in the formation of new substances with new properties. The former are called physical changes, the latter chemical changes.

1. *Physical Changes.* When a stick is broken, the pieces do not differ from the original stick save in size; the position of substances often changes, as when the leaves fall or trees are blown down; a piece of iron may be magnetized; substances may be changed from cold to hot as the iron heated by the blacksmith in his forge, or the filament of the incandescent lamp heated by the electrical current. In none of these changes is a new substance formed having a composition different from the substance undergoing the change. Such changes are called physical changes.

2. *Chemical Changes.* In many other cases the substances undergoing change lose their characteristic properties and are converted into new substances. When a piece of coal or a stick of wood burns, it disappears as such, and in its place we have ashes and invisible gases. Gunpowder, when ignited, explodes, and nothing but smoke and gases are found in its place. Sweet fruit juices ferment, and are changed into sour vinegar. Such changes are evidently quite different from the physical changes just mentioned. New substances are formed in place of the ones undergoing change. These changes are called chemical changes.

Changes in Physical State. It is not always easy to tell to which class a given change belongs, and many will require careful thought on the part of the student. One class of changes should be noted with especial care, since it is likely to prove misleading. It is a familiar fact that when water is cooled sufficiently it changes to ice; when heated to the boiling point it changes to steam. Here we have three different substances, water, ice and steam, one a liquid, one a solid and one a gas, the properties of which differ widely. Apparently these are chemical changes. A careful study, however, shows that the composition of the three is just the same: they are all composed of the same substances, and in the same proportion. Many other solids can be melted into liquids without undergoing change in composition. Familiar instances are the melting of butter, wax and metals. The change of liquids into vapors is quite as common, but not so often noticed. In general almost any substance can exist in the three conditions, solid, liquid and gas, and we speak of them as the three physical states of matter.

Chemical and Physical Properties. Many properties of a substance can be noted without causing the substance to undergo chemical change. Among these are its color, odor, taste, size, shape, weight, physical state. These are called its physical properties. Other properties are only discovered when the substance undergoes chemical change. These are called its chemical properties. Thus we find that coal burns in air, gunpowder explodes when fired, milk sours when exposed to air.

Two Factors in all Changes. In all the changes which matter can undergo, whether physical or chemical, two factors must be taken into account viz. energy and matter.

1. *Energy.* It is a familiar fact that certain bodies have the power to do work. Thus water falling from a height upon a water wheel turns the wheel and in this way does the work of the mills. Magnetized iron attracts iron to itself and the motion of the iron as it moves towards the magnet can be turned into work. Coal on burning causes the engine to move and transports the loaded cars from place to place. When a body has this power to do work it is said to possess energy.

Law of Conservation of Energy. Careful experiments have shown that when one body parts with its energy, the energy is not destroyed but is transferred to another body or system of bodies. Just as energy can not be destroyed, neither can it be created. If a body gains a certain amount of energy, some other body has lost an equivalent amount. These facts are summed up in the law of conservation of energy which states that *energy can neither be created nor destroyed, the amount of it in the universe being constant.*

Transformations of Energy. Although energy can neither be created nor destroyed, it is evident that it may assume many different forms. Thus the falling water may turn the electric generator and generate a current of electricity. The energy lost by the falling water is thus transformed into the energy of the electric current. This in turn may be changed into the energy of motion, as when the current is utilized for propelling the cars, or into the energy of heat and light, as when it is used for heating and lighting the cars. Again the energy of coal may be converted into energy of motion as when it is used as a fuel in steam engines.

Since the energy possessed by coal only becomes available when the coal is made to undergo a chemical change, it is sometimes called chemical energy. It is this form of energy with which we are especially interested in the study of chemistry.

2. *Matter.* At first sight there appears to be no limit to the kinds of matter of which the world is made. But it has been found that all these varieties may be divided into three classes, viz., mechanical mixtures, chemical compounds and elements. These will now be briefly discussed.

a. Mechanical Mixtures. If equal bulks of common salt and iron filings are thoroughly mixed together, a product is obtained, which, judging by its appearance, is a new substance. If it is examined more closely however, it will be seen to be merely a mixture of the salt and iron, each of which substances retains its own peculiar properties. The mixture tastes just like salt; the iron particles can be seen, and their gritty character detected. A magnet rubbed in the mixture draws out the iron just as if the salt were not there. The salt also can be separated from the iron quite easily. If several grams of the substance is placed in a test tube, and the tube half filled with water and thoroughly shaken, the salt disappears, or *dissolves* in the water. The iron particles can then be filtered from the liquid by pouring the entire mass upon a piece of filter paper folded so as to fit into the interior of a funnel (Fig. 1). The paper retains the solid but allows the clear liquid to drain through. The iron particles so obtained will be found to be identical with the original iron. The iron has undergone no change. The water of the salt solution can be removed by evaporation. To accomplish this, the solution is poured into a small evaporating dish and gently heated (Fig. 2) until the water has all disappeared, or *evaporated*. The salt is left in the dish and on comparing it with the original salt, it is found to be identical with it. No new substance has been formed by mixing the salt and iron, and the mixture is called a mechanical mixture.

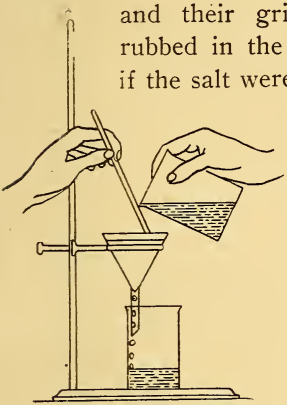


Fig. 1

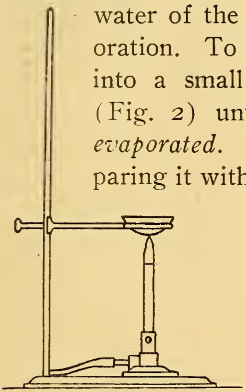


Fig. 2

Such mixtures are very common in nature. Thus in a piece of coarse grained granite, three quite different substances can be seen and picked out. Gold and sand is a mechanical mixture, for the miner separates them by merely shaking the mixture in a pan, allowing running water to wash away the lighter sand, while the heavier gold sinks to the bottom of the pan. Evidently the composition of such a mixture may vary greatly, and no two mixtures are likely to have the same composition. The ingredients of a mechanical mixture can often, though not always, be separated by mechanical means, such as sifting, sorting, magnetic attraction, or by dissolving one constituent and leaving the other undissolved.

b. Chemical Compounds. If iron filings and powdered sulphur are thoroughly ground together in a mortar, a yellowish green substance results. It might easily be taken to be a new compound; but as in the case of the iron and salt, the ingredients can be readily separated. A magnet draws out the iron. Water does not dissolve the sulphur, but other liquids do, as for instance the liquid called carbon disulphide. When treated with carbon disulphide, the iron is left unchanged, and the sulphur can be obtained again, after filtering off the iron, by evaporating the liquid. The substance is therefore a mechanical mixture. If now a new portion of the mixture is placed in a dry test tube and carefully heated in the flame of the Bunsen burner, as shown in Fig. 3, a striking change takes place. The mixture begins to glow at some point, the glow rapidly extending through the whole mass. If the test tube is broken and the product examined, it will be found to be a hard, black, brittle substance, in no way recalling the iron or the sulphur. The magnet no longer attracts it; carbon disulphide will not dissolve sulphur from it. It is a new sub-

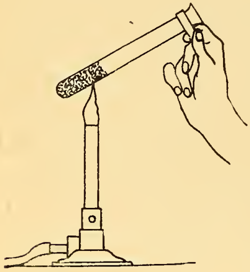


Fig. 3

stance with new properties, resulting from the chemical union of iron and sulphur.

Again if a small quantity of red oxide of mercury is heated in a hard glass test tube, it will be noticed that a bright silvery mirror gradually forms on the walls of the tube a little above the oxide. A glowing spark on a splint of wood, held at the mouth of the tube, bursts into flame, showing that a new, gaseous substance is being produced in the tube. On cooling the tube, the substance forming the silvery mirror does not change back again into the red oxide of mercury. It is a permanent new substance. By heating the red oxide, then, two new substances have been produced: the metallic substance forming the silvery mirror, and the gas which caused the spark to burst into flame.

When a substance contains two or more kinds of matter, which are united chemically and cannot be separated by mechanical means, we say that it is a chemical compound. Thus the iron and the sulphur formed a chemical compound when they were heated together; the red oxide of mercury is a chemical compound, because by chemical decomposition two very different substances can be obtained from it. We shall see later that a chemical compound differs markedly from a mechanical mixture, in that its composition is always exactly the same.

Chemical Affinity the Cause of Chemical Combination. The agency which causes substances to combine, and which holds them together when combined, is called chemical affinity. Yet the experiments just described show that heat is often necessary to bring about chemical action, and that it can also decompose some chemical compounds. The distinction between the cause producing chemical action, and the circumstances favoring it must be clearly made. Chemical affinity is always the cause of chemical union. Many agencies may make it possible for chemical affinity to act by overcoming circumstances which stand in its way. Among these agencies are heat, electricity, and sometimes light. As a rule, solution also promotes action between two substances. Sometimes these agencies may overcome chemical attraction, and so occasion decomposition of a compound, as in the case of the decomposition of the red oxide of mercury by heat.

c. Elements. It has been seen that strong heating of red oxide of mercury leads to the formation of two new substances. The question arises do these substances likewise contain other substances; that is are they also chemical compounds? All efforts have failed to get anything else from them but the metallic substance and the gas. Such substances are called elements. An element then is a substance from which no other substance can be obtained by any known means. It is not always easy to be certain that a given substance is really an element. Some way, as yet untried, may be successful in decomposing it into other simpler forms of matter, and the supposed element will then prove to be a compound. Water, lime and many other familiar compounds were at one time thought to be elements.

Alchemy. In olden times it was thought that some way could be found to change one element into another, and a great many efforts were made to accomplish this transformation. Most of these efforts were directed toward changing the commoner metals into gold, and many fanciful ways for doing this were described. The chemists of that time were called Alchemists, and the art which they practiced was called Alchemy. The Alchemists gradually became convinced that the only way common metals could be changed into gold was by the wonderful power of a magic substance which they called the Philosopher's Stone, which would accomplish this transformation by its mere touch, and would in addition give perpetual youth to its fortunate possessor. No one has ever found such a stone, and no one has succeeded in changing one metal into another.

Number of Elements. The number of substances now considered to be elements is not large — about eighty in all. Many of these are rare and very few of them make any large fraction of the materials in the earth's crust. Clark gives the following estimate of the composition of the earth's crust:

Oxygen	47.0%	Calcium	3.5%
Silicon	27.9%	Magnesium	2.5%
Aluminium	8.1%	Sodium	2.7%
Iron	4.7%	Potassium	2.4%
		Other elements	1.2%

It is not necessary to study more than a third of the total number of elements to gain a very good knowledge of chemistry.

Physical State of the Elements. About ten of the elements are gases at ordinary temperatures. Two — mercury and bromine — are liquids. The others are all solids, though their melting points vary through wide limits, from caesium which melts at 26° to elements which do not melt save in the intense heat of the electric furnace.

Occurrence of the Elements. Comparatively few of the elements occur as uncombined substances in nature, most of them being found in the form of chemical compounds. When an element does occur by itself, such as gold, we say that it occurs in the free state or native; when it is combined with other substances in the form of compounds, we say that it occurs in the combined state, or in combination. In the latter case there is usually little about the compound to suggest that the element is present in it; for we have seen that elements lose their own peculiar properties when they enter into combination with other elements.

It would never be suspected that the red oxide of mercury contains a bright silvery metal, or that the reddish, earthy looking iron ore contains iron.

Names of Elements. The names given to the elements have been selected in a great many different ways. Some are very old and their original meaning is obscure. Such names are iron, gold, copper. Many indicate some striking physical property of the element. The name bromine is derived from a Greek word meaning a stench, referring to the extremely unpleasant odor of the substance. The name iodine comes from a word meaning violet, alluding to the beautiful violet color of iodine vapor. Some names indicate prominent chemical properties of the elements. Nitrogen means the producer of nitre, nitrogen being a constituent of nitre or saltpetre. Hydrogen means the producer of water, since the element forms water when burned. Others are named from mythology, as tantalum; or from countries or localities, as germanium, and columbium.

Symbols. In indicating the elements found in compounds it is inconvenient to use such long names; hence chemists have adopted a system of abbreviations. Sometimes the initial letter of the name will suffice to indicate the element. Thus I stands for iodine, C for carbon. Usually it is necessary to add some other characteristic letter of the name. since several names may begin with the same letter. Thus C stands for carbon, Cl for chlorine, Cd for cadmium, Ce for cerium, Cb for columbium. Sometimes the symbol is an abbreviation of the old Latin name. In this way Fe (ferrum) indicates iron, Cu (cuprum) copper, Au (aurum) gold. These abbreviations are called symbols. They will become familiar through constant use.

Law of Conservation of Matter. It has been seen that matter often changes much in appearance; elements unite to form compounds which can be decomposed again into elements. In all such transformations it has been found that the amount of matter, or its mass, does not change at all. No matter is ever lost or created in these changes. This important truth is called the law of conservation of matter. The total amount of matter and of energy in the universe thus remains constant, though the form of each may suffer many changes.

CHAPTER II.

OXYGEN.

History. The discovery of oxygen is generally attributed to the English chemist Priestley, who in 1774, obtained it by heating a compound of mercury and oxygen known as mercuric oxide, the oxygen being expelled by the heat. It is probable however that the Swedish chemist Scheele had previously obtained it although an account of his experiments was not published until 1775. The name oxygen signifies "to make acid." It was given to the element by the French chemist Lavoisier, since he believed that all acids owe their characteristic properties to its presence — a view which we now know to be incorrect.

Occurrence. Oxygen is by far the most abundant of all the elements. It occurs both in the free and in the combined state. 100 volumes of air contain about 21 volumes of free oxygen. In the combined states it forms eight-ninths of water and nearly one-half of the rocks composing the earth's crust. It is also an important constituent of the compounds which compose plant and animal tissues.

Preparation. Although oxygen occurs in the free state in the atmosphere, its separation from the nitrogen and other gases with which it is mixed is such a difficult matter that in the laboratory it has been found more convenient to prepare it from its compounds. The most important of the laboratory methods are the following:

1. *Preparation from Water.* Water is a compound containing 11.18% of hydrogen and 88.82% of oxygen. It is easily separated into these constituents by passing a current of electricity through it under suitable conditions. The process will be described in the chapter on water.

While this method of preparation is a simple one, it is not economical, on account of the cost of the electric current.

2. *Preparation from Mercuric Oxide.* This method is of interest since it is the one which led to the discovery of oxygen. The oxide is placed in a small glass test tube and heated. The compound is thereby decomposed into mercury which collects on the sides of the glass tube forming a silvery mirror, and oxygen which, being a gas, escapes from the tube. The presence of the oxygen is shown by lighting the end of a splint, extinguishing the flame and bringing the glowing coal into the mouth of the tube. The oxygen causes the glowing coal to burst into a flame.

In a similar way, oxygen may be obtained from its compounds with some of the other elements. Thus manganese dioxide, a black compound of manganese and oxygen, when heated to a high temperature, loses one-third of its oxygen, while barium dioxide, on heating, loses one-half of its oxygen.

3. *Preparation from Potassium Chlorate.* This is the method usually employed in the laboratory. Potassium chlorate is a white solid composed of 31.9% potassium, 28.9% chlorine and 39.1% oxygen. When heated it undergoes a series of changes in which the oxygen is finally all set free, leaving a compound of potassium and chlorine called potassium chloride. The change may be represented as follows:

$$\underset{\text{(potassium chlorate)}}{\left\{\begin{array}{l}\text{potassium}\\ \text{chlorine}\\ \text{oxygen}\end{array}\right.} = \underset{\text{(potassium chloride)}}{\left\{\begin{array}{l}\text{potassium}\\ \text{chlorine}\end{array}\right.} + \text{oxygen}$$

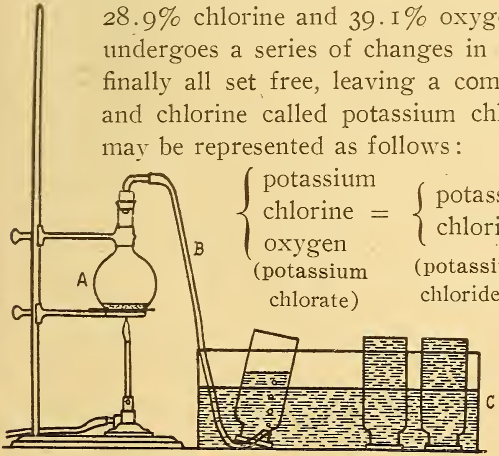


Fig. 4

The evolution of the oxygen begins at about 400°. It has been found however that if the potassium chlorate is mixed with about one-fourth its weight of manganese dioxide, the oxygen is given off at a much lower temperature. Just how the manganese dioxide brings about this result is not definitely known. The amount of oxygen obtained from a given weight of potassium chlorate is exactly the same whether the manganese dioxide is present or not. So far as can be detected the manganese dioxide undergoes no change.

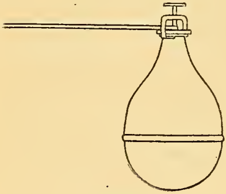


Fig. 5

The manner of preparing oxygen by this process is illustrated in the accompanying diagram (Fig. 4). A mixture composed of 1 part of manganese dioxide and 4 parts of potassium chlorate is placed in the flask A and gently heated. The oxygen is evolved and escapes through the tube B. It is collected by bringing over the end of the tube, the mouth of a bottle completely filled with water and inverted in a vessel of water as shown in the figure. The gas rises in the bottle and displaces the water.

In the preparation of large quantities of oxygen, a copper retort, (Fig. 5) is often substituted for the glass flask.

This method of collecting oxygen illustrates the general method used for collecting such gases as are insoluble in water or nearly so. The vessel C, (Fig. 4), containing the water in which the bottles are inverted, is called a "pneumatic trough."

4. **Commercial Methods of Preparation.** Oxygen can now be purchased stored under great pressure in strong steel cylinders. This is prepared either by heating a mixture of potassium chlorate and manganese dioxide or by separating it from the nitrogen and other gases with which it is mixed in the atmosphere. Different methods have been employed for accomplishing this separation. The most important of these at the present time consists in liquifying the air by subjecting it to intense cold and great pressure. When the pressure is removed, the liquid nitrogen present evaporates first, leaving the liquid oxygen. As this evaporates the gas is pumped under high pressure into a strong steel cylinder

Fig. 6

(Fig. 6) provided with a screw valve, so that the oxygen may be drawn off at will. Oxygen so prepared is never entirely free from nitrogen, often containing as much as 15 to 20% of it.

Physical Properties. Oxygen is a colorless, odorless, tasteless gas, slightly heavier than air. One liter of it weighs 1.428 grams, at a temperature of 0° and under a pressure of one atmosphere (1033 grams per square centimeter), while under similar conditions one liter of air weighs 1.292 grams. It is but slightly soluble in water. As in the case of other gases, oxygen may be liquefied by applying very great pressure to the highly cooled gas. When the pressure is removed, the liquid oxygen rapidly boils, passing again into the gaseous state, since its boiling point under ordinary pressure is — 181.4°.

Chemical Properties. At ordinary temperatures oxygen is not very active chemically. Most substances are either not affected by it at all, or the action is so slow as to escape notice. At higher temperatures however it is very active, forming compounds with all of the common elements except fluorine and bromine. This activity may be shown by heating various substances until just ignited and then bringing them into vessels of the gas, when they will burn with great brilliancy. Thus, as previously stated, a glowing splint if introduced into a jar of oxygen bursts into flame. Sulphur burns in the air giving a feeble light only; in oxygen however the flame is increased in size and brightness. Substances like phosphorus which readily burn in air, burn in oxygen with dazzling brilliancy. Even substances like iron which burn in air with great difficulty, readily burn in oxygen.

The burning of a substance in oxygen is due to the rapid combination of the substance or of the elements composing it with the oxygen. Thus when sulphur burns both the oxygen and sulphur disappear as such and there is formed a compound of the two which is an invisible gas, having the characteristic odor of burning sulphur. Similarly phosphorus on burning forms a white solid compound of phosphorus and oxygen, while iron forms a reddish black compound of iron and oxygen.

Oxidation. The term oxidation is applied to the chemical change which takes place when a substance combines with oxygen. This process may take place rapidly as in the burning of phosphorus, or slowly as in the oxidation (or rusting) of iron when exposed to the air. It is always accompanied by the liberation of heat. The amount of heat liberated by the oxidation of a definite weight of any given substance is always the same, being entirely independent of the rapidity of the process. If the oxidation takes place slowly, the heat is generated slowly so that it is difficult to detect it. If the oxidation takes place rapidly however, the heat is generated in such a short interval of time that the substance may become white hot and even burst into a flame.

Combustion. Kindling Temperature. When oxidation takes place so rapidly that the heat generated is sufficient to cause the substance to glow or burst into a flame the process is called combustion. In order that any substance may undergo combustion it is necessary that it should be heated to a certain temperature known as the kindling temperature. This temperature varies widely for different bodies but is always definite for the same body. Thus the kindling temperature of phosphorus is far lower than that of iron but is definite for each. When any portion of a substance is heated until it begins to burn, the combustion will continue without the further application of heat provided the heat generated by the process is sufficient to bring other parts of the substance to the kindling temperature. On the other hand if the heat generated is not sufficient to maintain the kindling temperature combustion ceases.

Oxides. The compounds formed by the oxidation of any element belong to the class of compounds called *oxides.* Thus in the combustion of sulphur, phosphorus and iron, the compounds formed are called respectively oxide of sulphur, oxide of phosphorus and oxide of iron. In general then an oxide is a compound of oxygen with another element. A great many of these are known; in fact the oxides of all the common elements have been prepared with the exception of those of fluorine and bromine. Some of these are familiar compounds. Water for example is an oxide of hydrogen.

Products of Combustion. The particular oxides formed by the combustion of any substance are called the products of combustion of that substance. Thus oxide of sulphur is the product of the combustion of sulphur; oxide of iron is the product of the combustion of iron. It is evident that the products of the combustion of any substance must weight more than the original substance, the increase in weight corresponding to the amount of oxygen combined. For example, when iron burns the oxide of iron formed weighs more than the iron which has undergone combustion. In some cases the products of combustion are invisible gases, so that the substance undergoing combustion is apparently destroyed. Thus when a candle burns, it is consumed and so far as the eye can judge, nothing is formed during combustion. That invisible gases are formed however, and that the weight of these is greater than the weight of the candle may be shown by the following experiment.

Two lamp chimneys are filled with the same amounts of the compound known as sodium hydroxide (caustic soda), and suspended from the beams of the balance as shown in Fig. 7. A piece of candle is placed on one of the balance pans so that the wick comes just below the chimney, and the balance is brought to a level by adding weights to the other pan. The candle is then lighted. The products formed pass up through the chimney and are absorbed by the sodium hydroxide. Although the candle burns away, the pan upon which it rests slowly sinks, showing that the combustion is attended by an increase in weight.

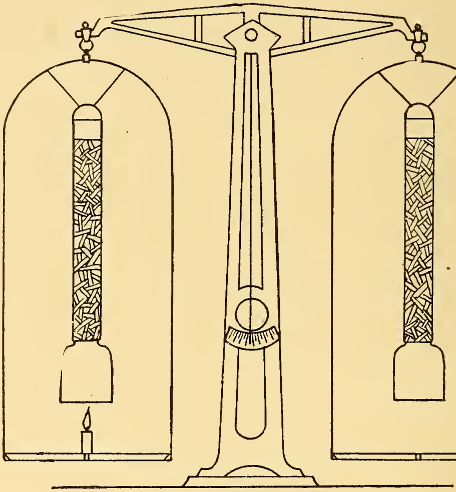


Fig. 7

Combustion in Air and in Oxygen. Combustion in air and in oxygen differ only in rapidity, the products formed being exactly the same. That the process should take place less rapidly in the former is readily understood, for the air is only about one-fifth oxygen, the remaining four-fifths being inert gases. Not only is less oxygen available therefore, but much of the heat is dissipated in raising the temperature of the inert gases surrounding the substance undergoing combustion.

Combustion in the Broad Sense. According to the definition given above the presence of oxygen is necessary for combustion. The term is sometimes used however in a broader sense to designate any chemical change attended by the evolution of heat and light. Thus iron and sulphur, or hydrogen and chlorine under certain conditions will combine so rapidly that light is evolved. Whenever combustion takes place in the air however, the process is one of oxidation.

Spontaneous Combustion. Some substances like phosphorus combine rapidly with oxygen even at ordinary temperatures. The heat generated by the process increases the rapidity of oxidation which in turn increases the amount of heat liberated so that the kindling temperature is soon reached and the substance bursts into a flame. This is an example of spontaneous combustion. Certain kinds of oils readily combine with oxygen at ordinary temperatures and not infrequently fires are traced to the presence of oily rags. Barns have been set on fire by the rapid oxidation of hay contained in them, while even heaps of coal have been known to undergo spontaneous combustion.

The French chemist, Lavoisier (1743-1794), who gave to oxygen its name, was the first to show that combustion is due to union with oxygen. Previous to this, combustion was supposed to be due to the presence of a substance called phlogiston. One substance was thought to be more combustible than another because it contained more phlogiston. When a substance burned, the phlogiston was supposed to escape. In accordance with this view, a substance on burning ought to lose in weight. As has been shown, however, the opposite is true.

Importance of Oxygen. Oxygen plays a very important part in the processes of nature. Its presence in the air is essential to all forms of life except certain minute forms of plant life. In respiration the air is taken into our lungs where a certain amount of the oxygen is absorbed by the blood. It is thus conveyed to all parts of the body where it combines with the worn-out tissue, oxidizing it into compounds which may readily be eliminated from the body. The heat generated by the oxidation is the source of the heat of the body. It was formerly thought that animals could not live in pure oxygen, on account of its great activity. Recent experiments seem to show however that this view is erroneous since the blood is capable of absorbing only a definite amount of oxygen; hence any excess present in the lungs is without effect.

The process of decay is also essentially one of oxidation. It will only take place however in the presence of certain minute forms of life known as bacteria. Just how these assist in the oxidation is not known. By this process the debris which collects on the surface of the earth such as leaves and dead forms of animal life are slowly oxidized and changed into harmless products. Thus oxygen acts as a great purifying agent.

Attention has been called to the fact that water dissolves a small amount of oxygen. All waters that come in contact with the air take up a certain amount of oxygen and this amount although small is essential to all forms of aquatic life. Moreover the oxygen dissolved in water tends to purify it by oxidizing the impurities nearly always present in natural waters.

Oxygen finds an important application in medicine in the treatment of such diseases as asthma where the patient is unable to inhale air sufficient to supply the necessary amount of oxygen.

OZONE.

When electric sparks are passed through oxygen it undergoes a remarkable change, being converted into a new substance called ozone. Ozone differs noticeably from oxygen in possessing a characteristic odor, which is often perceived near electric machines. It also has different chemical properties, being much more active than oxygen. For example, oxygen has no action upon a silver coin, while ozone quickly colors it brown.

Preparation. A convenient form of apparatus for the preparation of ozone in the laboratory is shown in Fig. 8. Two glass tubes are joined in the manner indicated and one surface of each coated with tin foil in such a manner that an electric discharge may be made to pass from one to the other by an electric machine or coil. A slow current of oxygen is admitted at A, and passing between the two tubes, is subjected to the action of the electric discharge until it escapes at B. Only a small amount of the oxygen is changed into ozone by this treatment. The pure ozone may be obtained by cooling the mixture of oxygen and ozone escaping at B by means of liquid oxygen. Ozone being much more easily liquified than oxygen is thus changed to the liquid state, and by its evaporation the pure gas is obtained. Ozone is also formed in certain chemical processes. Thus if some pieces of phosphorus are placed in a bottle and partially covered with water, the presence of ozone may soon be detected in the air contained in the bottle.

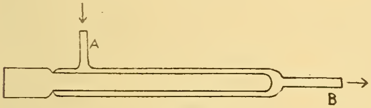


Fig. 8

The Composition of Ozone. In the conversion of oxygen into ozone, it is possible to show by experiment that three volumes of oxygen form two volumes of ozone. The change moreover is a reversible one, the two volumes of ozone by heating being changed back into the three volumes of oxygen. In changing oxygen into ozone no other substance is added to it and of course none is removed, since it is an element. How then can we account for this change in properties? It can be shown that in the conversion of a given amount of oxygen into ozone a definite amount of heat is absorbed; moreover, if the ozone formed is converted again into oxygen, exactly the same amount of heat is liberated. Oxygen differs from ozone therefore in its energy content, that of the ozone being greater, as indicated by the fact that more heat can be obtained from a given weight of it than from an equal weight of oxygen. The significance of this fact will be discussed in a later chapter. It is simply necessary here to note the fact that oxygen as well as a number of other elements exist in different forms or states, and that the conversion of the one state into another is always attended by the absorption or generation of heat. Such states are called allotropic states. Thus ozone is said to be an allotropic state of oxygen.

Properties. Pure ozone is a gas having a bluish tint and characteristic odor. Its chemical properties are similar to those of oxygen, except that it is far more active. The pure gas is very explosive, breaking down into oxygen with the liberation of a large amount of heat. On account of its activity it is now prepared commercially and used in place of oxygen in a number of manufacturing processes. It is possible that traces of it may exist in the atmosphere, although its presence there has not been definitely established, the tests formerly used for its detection having been proved to be unreliable.

Measurement of Gas Volumes.

It is a well known fact that the volume of a gas is not constant, but varies with the temperature of the gas and the pressure to which it is subjected. It follows, therefore, that the weight of any definite volume of gas, say one liter, varies with the conditions of temperature and pressure. It has been agreed that the figures given to represent the weight of a definite volume of any gas shall be its weight when the temperature of a gas is 0° and when it is under a pressure equal to that exerted by the atmosphere at the sea level, viz: 1033 grams per square centimeter. These conditions of temperature and pressure are known as the standard conditions, and when the weight or volume of a gas is given, it is understood that the measurement was made under these conditions unless it is otherwise stated. Thus the weight of a liter of oxygen has been given as 1.428 grams, i. e., one liter at a temperature of 0° and under a pressure of one atmosphere, weighs 1.428 grams.

Since the conditions of temperature and pressure under which gases are measured in the laboratory are different from the standard conditions, it becomes necessary to be able to reduce the volume which a gas occupies under any given conditions of temperature and pressure to the volume it will occupy under standard conditions. This may be done in accordance with the following laws.

1. **Variations in the Volume of a Gas Due to Change of Temperature.** Law of Dalton and Gay Lussac. Increasing the temperature of a gas tends to increase its volume. The relation between the rise in temperature and in the increase in volume was discovered independently by Dalton and by Gay Lussac in 1801. They were able to show by experiment the following fact or law: If a gas, having a temperature of 0° is heated, for a rise of each degree in temperature its volume is increased by $\frac{1}{273}$ of the volume which it occupied at 0°, provided the pressure upon the gas remains unchanged. Similarly, if cooled below 0° its volume is decreased by $\frac{1}{273}$ of the volume which it occupied at 0° for each degree through which the temperature has been lowered. If V represents the volume of gas at 0°, then the volume at 1° will be $V + \frac{1}{273}V$; at 2°, it will be $V + \frac{2}{273}V$; or in general the volume, v, at the temperature t will be expressed by the formula

$$(1) \quad v = V + \frac{t}{273}V$$

or

$$(2) \quad v = V\left(1 + \frac{t}{273}\right)$$

Since $\frac{1}{273} = 0.00366$, the formula may be written

$$(3) \quad v = V(1 + 0.00366t)$$

Since the value of V (volume under standard conditions) is the one generally sought, it is convenient to transpose the equation to the following form:

$$(4) \quad V = \frac{v}{1 + 0.00366t}$$

The following problem will serve as an illustration: The volume of a gas at 20° is 750 cubic centimeters. Find the volume it will occupy at 0°, the pressure remaining constant.

In this case, $v=750$ c.c. and $t=20$. By substituting these values, equation (4) becomes

$$V=\frac{750}{1+0.00366\times 20}=698.8 \text{ c. c.}$$

2. Variations in the Volume of a Gas Due to Change of Pressure. Boyle's Law. The English scientist, Robert Boyle, as a result of his experiments, was the first to show that the volume of a gas varies inversely with the pressure to which it is subjected. This is known as Boyle's law. If the volume of a gas under a certain pressure is 4 liters, doubling the pressure will reduce the volume to 2 liters; or halving the pressure will increase it to 8 liters, provided of course that the temperature remains constant. If V represent the volume when subjected to a pressure P and v represents its volume when the pressure is changed to p, then in accordance with the above law, $V:v::p:P$ or $VP=vp$. In other words the product of the numbers representing the volume of a gas and the pressure to which it is subjected is a constant.

Since the pressure of the atmosphere at any point is indicated by the barometric reading, it is convenient to substitute the latter for the actual pressure, in the solution of problems. The average reading of the barometer at the sea level is 760 millimeters, which corresponds to a pressure of 1033 grams per square centimeter. The following problem will serve as an illustration:

A gas occupies a volume of 500 c.c. in a laboratory where the barometric reading is 740 mm. What volume would it occupy if the atmospheric pressure changed so that the reading became 750 mm.?

Substituting the values in the equation $VP=vp$, we have $500\times 740=v\times 750$, or $v=493.3$ c.c.

Inasmuch as corrections must as a rule be made for both temperature and pressure, it is convenient to combine the equations given above for the corrections of each, so that the two corrections may be made in one operation. The following equation is thus obtained:

$$(5) \quad V=\frac{v\,p}{760\,(1+0.00366t)}$$

in which V represents the volume of a gas under standard conditions and v, the volume which it occupies when subjected to pressure p and temperature t.

The following problem will serve to illustrate the application of this equation.

A gas having a temperature of 20° occupies a volume of 500 c.c. when subjected to a pressure indicated by a barometric reading of 740 mm. What volume would this gas occupy under standard conditions?

In this problem $v=500$, $p=740$ and $t=20$. Substituting these in the above equation we get

$$V = \frac{500 \times 740}{760\,(1 + 0.00366 \times 20)} = 453.6 \text{ c. c.}$$

In many cases, gases are collected over water as explained under the preparation of oxygen. In such cases there is present in the gas a certain amount of water vapor. This vapor exerts a definite pressure (called the tension of aqueous vapor) in opposition to the atmospheric pressure and hence must be subtracted from the latter in determining the effective pressure upon the gas. The figures representing this tension at different temperatures are given at the end of this chapter. They express the tension in millimeters of mercury, corresponding to the barometric reading.

In measuring the volume of a gas collected over water, the reading should be taken after raising or lowering the tube containing the gas until the level of the liquid inside and outside the tube is the same; for it is only under these conditions that the gas is subjected to the atmospheric pressure as indicated by the barometric reading. If the tube is not so adjusted, corrections must be made for the difference in pressure. The method of determining this correction may be illustrated by the following example:

A tube graduated in cubic centimeters is partially filled with a gas collected over water, as shown in Fig. 9. The volume of the gas, as indicated by the reading on the graduated tube, is 250 c. c. Its temperature, as indicated by the reading of the thermometer placed near it, is 20°. The barometric reading is 740 mm. The level of the water inside the tube is found by measurement to be 100 mm. above the level outside. The problem is to find the volume which this gas would occupy under standard conditions.

It is evident that the pressure upon the gas is not indicated by the reading of the barometer, for the atmosphere pressing down on the surface of the liquid in the vessel B is not only compressing the gas in the tube A, but in addition is holding up a column of water 100 mm. in height. The effective pressure upon the gas is equal therefore to the pressure as indicated by the barometric reading less the pressure spent in supporting the column of water. Since mercury is 13.6 times as heavy as water, a column of water 100 mm. in height would be equivalent to a column of mercury 7.3 mm. high. Subtracting this from the barometric reading we have 740 — 7.3=732.7 mm. The gas being collected over water, the pressure is still further diminished by the tension of aqueous vapor. The value of this at 20° is 17.4 mm. Substracting this from 732.7, we get 715.3 mm. as the actual pressure to which the gas is subjected. Now substituting in equation (5) given above, the values for v, t and p, we get

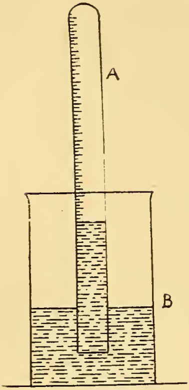


Fig. 9

$$V = \frac{250 \times 715.3}{760\,(1 + 0.00366 \times 20)} = 219.2 \text{ c. c.}$$

Tension of Aqueous Vapor Expressed in Millimeters of Mercury

Temp.	Pressure.	Temp.	Pressure.
16	13.5	21	18.5
17	14.4	22	19.7
18	15.4	23	20.9
19	16.3	24	22.2
20	17.4	25	23.6

CHAPTER III.

HYDROGEN.

Historical. Hydrogen was first clearly recognized as an element by the English investigator Cavendish, who, in 1776, obtained it in a pure state, and showed it to be different from the other inflammable airs or gases which had long been known. Lavoisier gave it the name hydrogen, signifying "water producer" since it had been found to be a constituent of water.

Occurrence. In a free state hydrogen is found in the atmosphere but only in traces. Large quantities of it occur however in the gaseous matter surrounding the sun and certain other stars. In the combined state it is widely distributed, being a constituent of water as already indicated. Combined with carbon it occurs in crude petroleum and natural gas. Nearly all of the products of the animal and vegetable kingdoms, such as sugar and starch, also contain it.

Preparation from Water.

a. By the Electric Current. As already indicated in the preparation of oxygen, water is easily separated into its constituents, hydrogen and oxygen by passing an electric current through it under certain conditions.

b. By the Action of Metals. When brought in contact with certain metals under appropriate conditions, water gives up a portion or the whole of its hydrogen, its place being taken by a definite amount of the metal. In the case of the metal sodium, this change occurs at ordinary temperatures. Thus if a bit of sodium is thrown on water an action is seen to take place at once, sufficient heat being generated to melt the sodium which runs about on the surface of the water. The change consists in the displacement of one-half of the hydrogen of the water by the sodium, and may be represented as follows:

$$\text{sodium} + \underset{\text{(water)}}{\left\{\begin{array}{l}\text{hydrogen}\\ \text{hydrogen}\\ \text{oxygen}\end{array}\right.} = \text{hydrogen} + \underset{\text{(sodium hydroxide)}}{\left\{\begin{array}{l}\text{sodium}\\ \text{hydrogen}\\ \text{oxygen}\end{array}\right.}$$

The sodium hydroxide formed is a white solid which remains dissolved in the undecomposed water and may be obtained by evaporating the solution to dryness.

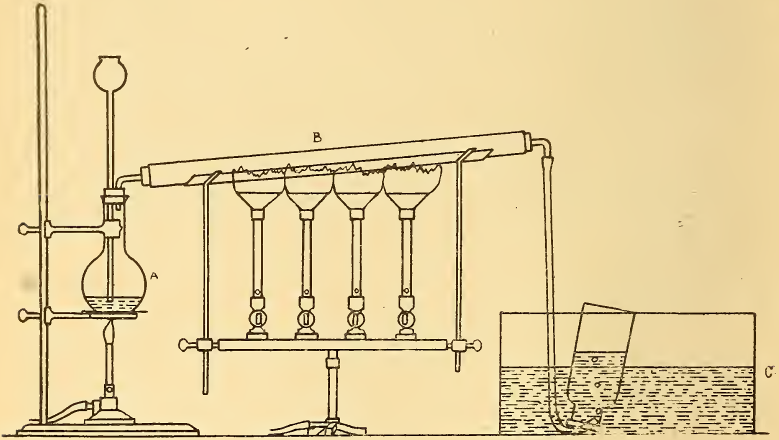


Fig. 10

Other metals such as magnesium and iron decompose water rapidly, but only at higher temperatures. The method of effecting this decomposition and collecting the liberated hydrogen is illustrated in Fig. 10. A porcelain or iron tube, B, about 50 cm. in length and 2 or 3 cm. in width is partially filled with fine iron wire or tacks, and connected as shown in the figure.

The flask A is partially filled with water. The tube is heated, slowly at first, until the iron is red hot. Steam is then conducted through the tube by boiling the water in the flask A. The hot iron combines with the oxygen in the steam setting free the hydrogen which is collected over water. The gas which passes over first is mixed with the air previously contained in the flask and tube, and is allowed to escape *since a mixture of hydrogen and oxygen or air explodes with great violence when brought in contact with a flame.* It is evident that the flask A must be disconnected from the tube before the heat is withdrawn.

That the gas obtained is different from air and oxygen may be shown by holding a bottle of it mouth downward and bringing a lighted splint into it. The hydrogen is ignited and burns with an almost colorless flame.

If, at the close of the experiment the iron in the tube is examined, it will be found that at least a portion of it has been changed to a reddish black substance. This has been proved to be an oxide of iron, identical with that obtained by the combustion of iron in oxygen. The change which has taken place may be represented as follows:

$$\text{iron} + \underset{\text{(water)}}{\left\{\begin{matrix}\text{hydrogen}\\ \text{hydrogen}\\ \text{oxygen}\end{matrix}\right.} = \begin{matrix}\text{hydrogen}\\ \text{hydrogen}\end{matrix} + \underset{\text{(iron oxide)}}{\left\{\begin{matrix}\text{iron}\\ \text{oxygen}\end{matrix}\right.}$$

The iron has thus taken the place of the whole of the hydrogen in the water; in other words it has combined with the oxygen and liberated the hydrogen.

If the element carbon, in the form of charcoal or coke is substituted for the iron in the above experiment, the hot carbon, like the iron combines with the oxygen and liberates the hydrogen. The change may be represented as follows:

$$\text{carbon} + \underset{\text{(water)}}{\left\{\begin{array}{l}\text{hydrogen}\\ \text{hydrogen}\\ \text{oxygen}\end{array}\right.} = \begin{array}{l}\text{hydrogen}\\ \text{hydrogen}\end{array} + \underset{\text{(carbon monoxide)}}{\left\{\begin{array}{l}\text{carbon}\\ \text{oxygen}\end{array}\right.}$$

The carbon monoxide formed is a gas however, so that the product obtained by this method is not pure hydrogen but a mixture of two gases. Since both of these gases burn with a hot flame, the mixture is often manufactured on a large scale and used as a fuel under the name "water gas."

While hydrogen may thus be obtained readily from water the methods are not economical and are therefore little used.

Preparation from Acids.

a. Usual Laboratory Method. Among the most important compounds with which the chemist has to deal are those included under the name, "acids." Hydrogen is an essential constituent of all acids. Moreover when certain metals are brought in contact with an acid, the hydrogen contained in the acid is liberated, being replaced by a definite amount of the metal. Although this reaction is a general one, it has been found most convenient in preparing hydrogen by this method to use for the acid, either hydrochloric or dilute sulphuric and for the metal either zinc or iron, generally the former.

Both sulphuric acid and zinc, if impure, are likely to contain small amounts of arsenic. Such materials should not be used in preparing hydrogen since the arsenic present combines with a portion of the hydrogen to form a very poisonous gas known as arsine. On the other hand chemically pure sulphuric acid, i. e. sulphuric acid that is entirely free from impurities, will not act upon chemically pure zinc. The reaction may be started however by the addition of a few drops of a solution of copper sulphate.

To prepare hydrogen by this method the metal is placed in a flask or wide mouth bottle A (Fig. 11) and the acid slowly added through the funnel tube B. The metal dissolves in the acid. The hydrogen which is liberated escapes through the exit tube C and is collected over water. It is evident that the hydrogen which passes over first is mixed with the air contained in the bottle; hence care must be taken not to bring a flame near the exit tube, since as previously stated such a mixture explodes with great violence when brought in contact with a flame.

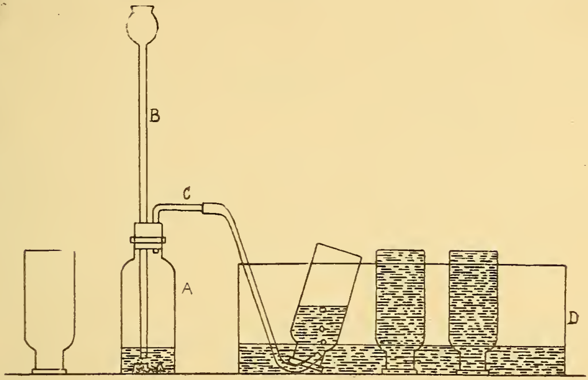


Fig. 11

The changes which take place when zinc and dilute sulphuric acid are used may be represented as follows:

$$\text{zinc} + \underset{\text{(sulphuric acid)}}{\left\{\begin{array}{l}\text{hydrogen}\\ \text{sulphur}\\ \text{oxygen}\end{array}\right.} = \text{hydrogen} + \underset{\text{(zinc sulphate)}}{\left\{\begin{array}{l}\text{zinc}\\ \text{sulphur}\\ \text{oxygen}\end{array}\right.}$$

In other words the zinc has taken the place of the hydrogen in sulphuric acid, which is a compound of hydrogen, sulphur and oxygen. The resulting compound contains zinc, sulphur and oxygen and is known as zinc sulphate. This is a white solid which is soluble in water and hence dissolves as fast as formed in the water present in the acid. It may be obtained by evaporating the liquid which is left in the flask A, Fig. 11, after the metal has passed into solution.

When zinc and hydrochloric acid are used the following changes take place.

$$\text{zinc} + \underset{\text{(hydrochloric acid)}}{\left\{\begin{matrix}\text{hydrogen}\\ \text{chlorine}\end{matrix}\right.} = \text{hydrogen} + \underset{\text{(zinc chloride)}}{\left\{\begin{matrix}\text{zinc}\\ \text{chlorine}\end{matrix}\right.}$$

The zinc chloride is a white solid, which dissolves in the water of the flask and may be obtained by evaporating the solution to dryness. When iron is used the changes which take place are exactly similar to those just given for zinc.

Physical Properties. Hydrogen is similar to oxygen in that it is a colorless, tasteless, odorless gas. It is characterized by its extreme lightness, being the lightest of all known substances. One liter of it weighs only 0.08984 grams. On comparing this weight with that of an equal volume of oxygen viz, 1.428 grams, the latter is found to be 15.8 or in round numbers 16 times as heavy. Similarly air is found to be 14.4 times as heavy as hydrogen. Its extreme lightness may be shown by blowing soap bubbles with it, the bubbles rising in the air with great rapidity. This suggests its use for the inflation of balloons. On account of its lightness it is possible to pour it "upward" from one bottle into another. Thus if the bottle A, (Fig. 12) is filled with hydrogen, placed mouth downward by the side of bottle B filled with air, and then gradually changed as indicated in the figure to an upright position the hydrogen will flow upward into bottle B displacing the air. Its presence in bottle B may be then shown by bringing a lighted splint to the mouth of the bottle, the hydrogen be-

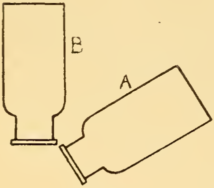


Fig. 12

ing ignited by the flame. It is evident from this experiment that in order to retain the gas in an open bottle, the bottle must be held mouth downward.

Hydrogen is far more difficult to liquify than any other gas, with the exception of the rare element helium which has as yet resisted all efforts to liquify it. The English scientist Dewar however in 1898 succeeded not only in obtaining it in liquid state but also in a solid state. Liquid hydrogen is colorless and has a density of only 0.07. Its boiling point under atmospheric pressure is —252°. Under diminished pressure the boiling point is lowered to —258°, a point only 15° above absolute zero.

The solubility of hydrogen in water is very slight being still less than that of oxygen.

Chemical Properties. At the ordinary temperature, hydrogen is an inactive element. At higher temperatures however it combines with a number of elements being remarkable for its affinity for oxygen. On account of this affinity, a mixture of hydrogen and oxygen or hydrogen and air, (which is about one-fifth oxygen) explodes with great violence when heated to the kindling temperature. Nevertheless under proper conditions, hydrogen may be made to burn quietly in either of these gases. To bring this about the hydrogen is generated in the bottle A, (Fig. 13) is dried by conducting it through the tube X, filled with some substance (generally calcium chloride) which has a great attraction for moisture, and escapes through the tube T, the end of which is drawn out to a jet. The hydrogen first liberated mixes with the air contained in the generator. If a flame is brought near the jet before this mixture has all escaped, a violent and very dangerous explosion results, since the entire apparatus is filled with the explosive mixture. On the other hand if the flame is not applied until all the air has been expelled the hydrogen is ignited and burns quietly, since only the small amount of it which escapes from the jet can come in contact with the oxygen of the air at any one time.

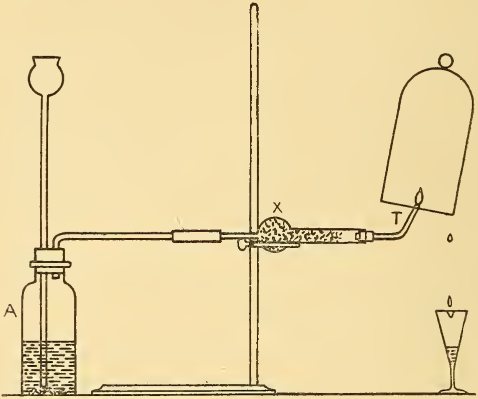


Fig. 13

Before igniting the hydrogen therefore it is absolutely necessary to know that it is free from air. This is determined by testing small amounts of the escaping gas. A convenient and safe method of doing this is to fill a test tube with the gas by bringing it down over the jet. The hydrogen on account of its lightness collects in the tube. After leaving it over the jet for a few moments in order that it may be filled with the gas, the tube is gently carried mouth downward to the flame of a burner placed not nearer than an arm's length from the jet. If the hydrogen is mixed with air a slight explosion occurs; but if pure, it burns quietly in the tube. The operation is repeated until the gas burns quietly, when the tube is quickly brought back over the jet for an instant, whereby the escaping hydrogen is ignited by the flame in the tube.

The hydrogen flame is almost colorless and very hot. The combustion of the gas is due, of course to its union with oxygen. The product of the combustion is therefore a compound of hydrogen and oxygen. That the compound formed is water which as already indicated is composed of these two elements, may be shown by holding over the flame a cold and dry bell jar or bottle (Fig. 13). The steam is condensed, the water collecting in drops on the sides of the jar.

That a mixture of hydrogen and air is explosive may be shown safely as follows. A cork through which passes a short glass tube about 1 cm. in diameter is fitted air tight into the tubule of a bell jar of two or three liters capacity. (A thick glass bottle with bottom removed may be used.) The tube is closed with a small rubber stopper and the bell jar filled with hydrogen, the gas being collected over water. When entirely filled with the gas the jar is removed from the water and supported by blocks of wood in order to leave the bottom of the jar open as shown in Fig. 14. The stopper is now removed from the tube in the cork and the hydrogen, which on account of its lightness escapes from the tube, is at once lighted. As the hydrogen escapes, the air flows in at the bottom of the jar and mixes with the remaining portion of the hydrogen, so that a mixture of the two soon forms and a loud explosion results. The explosion is not dangerous, since the bottom of the jar is open, thus leaving room for the expansion of the hot gas.

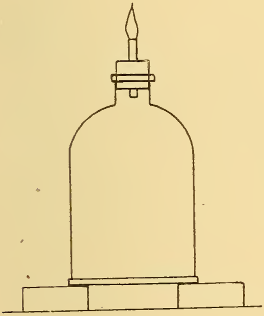


Fig. 14

Since air is only one-fifth oxygen the remainder being inert gases, it may readily be inferred that a mixture of hydrogen with pure oxygen would be far more explosive than a mixture of hydrogen with air. Such mixtures should not be made except in small quantities and by experienced teachers.

Hydrogen does not Support Combustion. While hydrogen is readily combustible it is not a supporter of combustion i. e., substances will not burn in it. This may be

Fig. 15

shown by bringing a lighted candle supported by a stiff wire into a bottle or cylinder of the pure gas as shown in Fig. 15. The hydrogen is ignited by the flame of the candle and burns at the mouth of the bottle. When the candle is thrust up into the gas, its flame is extinguished on account of the absence of oxygen. If slowly withdrawn the candle is relighted as it passes through the layer of burning hydrogen.

Reduction. On account of its great affinity for oxygen, hydrogen has the power of abstracting it from many of its compounds. Thus if a stream of hydrogen, dried by passing through the tube B (Fig. 16), filled with calcium chloride, is conducted through the tube C containing some copper oxide, heated to a medium temperature, the following change takes place.

$$\text{hydrogen} + \underset{\text{(copper oxide)}}{\left\{\begin{matrix}\text{copper}\\ \text{oxygen}\end{matrix}\right.} = \text{copper} + \underset{\text{(water)}}{\left\{\begin{matrix}\text{hydrogen}\\ \text{oxygen}\end{matrix}\right.}$$

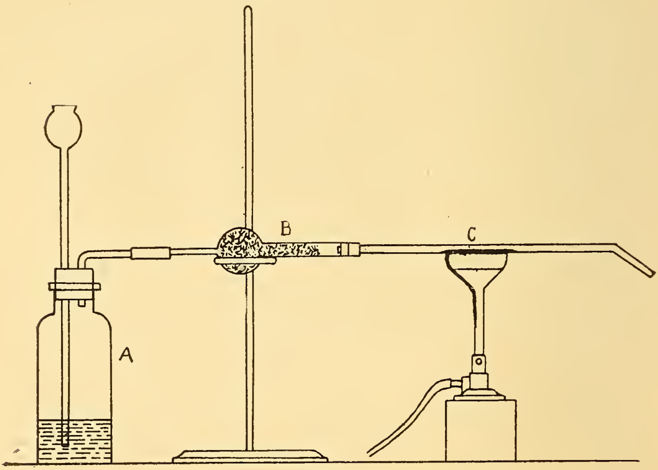


Fig. 16

The water formed collects in the cold portions of the tube C near its end.

In this experiment the copper oxide is said to undergo reduction. In other words its oxygen is withdrawn. The hydrogen used to effect this reduction is called a reducing agent. Oxidation and reduction are therefore complementary terms. The one consists in adding oxygen to a substance, the other in withdrawing it. Reduction as a rule is accompanied by oxidation. Thus in the above experiment, the copper oxide is reduced and the hydrogen is oxidized.

In addition to oxygen, hydrogen also combines with a number of other elements. Thus it combines with chlorine to form hydrochloric acid which is often used as a source of hydrogen; with nitrogen to form common ammonia; with sulphur to form the foul smelling gas, hydrogen sulphide.

Pure hydrogen produces no injurious results when inhaled. Of course one could not live in an atmosphere of it, since oxygen is essential to life.

The Oxyhydrogen Blowpipe. This is a form of apparatus used for burning hydrogen in pure oxygen. As previously stated, the flame produced by the combustion of hydrogen in air is very hot. It is evident that if pure oxygen is substituted for air, the temperature reached will be much greater, since there will be no inert gases to absorb the heat. The oxyhydrogen blowpipe, used to effect this combination, consists of a small tube placed within a larger one, as shown in Fig. 17.

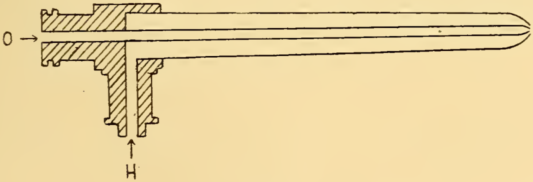


Fig. 17

The hydrogen, stored under pressure, generally in steel cylinders, is first passed through the outer tube and ignited at the end of the tube. The oxygen similarly stored is then conducted through the inner tube and mixes with the hydrogen at the end of the tube. In order to produce the maximum heat, the hydrogen and oxygen must be present in the exact proportion in which they combine, viz., 2 volumes of hydrogen to 1 of oxygen, or by weight, 2 parts of hydrogen to 15.8 parts of oxygen. The intensity of the heat may be shown by bringing into the flame pieces of metal such as iron wire or zinc. These burn with great brilliancy. Even platinum, having a melting point of 1770° may be melted by the heat of the flame.

While the oxyhydrogen flame is intensely hot it is almost non-luminous. If directed against some infusible substance like ordinary lime (calcium oxide) the heat is so intense that the lime becomes incandescent and glows with a brilliant light. This is sometimes used as a source of light under the name of "Drummond" or "lime light."

The Blast Lamp. A similar form of apparatus is commonly used in the laboratory as a source of heat under the name "blast lamp" (Fig. 18). This differs from the oxyhydrogen blowpipe, only in the size of the tubes. In place of the hydrogen and oxygen the more accessible coal gas and air are respectively used. The former is composed largely of a mixture of free hydrogen together with gaseous compounds of carbon and hydrogen. While the temperature of the flame is not so intense as that of the oxyhydrogen blowpipe it nevertheless suffices for most chemical operations carried out in the laboratory.

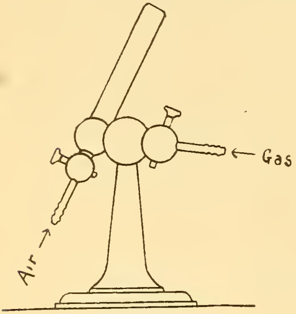


Fig. 18

Uses of Hydrogen. On account of its cost, hydrogen is but little used for commercial purposes. It has been used as a material for the inflation of balloons, but generally the much cheaper coal gas is now substituted for it.

Even hot air is often used when the duration of ascension is very short. It has also been largely used as a source of heat and light in the oxyhydrogen blowpipe. Where the electric current is available, however, this form of apparatus has been displaced almost entirely by the electric light and electric furnace which are much more economical and more powerful sources of light and heat.

CHAPTER IV.

COMPOUNDS OF HYDROGEN AND OXYGEN. WATER AND HYDROGEN DIOXIDE.

Historical. Water was long regarded as an element. In 1781, Cavendish, the discoverer of hydrogen showed that it was formed by the union of hydrogen and oxygen. Being a believer in the phlogiston theory however he failed to interpret his results correctly. A few years later, Lavoisier repeated Cavendish's experiments and asserted that water must be regarded as a compound of hydrogen and oxygen.

The Composition of Water. The composition of any substance is ordinarily determined by one of two processes. In the first place it may be possible to separate the substance into its constitutents and its composition may thus be determined. This process is called *analysis*. Thus we analyze water when we separate it into the elements which compose it. In the second place the substance may be formed by the union of its constituent parts. Such a process is called *synthesis*. Thus the composition of water may be demonstrated by showing that it is the product formed by the union of hydrogen and oxygen.

Analysis and synthesis are therefore opposite processes. The one is the separation of a substance into its constituents; the other is the formation of a substance by the union of its constituents. These processes may be either qualitative or quantitative. Thus qualitative analysis consists simply in ascertaining what elements are present: quantitative analysis on the other hand consists in determining the exact amount of each element present. Qualitative analysis must therefore precede quantitative analysis.

It has already been shown in the discussion of the combustion of hydrogen that water is a compound of hydrogen and oxygen. It remains to ascertain the exact proportions in which these elements combine to form water; in other words to determine the quantitative composition of water.

The methods employed in making this determination may be classed under the two general heads, (1) Methods based on analysis and (2) Methods based on synthesis.

1. *Methods Based on Analysis.* As has already been indicated, water may be separated into its component parts, by means of the electric current. The form of apparatus ordinarily used for effecting this change is shown in Fig. 19. A platinum wire, to the end of which is attached a small piece of platinum foil (about 15 by 25 mm.) is fused through each of the tubes B and D as shown in the figure.

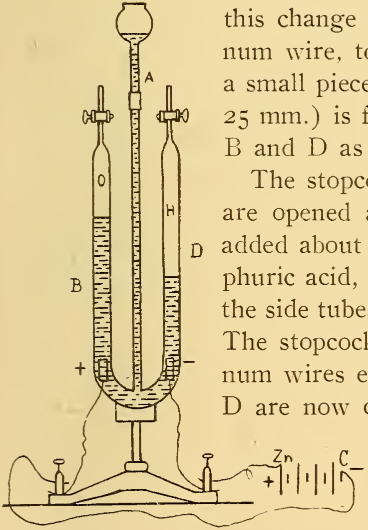


Fig. 19

The stopcocks at the ends of these tubes are opened and water, to which has been added about one-tenth of its volume of sulphuric acid, is poured into the tube A until the side tubes B and D are completely filled. The stopcocks are then closed. The platinum wires extending into the tubes B and D are now connected with the wires leading from two or three dichromate cells joined in series. The pieces of platinum foil within the tubes thus become the electrodes and the current flows from one to the other through the acidulated water. As soon as the current passes bubbles of gas rise from each of the electrodes and collect in the upper part of the tubes. The gas rising from the negative electrode will be found to have approximately twice the volume of that rising from the positive electrode. That the former is hydrogen and the latter oxygen may be verified by making the appropriate tests.

The process of decomposing a substance by means of the electric current is known as electrolysis. The positive electrode viz., the end of the wire connected with the carbon plate of the battery, is called the anode, while the negative electrode is called the cathode. As stated above, in the electrolysis of water the hydrogen escapes from the cathode and the oxygen from the anode. Pure water is a non-conductor of electricity, but can be made a conductor by the addition of a little sulphuric acid. The exact function of the acid will be discussed later in the chapter on solutions.

On close examination, the volume of hydrogen obtained by the electrolysis of water will be found to be slightly more than double that of the oxygen. As has been pointed out however oxygen is somewhat more soluble in water than hydrogen, and this tends to diminish its volume as compared with the volume of hydrogen. It has also been found that a small amount of the oxygen liberated is converted into ozone and hydrogen dioxide. When these facts are taken into consideration and appropriate corrections made, it can be shown that the volume of the hydrogen obtained is exactly twice that of the oxygen.

It is evident that this experiment in itself does not prove the composition of water. It simply shows that water contains hydrogen and oxygen. It does not prove the absence of other elements; indeed it does not prove the presence of hydrogen and oxygen in the proportion in which they are liberated.

That no other elements are present however and that water is composed of hydrogen and oxygen in the above proportions may be proved in two ways. In the first place it may be shown that the weight of the hydrogen and oxygen obtained by the decomposition of water is exactly equal to the weight of water decomposed. In the second place the two volumes of hydrogen and the one volume of oxygen may be reunited with the formation of water. This leads to the discussion of the second of the methods employed for the determination of the composition of water.

2. *Methods Based on Synthesis.* The determination of the composition of water by the union of hydrogen and oxygen is effected in the following way. The combination of the gases is brought about in a tube known as a eudiometer (Fig. 20). This is a graduated tube about 60 cm. long, 2 cm. wide and closed at one end. Near the closed end two platinum wires are fused through the glass, the ends of the wires within the tube being separated by a distance of 2 or 3 mm. The tube is entirely filled with mercury and inverted in a vessel of the same liquid. Pure hydrogen is passed into the tube until it is about one-fourth filled. The volume of the gas is then read off on the scale and reduced to standard conditions. About an equal volume of pure oxygen is then introduced, the volume again read off and reduced to standard conditions. This gives the total volume of the two gases and from this the volume of the oxygen introduced may be determined by subtracting from it the volume of the hydrogen. The combination of the two gases is now brought about by connecting the two platinum wires with an induction coil and passing a spark from one wire to the other. Immediately a slight explosion occurs. The mercury in the tube, at first depressed, at once rises taking the place of the gases which have combined to form water — the volume of the latter being so small in comparison with the volume of the gases from which it was formed that it may be disregarded. In order that the temperature of the residual gas and the liquid may become uniform, the apparatus is allowed to stand for a few minutes. The volume of the gas is then read off and reduced to standard conditions in order that it may be compared with those of the hydrogen and oxygen taken. The residual gas is then tested in order to ascertain whether it is hydrogen

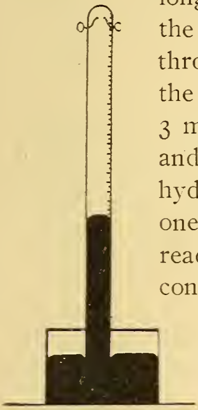


Fig. 20

or oxygen. From the data thus obtained the composition of the water may be calculated. Thus suppose the data obtained were as follows:

Volume of hydrogen taken	20.3 c.c.
Volume of hydrogen and oxygen	38.7 c.c.
Volume of oxygen	18.4 c.c.
Volume of gas left after combination has taken place (oxygen)	8.3 c.c.

Hence the 20.3 c.c. of hydrogen has combined with 18.4 — 8.3 or 10.1 c.c. of oxygen; or approximately 2 volumes of hydrogen have combined with 1 of oxygen. Since oxygen is 15.88 times as heavy as hydrogen the proportion by weight in which the two gases combine is 2 parts of hydrogen to 15.88 of oxygen.

If the two gases are introduced into the eudiometer in the exact proportions in which they combine, after the combination has taken place the liquid will rise and completely fill the tube. Under these conditions, however, the tube is very likely to be broken by the sudden upward-rush of the liquid. Hence in performing the experiment care is taken to introduce an excess of one of the gases.

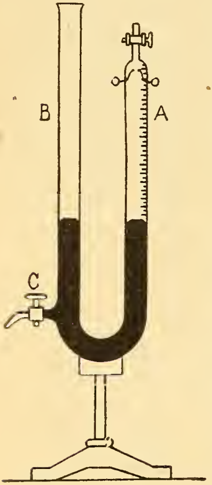


Fig. 21

A form of eudiometer (Fig. 21) different from that given above, is sometimes used to avoid the calculations necessary to reduce the volumes of the gases to the same conditions of temperature and pressure in order to make comparisons. With this form it is possible to make the readings of the volumes under the same conditions of temperature and pressure, and thus compare them directly. The apparatus (Fig. 21) is filled with mercury and the gases introduced into the tube A. The experiment is carried out as in the preceding one, except that before taking the reading of the gas volumes mercury is either added to the tube B or withdrawn from it by means of the stopcock C until it stands at exactly the same height in both tubes. The gas enclosed in tube A is then under atmospheric pressure; and since only a few minutes are required for performing the experiment, the conditions of temperature and pressure may be regarded as constant. Hence the volumes of the hydrogen and oxygen and of the residual gas may be read off from the tube and directly compared.

By the above method it is possible to determine the proportion by volume in which hydrogen and oxygen combine. From these results, the proportion by weight can be readily deduced, knowing the relative weights of the two gases. It is possible however to determine directly the proportion by weight in which the elements combine. Fig. 22 illustrates the apparatus used in making this determination. B represents a glass tube containing copper oxide. C and D are glass tubes filled with calcium chloride, which has a great affinity for water. The tubes B and C including their contents are carefully weighed, and the apparatus connected as shown in the figure. A slow current of pure hydrogen is then passed through A, and that part of the tube B which contains copper oxide is carefully heated. The hydrogen combines with the oxygen present in the copper oxide to form water which is absorbed by the calcium chloride in tube C. The operation is continued until an appreciable

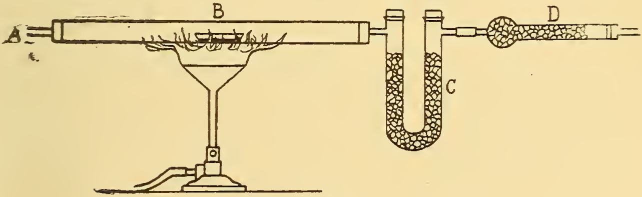


Fig. 22

amount of water has been formed. The tubes B and C are then again weighed. The loss of weight in the tube B will exactly equal the amount of oxygen taken up from the copper oxide in the formation of the water. The gain in weight in the tube C will exactly equal the weight of water formed. The difference in these weights will of course equal the weight of the hydrogen present in the water formed.

This method for the determination of the composition of water was first used by Berzelius in 1820. The work was repeated in 1843 by Dumas the average of whose results is as follows:

Weight of water formed............	236.36 grains.
Oxygen given up by the copper oxide	210.04 grains.
Weight of hydrogen present in water	26.32 grains.

Hence, according to this experiment, the ratio of hydrogen to oxygen in water is as 26.32 to 210.04 or as 2 to 15.96.

Morley's Results. The most accurate determination of the ratio of hydrogen to oxygen in water ever made has been recently carried out by the American chemist, Morley. The hydrogen and oxygen which combined as well as the water formed, were all accurately weighed. Extreme precautions were taken to insure pure materials and to eliminate all sources of error. Morley's results show that 2 parts of hydrogen by weight combine with 15.88 parts of oxygen to form water.

Relation Between the Volume of Aqueous Vapor and the Volumes of the Hydrogen and Oxygen Which Combine to Form it.

It was stated above that when hydrogen and oxygen are introduced into an eudiometer tube and made to combine, the volume occupied by the resulting water is so

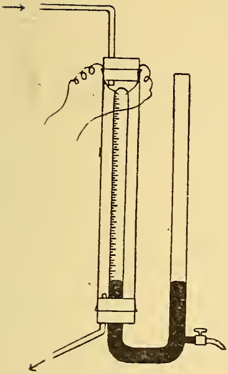


Fig. 23

small in comparison with the volumes of the gases which combined to form it that it could be disregarded. If, however the eudiometer tube is surrounded by a larger tube (Fig. 23) through which is passed the vapor of some liquid whose boiling point is above that of water, the vapor resulting from the union of the hydrogen and oxygen in the eudiometer tube does not condense but remains in the form of steam. It thus becomes possible to compare the volume of steam or water vapor with the volumes of the hydrogen and oxygen which combine to form it. In this way it has been shown that when two volumes of hydrogen and one volume of oxygen combine, exactly two volumes of water vapor are formed. It will be noted that the relation between these volumes may be expressed by whole numbers. The significance of this very important fact will be discussed in a subsequent chapter.

Occurrence of Water. Water not only covers about three-fourths of the surface of the earth, and is present in the atmosphere in the form of moisture but it is also a common constituent of the soil and rocks and almost every form of animal and vegetable organism. The human body is nearly 70% water. This is derived not only from the water which we drink but also from various forms of food which contain a large percentage of water. Thus potatoes contain about 78% of water, milk 85%, beef over 50%, apples 84%, tomatoes 94%.

Impurities in Water. As has already been shown, chemically pure water contains only hydrogen and oxygen. Such a water never occurs in nature, however, for being a good solvent, it takes up certain substances from the rocks and soil with which it comes in contact. When such waters are evaporated these substances are deposited in the form of a residue. Even rain water which is the purest form occurring in nature, since it does not come in contact with the earth, contains dust particles and gases dissolved from the atmosphere. The foreign matter in water is of two kinds viz., mineral, such as common salt and limestone, and organic i. e., the products of animal and vegetable life.

The amount and nature of the mineral matter present in different waters vary greatly, depending on the nature of the rocks and soil with which the waters come in contact. The more common of the substances present are common salt and compounds of calcium, magnesium and iron. One liter of the average river water contains about 175 mg. of mineral matter. Water from deep wells naturally contains more mineral matter than river water, generally two to three times as much, while sea water contains as much as 35,000 mg. to the liter.

The mineral matter in water does not, save in very exceptional cases, render the water injurious to the human system. In fact the presence of a certain amount of it is advantageous, supplying the mineral matter necessary for the formation of the solid tissues of the body. The presence of organic matter on the other hand must always be regarded with suspicion. Such organic matter may consist not only of the products of animal and vegetable life, but also of certain microscopic forms of living organisms which are likely to accompany such products. Contagious diseases are known to be due to the presence in the body of minute living organisms or germs. Each disease is caused by its own particular kind of germ. These germs often find their way through the sewage from persons afflicted with disease into the water supply and it is very often through the drinking water that certain of these diseases, especially typhoid fever, are spread. It becomes of great importance therefore to be able to detect such matter when present in drinking water as well as to devise methods whereby it can be removed or at least rendered harmless.

The mineral analysis of a water is, as the name suggests, simply the determination of the mineral matter present. Sanitary analysis, on the other hand, is the determination of the organic matter present. The physical properties of a water give no conclusive evidence as to its purity, since a water may be unfit for drinking purposes and yet be perfectly clear and odorless. Neither can any reliance be placed on the simple methods often given for testing the purity of water. Only the trained chemist can carry out such methods of analysis as can be relied upon.

The Purification of Water. The most effective way of purifying natural waters is by the process of distillation. This consists in boiling the water and condensing the steam. Fig. 24 illustrates the process of distillation as commonly conducted in the laboratory. Ordinary water is poured into the flask A and boiled. The steam is conducted through the condenser B which consists essentially of a narrow glass tube sealed within a larger one, the space be-

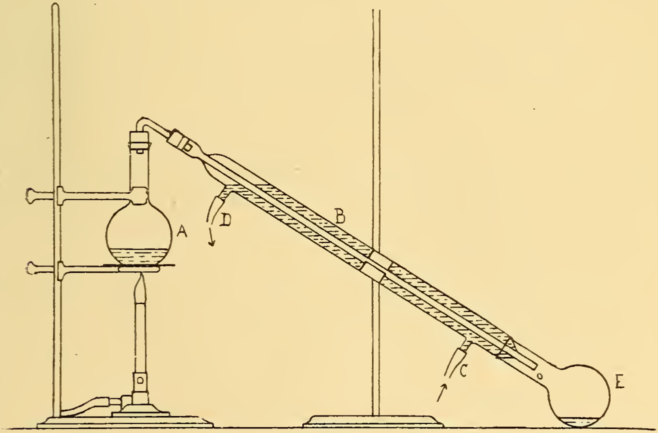


Fig. 24

tween the two being filled with cold water, which is admitted at C and escapes at D. The inner tube is thus kept cool and the steam in passing through it is condensed. The water formed by the condensation of the steam collects in the receiver E and is known as distilled water. Such water is practically pure, since the impurities being non-volatile, remain in the flask A.

In preparing distilled water on a large scale, the steam is generated in a boiler or other metal container and condensed by passing it through a pipe made of metal, generally tin. This pipe is wound into a spiral and surrounded by a current of cold water. Distilled water is used by the chemist in almost all of his work. It is also used in the manufacture of artificial ice and for drinking water.

In preparing distilled water, it is evident that if the natural water contains some substance which is volatile, its vapor will pass over and be condensed with the steam, so that the distillate will not be pure water. Even such mixtures, however, may generally be separated by repeated distillation. Thus if a mixture of water (boiling point 100°) and alcohol (boiling point 78°) is distilled, the alcohol, having the lower boiling point, tends to distill first, followed by the water. The separation of the two is not perfect, however, but may be made nearly so by repeated distillations under certain conditions that can not properly be discussed in an elementary treatise. The process of separating a mixture of volatile substances by distillation is known as fractional distillation.

The process of distillation practically removes all non-volatile foreign matter, mineral as well as organic. In purifying water for drinking purposes however it is only necessary to eliminate the latter or to render it harmless. This is ordinarily done by either one of two different processes, viz., filtration and boiling. In filtration the water is passed through some medium which will retain the organic matter. Ordinary charcoal is a porous substance and will condense within its pores the organic matter in water if brought in contact with it; hence its use in the construction of filters.

Such filters in order to be effective must be kept clean, since it is evident that the charcoal is useless after its pores are filled. A more effective type of filter is the Chamberlain-Pasteur. In this, the water is forced through a porous, cylindrical cup, the pores being so minute as to strain out the organic matter.

A simpler and equally effective method for purifying water for drinking purposes consists in boiling the water. It is the germs in water that render it dangerous to health. These germs are living forms of matter. If the water is boiled, the germs are killed and the water rendered safe.

While these germs are destroyed by heat, cold has little effect upon them. Thus Dewar, in working with liquid hydrogen, exposed some of these minute forms of life to the temperature of boiling hydrogen (—252°) without killing them. It is clear from this that ice frozen from impure water can not be regarded as free from impurities.

The above processes, viz., filtration and boiling, remove at most only a small amount of the mineral matter dissolved in the water. The main mineral ingredient removed is limestone.

Reference was made under the discussion of the uses of oxygen, to the self-purification of running water, due to the oxidation of the organic matter present through the agency of the atmospheric oxygen. While water is purified in this way, yet the method can not be relied upon to purify a contaminated water so as to render it safe for drinking purposes.

Water which has percolated through the soil to any distance is purified by the absorbent action of the soil. Advantage is taken of this fact in purifying the water supply of cities. Large filtration beds are prepared from sand and gravel and the water is allowed to flow through these. Cities supplied with water purified in this way are practically free from typhoid fever.

Physical Properties. Pure water is an odorless and tasteless liquid, colorless in thin layers but having a bluish tinge when observed through a considerable thickness. Under the normal pressure of one atmosphere, water boils at 100° and solidifies at 0°. If the pressure is increased the boiling point is raised and the freezing point is lowered. When water is cooled it steadily contracts until a temperature of 4° is reached; it then expands. Hence ice is lighter than water and floats upon it.

Chemical Properties. It will be recalled that the union of hydrogen with oxygen to form water is attended by the liberation of a large amount of heat. Such a body is very difficult to decompose by heat alone since experiment has shown that it requires as much heat to effect the decomposition of a substance as is given off when the substance is formed. In the case of water, this decomposition begins near 1000° but is only about half complete at 2500°. If the heat is withdrawn combination of the elements of course takes place again. While water is thus very stable towards heat it may be decomposed as already pointed out, by the electric current and by the action of certain elements as sodium, iron and carbon.

Many substances such as sugar or salt, when brought into contact with water are taken up or dissolved by it, a solution of the substance in water being formed. The nature of solutions will be discussed later in the chapter devoted to this subject. It is only necessary to add here that compounds in solution undergo chemical changes much more readily than when in the dry or solid forms. Even the slightest trace of moisture, in some unexplained way, often materially assists in causing chemical changes to take place. Thus phosphorus usually burns in oxygen with great energy; but if extreme precautions are taken to remove all traces of moisture, the two elements will not combine at all. Again the kindling temperature of hydrogen and oxygen under ordinary conditions is about 600°; but if the gases are perfectly dry the kindling temperature is considerably raised. Many other examples of this kind might be given.

Water of Crystallization. When solutions of solid compounds are allowed to stand, the water evaporates and the solid compound separates out, often in the form of crystals. It has been found that the crystals of many compounds, although perfectly dry, give up a definite amount of water when heated, the substance at the same time losing its crystalline form. Such water is called water of crystallization. This varies in amount with different compounds but is perfectly definite for the same compound. Thus if a crystal of copper sulphate is strongly heated in a tube, water is evolved and condenses on the sides of the tube, the crystal crumbling to a light powder. The weight of the water evolved is always equal to exactly 36.07 % of the weight of copper sulphate crystals heated. The water must therefore be in chemical combination with the substance composing the crystal; for if simply mixed with it or adhering to it, not only would the substance appear moist but the amount present would undoubtedly vary. The combination however must be a very weak one since the water is often expelled by even a gentle heat. Indeed in some cases, the water is evolved on simple exposure to air. Such compounds are said to be *efflorescent*. Thus a crystal of ordinary sodium sulphate (Glauber's salt) on exposure to air crumbles to a fine powder, owing to the escape of its water of crystallization. Other substances have just the opposite property, viz., they absorb moisture when exposed to the air. Thus if a bit of dry calcium chloride is exposed to the air, in the course of a few hours it will have absorbed sufficient moisture to dissolve it. Such substances are said to be *deliquescent*. A deliquescent body serves as a good drying or desiccating agent. Thus we have already employed calcium chloride as an agent for absorbing the moisture from hydrogen.

Water of crystallization must be carefully distinguished from water which is mechanically inclosed in a crystal and which can be removed by powdering the crystal and drying. Thus when crystals of common salt are heated, the water inclosed in the crystal is changed into steam and bursts the crystal with a crackling sound. Such crystals are said to decrepitate. That this water is not combined is proven by the fact that the amount of it present varies and that it has all the properties of water.

Uses of Water. The importance of water in its relation to life and commerce is too well known to require comment. Its importance to the chemist has also been pointed out. It simply remains to call attention to the fact that it is used as a standard in many physical measurements. Thus 0° and 100° on the centigrade scale are respectively the freezing and the boiling points of water under normal pressure. The weight of 1 c.c. of water at its point of greatest density is the unit of weight in the metric system viz., the gram. It is also taken as the unit for the determination of the density of liquids and solids as well as for the measurement of amounts of heat.

HYDROGEN DIOXIDE.

As has been shown, two parts by weight of hydrogen combine with 15.88 parts by weight of oxygen to form water. It is possible however to obtain a second compound of hydrogen and oxygen differing from water in composition in that two parts by weight of hydrogen are combined with 2×15.88 or 31.76 parts of oxygen. This compound is called hydrogen dioxide or hydrogen peroxide the prefixes "di" and "per" signifying that it contains more oxygen than hydrogen oxide which is the chemical name for water.

Preparation. Hydrogen dioxide can not be prepared economically by the direct union of hydrogen and oxygen; indirect methods must therefore be used. It is commonly prepared by the action of sulphuric acid on barium dioxide. The change which takes place may be indicated as follows:

$$\underset{\substack{\text{(sulphuric}\\\text{acid)}}}{\left\{\begin{array}{l}\text{hydrogen}\\\text{sulphur}\\\text{oxygen}\end{array}\right.} + \underset{\substack{\text{(barium}\\\text{dioxide)}}}{\left\{\begin{array}{l}\text{barium}\\\text{oxygen}\end{array}\right.} = \underset{\substack{\text{(barium}\\\text{sulphate)}}}{\left\{\begin{array}{l}\text{barium}\\\text{sulphur}\\\text{oxygen}\end{array}\right.} + \underset{\substack{\text{(hydrogen}\\\text{dioxide)}}}{\left\{\begin{array}{l}\text{hydrogen}\\\text{oxygen}\end{array}\right.}$$

In other words the barium and hydrogen in the two compounds exchange places. By this method a dilute solution of the dioxide in water is obtained. Inasmuch as the boiling point of the dioxide is higher than that of water it is possible to separate the two by fractional distillation. This is attended with great difficulties however, since the pure dioxide is explosive. The distillation is carried on under diminished pressure so as to lower the boiling points as much as possible; otherwise the high temperature will decompose the dioxide.

Properties and Uses. The pure hydrogen dioxide is a colorless syrupy liquid having a density of 1.49. Its most characteristic property is the ease with which it decomposes into water and oxygen. Two parts by weight of hydrogen are capable of holding firmly only 15.88 parts of oxygen. The extra 15.88 parts present in hydrogen dioxide are therefore easily evolved, the compound breaking down into water and oxygen. This decomposition is attended by the evolution of considerable heat. In dilute solutions hydrogen dioxide is fairly stable, although such solutions should be kept in a dark cool place since both heat and light aid in its decomposition. These solutions are used largely as oxidizing agents i. e., they readily give up oxygen to other substances which have an affinity for it. A 3%

solution in water is commonly used in medicine as an antiseptic. When brought in contact with organic matter, it decomposes, the evolved oxygen destroying the germs of disease.

It is a noteworthy fact that the decomposition of hydrogen dioxide may be brought about by the presence of certain metals. Thus if a piece of platinum is introduced into a concentrated solution of the dioxide the decomposition takes place with explosive violence. Just how the metal effects this change is not understood, since it undergoes no apparent change.

CHAPTER V.

THE ATOMIC THEORY.

Fundamental Laws of Matter.

1. *Law of Conservation of Matter.* In the introductory chapter reference was made to the law of conservation of matter, which states that in all the changes which substances can be made to undergo, no matter is either created or destroyed. Attention must now be directed to two equally important laws relating to the composition of chemical compounds.

2. *Law of Definite Composition.* In the earlier days of chemistry there was much discussion as to whether the composition of a given compound is always precisely the same, or whether it is subject to some variation. Two Frenchmen, Berthollet and Proust, were the leaders in this discussion, and a great deal of most useful experimenting was done to decide the question. Their experiments, as well as all succeeding ones, have shown that the composition of a pure chemical compound is always exactly the same. Water obtained by melting pure ice, condensing steam, burning hydrogen in oxygen, has always 11.19% hydrogen, and 88.81% oxygen in it. Red oxide of mercury from whatever source it is obtained, contains 92.6% mercury and 7.4% oxygen. This truth may be summed up in the statement that the composition of a chemical compound never varies. This statement is called the law of definite proportion.

3. *Law of Multiple Proportion.* It has already been noted however, that hydrogen and oxygen combine in two different proportions to form water and hydrogen dioxide. It will be observed that this fact does not contradict the law of definite proportions, for entirely different substances are

formed. These compounds differ from each other in composition, but the composition of each one is always constant. This ability of two elements to unite in more than one proportion is very frequently observed. Carbon and oxygen combine in two different proportions; nitrogen and oxygen combine to form as many as five distinct compounds each with its own precise composition.

In the first decade of the last century, John Dalton, an English school teacher and philosopher, endeavored to find some rule which holds between the ratios in which two given substances combine. His studies brought to light a very simple relation which the following examples will make clear. In water, as has been already stated, the hydrogen and oxygen are combined in the ratio of 2 parts by weight of hydrogen to 15.88 parts by weight of oxygen. In hydrogen dioxide the 2 parts by weight of hydrogen are combined with 31.76 parts by weight of oxygen. The ratio between the amounts of oxygen which combine with the same amount of hydrogen to form respectively water and hydrogen dioxide is therefore 15.88 : 31.76, or 1 : 2.

Similarly, the element iron combines with oxygen to form two oxides, one of which is black and the other red. By analysis it has been shown that the former contains 2 parts by weight of oxygen combined with 7 parts by weight of iron, while the latter contains 3 parts by weight of oxygen combined with 7 parts by weight of iron. Here again we find that the amounts of oxygen which combine with the same amount of iron to form the two compounds are in the ratio of small whole numbers, viz. 2 : 3.

Many other examples of this simple relation might be given, since it has been found to hold true in all cases where more than one compound is formed from the same elements. Dalton's law of multiple proportion states these facts as follows: When any two elements, A and B are able to form more than one compound, the amounts of B which unite with any fixed amount of A bear the ratio of small, whole numbers to each other.

The Atomic Theory. These three generalizations are called *laws*, because they express in concise language truths which are found by careful experiment to hold good in all cases. They do not offer any explanation of the facts, but merely state them. The human mind, however, does not rest content with the mere bare facts, but seeks ever to learn the explanation of the facts. A suggestion which is offered to explain such a set of facts is called an hypothesis. The suggestion which Dalton offered to explain the three laws of matter was prompted by his view of the constitution of matter, and it involves three distinct assumptions in regard to the nature of matter and chemical action. Dalton could not prove these assumptions to be true, but he saw that if they were true, the laws of matter become very easy to understand.

Three Assumptions upon which Dalton's Hypothesis Rests. The three assumptions which are involved in Dalton's atomic hypothesis are these:

1. All elements consist of minute particles which Dalton called atoms. According to this view matter is not continuous, but is made up of minute units.

2. All atoms of the same element have equal masses; those of different elements have different masses. In any change to which an atom is subjected, its mass does not change.

3. When chemical union takes place between two elements, the action consists in a definite number of atoms of the one element uniting with a definite number of the atoms of the other element to form a small particle of the compound.

Dalton called the particles of the compound, as well as those of the elements, atoms. Later Avogadro, an Italian scientist, pointed out the fact that the two are different, since the smallest particle of an element is a unit, while that of a compound must have at least two units in it. He suggested the name molecule for the least particle of a compound which can exist, retaining the name atom for the smallest particle of an element.

Supposing these three assumptions to be true, let us now see how they serve to explain the laws of matter.

1. *Explanation of the Law of Conservation of Mass.* It is evident that if the atoms never change their masses in any change which they undergo, the total mass of matter can never change and the law of conservation of mass must follow.

2. *Explanation of the Law of Definite Proportion.* According to the third supposition, when iron combines with sulphur the union is between definite numbers of the two kinds of atoms. In the simplest case one atom of the one element combines with one atom of the other. If the sulphur and the iron atoms never change their respective masses when they unite to form a molecule of iron sulphide, all iron sulphide molecules will have equal amounts of iron in them, and also of sulphur. Consequently any mass made up of iron sulphide molecules, will have the same fraction of its weight iron as do the individual iron sulphide molecules. Iron sulphide, from whatever source will have the same composition, which is the law of definite proportion.

3. *Explanation of the Law of Multiple Proportion.* But this simplest case may not always be the only one. Under other conditions one atom of iron might combine with two of sulphur to form a molecule of a second compound. In such a case the one atom of iron would be in combina-

tion with twice the mass of sulphur that is in the first compound, since the sulphur atoms all have equal masses. What is true for one molecule will be true for any number of them; consequently when definite quantities of these two compounds are found to contain the same amount of iron, one will have twice as much sulphur as the other.

The combination between the atoms might occur in other simple ratios. Thus two atoms of the one element might combine with three of the other or two with five. In any case the union would produce compounds having definite composition, and on selecting such numbers of molecules of the two compounds as would contain equal numbers of the atoms of one constituent, the numbers of the atoms of the other constituent would have to bear simple ratios to each other. And if the numbers of the atoms are in simple ratio to each other, the masses of them would have to be, since the weights of the atoms of a given element are all equal. Consequently if we select such amounts of the two compounds as will contain equal masses of one of the elements, the masses of the other element in the two compounds will have to bear a simple ratio to each other.

Testing the Hypothesis. Efforts have been made to find compounds which do not conform to these laws, but all such attempts have resulted in failure. If such compounds were to be found, the laws would be no longer true, and the hypothesis of Dalton would cease to possess value. When an hypothesis has been tested in every way that experiment can test it, and is still found to be in harmony with the facts in the case it is termed a theory. We now speak of the atomic theory rather than of the atomic hypothesis.

Value of a Theory. The value of a theory is twofold. It aids in the clear understanding of the laws of nature because it gives an intelligent idea as to why these laws should be in operation.

A theory also adds much to our knowledge. It usually happens that in testing a theory much valuable work is done, and many new facts are discovered. Almost any theory in explaining given laws, will involve a number of consequences apart from the law it seeks to explain. Experiment will soon show whether these facts are as the theory predicts they will be. Thus Dalton's atomic theory predicted many properties of gases which experiment has since verified.

Atomic Weights. It would be of great advantage in the study of chemistry if we could determine the weights of the different kinds of atoms. That this cannot be done directly is evident. They are so small that they cannot be seen even with a most powerful microscope. No balance can weigh such minute objects. It is possible, however, to determine their relative weights — that is how much heavier one is than another. These relative weights of the atoms are spoken of as the atomic weights of the elements.

If elements were able to combine in only one way — one atom of one with one atom of another — the problem of determining the atomic weights would be very simple. We should merely have to take some one convenient element as a standard, and find by experiment how much of each other element would combine with a fixed amount of it. The ratios thus formed would be the same ratios as those between the atoms of the elements, and thus we should have their relative atomic weights. The law of multiple proportion calls attention to the fact that the atoms combine in other ratios than 1 :1, and there is no direct way of telling which one of the several compounds in a given case is the one consisting of a single atom of each element. If some way were to be found of telling how much heavier the entire molecule of a compound is than the atom chosen as standard, that is of determining the molecular weights of compounds, the problem could be solved, though its solution would not be an entirely simple matter. There are ways of obtaining this information, that is of determining the relative molecular weights of compounds, and there are other experiments which throw light upon the relative weights of the atoms directly. These methods cannot be described until the facts upon which they rest have been studied. It will be sufficient for the present to assume that these methods are trustworthy.

Standard for Atomic Weights. The figures following the symbols of the elements in the table on the front cover of the book give the relative weights of the atoms of the elements. They are not weights in grams or any other system of units. They merely mean that if we were to assign the arbitrary value of one unit of any kind to the atom of hydrogen, we should have to give the value 55.6 to the atom of iron, 31.83 to the atom of sulphur, etc. Whatever may be the actual weight of the atom of hydrogen and of the atom of iron, the ratio of their weights is 1 : 55.6.

Since the atomic weights are merely relative to some one element chosen as a standard, it is evident that any one of the elements may serve as this standard, and that any convenient value may be assigned to its atom. At one time oxygen was taken as the standard with the value 100 and the other elements were given weights to agree with this. It would seem to be more rational to take the element of smallest atomic weight as the standard, and give it unit value; accordingly hydrogen is assumed as the standard, with an atomic weight of 1. On this basis oxygen is 15.88. For many reasons oxygen serves better as a standard, and if the value 16 is given to it, hydrogen becomes 1.008. There is little difference in the two sets of values which will be obtained from these two standards, and since the reason for assuming hydrogen as the unit is a little easier to understand, we shall keep it as the standard in the chapters which follow.

CHAPTER VI.

CHEMICAL EQUATIONS AND CALCULATIONS.

Formulas. Since the molecule of any chemical compound consists of a definite number of atoms, and this number never changes without destroying the identity of the compound, it is very convenient to represent the composition of a compound by indicating the composition of its molecules. This can easily be done by using the symbols of the atoms to indicate the number and the kind of the atoms which constitute the molecule. HgO will in this way represent mercuric oxide, a molecule of which has been found to contain one atom each of mercury and oxygen. H_2O will represent water, the molecules of which consist of one atom of oxygen and two of hydrogen, the subscript figure indicating the number of the atoms of the element whose symbol precedes it. H_2SO_4 will stand for sulphuric acid, the molecules of which contain two atoms of hydrogen, one of sulphur and four of oxygen. The combination of symbols which represents the molecule of a substance is called its formula.

Equations. When a given substance undergoes a chemical change, it is possible to represent this change by the use of such symbols and formulas. It has already been seen that mercuric oxide decomposes when heated to form mercury and oxygen. This may be expressed very briefly in the form of an equation:

$$(1) \quad HgO = Hg + O.$$

When water is electrolyzed, two new substances, hydrogen and oxygen, are formed from it. This statement in the form of an equation is:

$$(2) \quad H_2O = 2H + O.$$

The coefficient before the symbol for hydrogen indicates that a single molecule of water yields two atoms of hydrogen on decomposition. In like manner the combination of sulphur with iron is expressed by the equation:

$$(3) \quad Fe + S = FeS.$$

The decomposition of potassium chlorate by heat takes place as represented by the equation:

$$(4) \quad KClO_3 = KCl + 3\ O.$$

Reading of Equations. Since equations are simply a kind of short hand way of indicating chemical changes which occur under certain conditions, in reading an equation the full statement for which it stands should be given. Equation (1) should be read "mercuric oxide when heated gives mercury and oxygen." Equation (2) is equivalent to the statement "when electrolysed, water produces hydrogen and oxygen." Equation (3), "when heated together, iron and sulphur unite to form iron sulphide;" equation (4), "potassium chlorate when heated yields potassium chloride and oxygen."

How Equations are Derived. In order to write such equations correctly a considerable amount of exact knowledge is required. Thus in equation (1) the fact that red oxide of mercury has the composition represented by the formula HgO, that it is decomposed by heat, that in this decomposition mercury and oxygen are formed and no other products — all these facts must be ascertained by exact experiment before the equation can be written. An equation expressing these facts will then have much value.

Having obtained an equation describing the conduct of mercuric oxide on being heated, it will not do to assume that similar oxides will behave in like manner. Iron oxide, FeO, resembles mercuric oxide in many respects, but it undergoes no change at all when heated. Manganese dioxide, the black substance used in the preparation of oxygen, has the formula MnO_2. When this substance is heated, oxygen is set free, but none of the metal manganese is formed. Instead a different oxide of manganese containing less oxygen is produced. The equation representing the reaction is:

$$3MnO_2 = Mn_3O_4 + 2O.$$

Substitution. The equations so far considered, represent the simple union of two elements, or the decomposition of a compound into other substances. It is sometimes possible for an element in the free state to act in such a way upon a compound that it takes the place of one of the elements of the compound, liberating it in turn. In the study of the element hydrogen it was pointed out that hydrogen is most easily prepared by the action of sulphuric or hydrochloric acid upon zinc. When sulphuric acid is used, a substance called zinc sulphate, having the composition represented by the formula $ZnSO_4$ is formed, together with hydrogen. The equation is:

$$(5) \quad Zn + H_2SO_4 = ZnSO_4 + 2H.$$

When hydrochloric acid is used, zinc chloride and hydrogen are the products of reaction.

$$(6) \quad Zn + 2HCl = ZnCl_2 + 2H.$$

These two reactions are quite similar as is apparent from an examination of the two equations. In both cases an atom of zinc replaces two atoms of hydrogen in the acid, and the hydrogen escapes as a gas. When an element in the free state, such as zinc, takes the place of some one element in a compound, setting it free from chemical combination, the act is called substitution.

Other reactions illustrating substitution are the action of sodium on water,

$$(7)\quad \mathrm{Na} + \mathrm{H_2O} = \mathrm{NaOH} + \mathrm{H}$$

and the reaction of water upon heated iron:

$$(8)\quad 3\mathrm{Fe} + 4\mathrm{H_2O} = \mathrm{Fe_3O_4} + 8\mathrm{H}.$$

Double Decomposition. When barium dioxide, which has the composition represented by the formula BaO_2, is treated with sulphuric acid, two compounds are formed, viz., hydrogen dioxide, H_2O_2, and barium sulphate, $BaSO_4$. The equation is

$$(9)\quad \mathrm{BaO_2} + \mathrm{H_2SO_4} = \mathrm{BaSO_4} + \mathrm{H_2O_2}.$$

In this reaction it will be seen that the two elements barium and hydrogen simply exchange places. Such a reaction is called a double decomposition or metathesis. We shall meet with many examples of this kind of chemical reactions.

These four kinds of chemical reactions, viz., direct combination, decomposition, substitution and double decomposition, are the most common types of chemical reactions.

Chemical Equations are Quantitative. The use of symbols and formulas in expressing chemical changes has another great advantage. Thus according to the equation, $H_2O = 2\,H + O$, 1 molecule of water is decomposed into 2 atoms of hydrogen and 1 atom of oxygen. But as already stated, the relative weights of the atoms are known, that of hydrogen being 1 while that of oxygen is 15.88. The molecule of water being composed of 2 atoms of hydrogen and 1 atom of oxygen must therefore weigh relatively $2 + 15.88$ or 17.88. The amount of hydrogen in this molecule must therefore be $\frac{2}{17.88}$ or 11.18% of the whole while the amount of oxygen must be $\frac{15.88}{17.88}$ or 88.82% of the whole. Now since any amount of water is simply the sum of a certain number of molecules of water, it is plain that the numbers representing the relative amounts of hydrogen and oxygen present in a molecule must likewise express the relative amounts of hydrogen and oxygen present in any quantity of water. Thus for example, in 20 grams of water there are $\frac{2}{17.88} \times 20$ or 2.236 grams of hydrogen and $\frac{15.88}{17.88} \times 20$ or 17.764 grams of oxygen. It will be observed that these results in reference to the composition of water express the facts obtained by direct experiment as given in the chapter on water.

It may be easier for some students to make the above calculation by proportion. Since the molecule of water and the two atoms of hydrogen which it contains have the ratio by weight of 17.88 : 2, any mass of water has the same ratio between its total weight and the weight of the hydrogen in it. Hence to find the number of grams (x) of hydrogen in 20 grams of water, we have the proportion

17.88 : 2 :: 20 grams : x (grams of hydrogen).

Solving for x we get 2.236 for the number of grams of hydrogen. Similarly to find the amount (x) of oxygen present in the 20 grams of water we have the proportion

$$17.88 : 15.88 :: 20 : x$$

from which we find that $x = 17.764$ grams.

Again, suppose we wish to find how much oxygen can be obtained from 15 grams of mercuric oxide. The equation representing the decomposition of mercuric oxide is $HgO = Hg + O$. The relative weights of the mercury and oxygen atoms are in round numbers respectively 199 and 16. The relative weight of the mercuric oxide molecule must therefore be the sum of these, or 215. The molecule of mercuric oxide and the atom of mercury which it contains have the ratio 215:16. This same ratio must therefore hold between the weight of any given quantity of mercuric oxide and the oxygen which it contains. Hence to find the weight of oxygen in 15 grams of mercuric oxide we have the proportion 215 : 16 :: 15 : x (grams of oxygen).

On the other hand suppose we wish to prepare say 20 grams of oxygen. The problem is to find out what quantity of mercuric oxide will yield 20 grams of oxygen. The following proportion evidently holds good:

215 : 16 : : x (grams of mercuric oxide) :20,

from which we get $x = 268.7$.

In the preparation of hydrogen by the action of sulphuric acid upon zinc, according to the equation

$$Zn + H_2SO_4 = ZnSO_4 + 2H,$$

suppose that 50 grams of zinc are available; let it be required to calculate the weight of hydrogen which can be obtained. It will be seen that one atom of zinc will liberate two atoms of hydrogen. The ratio by weight of a zinc to an hydrogen atom is 65 : 1; of a zinc atom to two hydrogen atoms, 65 : 2. Zinc and hydrogen will be related in this reaction in this same ratio, however many atoms of zinc are concerned. Consequently in the proportion

$$65 : 2 :: 50 : x,$$

x will be the amount of hydrogen set free by 50 grams of zinc. The amount of zinc sulphate produced at the same time can be found from the proportion 65 : 161 :: 50 : x, where 161 is the molecular weight of the zinc sulphate, and x the weight of zinc sulphate formed. In like manner the amount of sulphuric acid used up can be calculated from the proportion

$$65 : 98 :: 50 : x.$$

These simple calculations are possible because the symbols and formulas in the equations represent the relative quantities of substances concerned in a chemical reaction. When once the relative weights of the atoms have been determined, and it has been agreed to allow the symbols to stand for these relative weights, an equation or formula making use of the symbols becomes a statement of a definite numerical fact, and calculations can be based on it.

Chemical Equations Not Algebraic. Although chemical equations are quantitative, it must be clearly understood that they are not algebraic. A glance at the equations $7 + 4 = 11$, $8 + 5 = 9 + 4$ will show at once that they are true. The equations $HgO = Hg + O$, $FeO = Fe + O$ are equally true in an algebraic sense, but experiment shows that only the first is true chemically. Only such equations as have been found by careful experiment to express a real chemical transformation, true both for the kinds of substances as well as for the amounts, have any value.

Chemical formulas and equations therefore, are a concise way of representing qualitatively and quantitatively facts which have been found by experiment to be true in reference to the composition of substances and the changes which they undergo.

Heat of Reaction. Attention has frequently been directed to the fact that chemical changes are usually accompanied by heat changes. In general it has been found that in every chemical action heat is either absorbed or given off. The equations so far employed take no notice of these heat changes; and in order to record them it is first necessary to find a way to measure heat accurately. This cannot be done by the use of a thermometer alone, since the thermometer measures the intensity of heat, not its quantity.

The easiest way to measure a quantity of heat is to note how warm it will make a definite amount of a given substance chosen as a standard. Water has been chosen as the standard and the unit of heat, called a calorie, is defined as the amount of heat required to raise the temperature of 1 gram of water from 0° to 1°.

By means of this unit it is easy to indicate the heat changes in a given chemical reaction. The reaction

$$2\ H + O = H_2O + 68300\ \text{cal},$$

means that when 2 grams of hydrogen combines with 15.88 grams of oxygen, to form 17.88 grams of water, 68300 units of heat are set free.

$$C + 2S = CS_2 - 19000 \text{ cal.}$$

means that an expenditure of 19000 heat units is required to cause 12 grams of carbon to unite with 64 grams of sulphur, to form 76 grams of carbon disulphide.

Conditions of a Chemical Action not Indicated by Equations. Equations do not tell the conditions under which a reaction will take place. The equation

$$HgO = Hg + O$$

does not tell us that it is necessary to keep the mercuric oxide at a high temperature that the decomposition may go on. The equation

$$Zn + 2\ HCl = ZnCl_2 + 2\ H$$

in no way indicates the fact that the hydrochloric acid must be dissolved in water before it will act upon the zinc. From the equation

$$H + Cl = HCl$$

it would not be suspected that the two gases hydrogen and chlorine will unite instantly in the sunlight, but will stand mixed in the dark a long time without change. It will therefore be necessary to pay much attention to the details of the conditions under which a given reaction occurs, as well as to the expression of the reaction in the form of an equation.

CHAPTER VII.

NITROGEN AND THE RARE ELEMENTS, ARGON — NEON — HELIUM — KRYPTON — XENON.

Historical. Nitrogen was discovered by the English chemist Rutherford in 1772. A little later Scheele showed it to be a constituent of air and Lavoisier gave it the name azote, signifying that it would not support life. The name nitrogen was afterwards given it because of its presence in saltpetre or nitre. The term azote and symbol Az are still retained by the French chemists.

Occurrence. Attention has already been called to the fact that the air is composed principally of oxygen and nitrogen in a free state, about 78 parts by volume out of every 100 parts being nitrogen. Nitrogen also occurs in nature in the form of potassium nitrate, KNO_3, (commonly called saltpetre or nitre) as well as in sodium nitrate, $NaNO_3$. Nitrogen is also a necessary constituent of living forms of matter.

Methods of Preparation.

1. *Preparation from Air.* Usual laboratory method. Nitrogen is commonly prepared in the laboratory by removing the oxygen from a confined portion of air. This may be done by burning some substance in the confined air which has a very strong affinity for oxygen. Such a substance must be chosen however as will combine with the oxygen to form a product which is not a gas; otherwise the nitrogen present will be mixed with the gaseous products of combustion. The substance ordinarily used is phosphorus. This is placed in a little porcelain dish attached to a cork

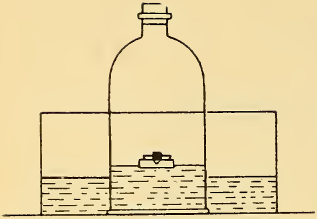


Fig. 25

and floated on water. (Fig. 25.) It is then ignited by contact with a hot wire and immediately a bell jar or bottle is brought over it so as to confine a portion of the air. The phosphorus combines with the oxygen to form an oxide of phosphorus known as phosphorus pentoxide. This is a white solid which floats about in the bell jar but on standing is all absorbed by the water, leaving the nitrogen. The withdrawal of the oxygen is indicated by the rising of the water in the bell jar.

The oxygen present in the air may also be removed by passing air slowly through a heated tube containing copper. The copper combines with the oxygen to form copper oxide.

Inasmuch as air, in addition to oxygen and nitrogen contains small amounts of other gases, and since the phosphorus as well as the copper removes only the oxygen, it is evident that the nitrogen obtained by this method is never quite pure. About 1% of the product is composed of other gases from which it is very difficult to separate the nitrogen. The nitrogen so obtained however may be used for a study of some of its properties since these are not materially affected by the presence of the other gases.

2. *Preparation from Compounds of Nitrogen.* Pure nitrogen may be obtained from certain compounds of the element. Thus if heat is applied to the compound, ammonium nitrite, NH_4NO_2, the change represented in the following equation takes place:

$$NH_4NO_2 = 2H_2O + 2N.$$

Physical Properties. Nitrogen is similar to oxygen and hydrogen in that is a colorless, odorless and tasteless gas. 1 liter of it weighs 1.2501 grams; hence it is about 14 times as heavy as hydrogen and slightly lighter than oxygen. It can be obtained in the form of a colorless liquid having a boiling point of –195°. At –214° it becomes a solid.

Chemical Properties. Nitrogen is characterized by its inertness. It has but slight activity even when heated to high temperatures. It is neither combustible nor a supporter of combustion. At ordinary temperatures it will not combine directly with any of the elements. At higher temperatures it combines with magnesium, lithium, titanium and a few other elements. The compounds formed are called nitrides, just as compounds of an element with oxygen are called oxides. When mixed with oxygen and subjected to the action of electric sparks combination slowly takes place with the formation of oxides of nitrogen. A mixture of nitrogen and hydrogen when treated similarly forms ammonia, a gaseous compound of nitrogen and hydrogen.

Since we are constantly inhaling nitrogen, it is evident that it is not poisonous. Nevertheless life would be impossible in an atmosphere of pure nitrogen on account of the exclusion of the necessary oxygen.

Argon, Neon, Helium, Krypton, Xenon. These are all rare elements, recently discovered in the atmosphere, in which they occur in very small quantities. Argon, discovered in 1894, was the first one obtained. Lord Rayleigh, an English scientist, while engaged in determining the exact weights of various gases, observed that nitrogen obtained from the air is slightly heavier than the pure nitrogen obtained from its compounds. After repeating his experiments many times, always with the same results, Rayleigh finally concluded that the nitrogen obtained from the air is not pure, but is mixed with a small amount of some unknown gas, the density of which is greater than that of nitrogen. Acting on this assumption, Rayleigh, together with the English chemist Ramsay, attempted to separate the nitrogen from the unknown gas. Knowing that nitrogen would combine with magnesium, they passed the nitrogen obtained from the air and freed from all known substances, through tubes containing magnesium heated to the necessary temperature. After repeating this operation, they finally succeeded in obtaining from the atmospheric nitrogen a small volume of gas which would not combine with the magnesium and hence was not nitrogen. This proved to be a new element to which they gave the name argon. As predicted, this new element was found to be heavier than nitrogen, its density as compared with hydrogen as a standard being approximately 20, that of nitrogen being only 14. About 1% of the atmospheric nitrogen proved to be argon. The new element is characterized by having no affinity for other elements. Even under the most favorable conditions, it can not be made to combine with any other elements. On this account it was given the name argon, signifying "lazy" or "idle." Like nitrogen, it is colorless, odorless, and tasteless. It has been liquefied and solidified. Its boiling point is —187°.

The remaining elements of this group have been obtained from liquid air. Under the subject of distillation attention was called to the fact that by repeated distillation a mixture of liquids of different boiling points can be separated from each other. In this way, by liquefying air and then allowing it to boil, those constituents having the lowest boiling points, and hence the most difficult to liquefy, tend to escape first, followed by the others in the order of their boiling points. In this way Ramsay succeeded in obtaining from liquid air not only the known constituents, including argon and helium, but also the new elements neon, krypton and xenon. These new elements all proved to be similar to argon in that they are without chemical activity, apparently forming no compounds whatever. The amounts present in the air are very small.

Helium was first found in the gases expelled from certain minerals by heating. Through the agency of the spectroscope it had been known to exist in the sun long before its presence on the earth had been recognized—hence the name helium, signifying the sun. It is the only gas which has not yet been liquefied, so that its boiling point must be below that of hydrogen. The names, neon, krypton, xenon, signify respectively, "new," "hidden," "stranger."

CHAPTER VIII.

THE ATMOSPHERE.

Many references have already been made to the composition and properties of the atmosphere. These statements must now be collected and discussed somewhat more in detail.

The term atmosphere is applied to the gaseous envelope surrounding the earth. The term air is generally applied to a limited portion of this gas although often used synonomously with the term atmosphere.

Air Formerly Regarded as an Element. Like water air was at first regarded as elementary in character.. Near the close of the eighteenth century, Priestley, Lavoisier and Scheele showed by their experiments that it is a mixture of at least two gases, those which we now call oxygen and nitrogen. By burning substances in an enclosed volume of air and noting the contraction in volume due to the removal of the oxygen, they were able to determine with some accuracy the relative volumes of these gases present in the air.

The Constituents of the Atmosphere.

1. *Constituents Essential to Life.* In addition to oxygen and nitrogen at least two other substances, namely, carbon dioxide and water vapor must be present in the atmosphere in order that life may exist. The former of these is a gaseous compound of carbon and oxygen having the formula CO_2. Its properties will be discussed in detail in the chapter on the compounds of carbon. Its presence in the air may be shown by causing the air to bubble through a solution of calcium hydroxide, $Ca(OH)_2$, commonly called

lime water. The carbon dioxide combines with the calcium hydroxide in accordance with the following equation:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

The calcium carbonate, $CaCO_3$, is insoluble in water and separates in the form of a white powder which causes the solution to appear milky. The presence of water vapor is readily shown by its condensation on cold objects as well as by exposing a bit of dry calcium chloride to the air, sufficient moisture soon being absorbed to dissolve the chloride.

Function of Each of the Essential Constituents. The oxygen directly supports life through respiration. The nitrogen, on account of its inactivity, serves to dilute the oxygen, and while contrary to the older views, it is possible that life might continue to exist in the absence of the atmospheric nitrogen, yet the conditions of life would have to be entirely changed. Moreover, nitrogen is an essential constituent of all animal and plant life. It was formerly supposed that neither animals nor plants can assimilate the free nitrogen, but it has been shown recently that at least one order of plants, the leguminosiae, to which belong the beans and peas, has the power of directly assimilating the free nitrogen from the atmosphere.

The carbon dioxide in the air serves as a plant food. The plant absorbs it and decomposes it, utilizing the carbon in building up its tissues and liberating the oxygen. Water vapor is essential to both plants and animals, neither of which can exist for a long period in a perfectly dry atmosphere.

2. *Constituents not Essential to Life.* In addition to the oxygen, nitrogen, carbon dioxide and water vapor, the air contains small amounts of various other gases, the presence of which so far as known is not essential to life. This list includes the rare elements argon, helium, neon, krypton and xenon; also hydrogen, ammonia, hydrogen dioxide and probably ozone. Certain minute forms of life (germs)

are also present, the putrefaction of organic matter being due to their presence.

The Quantitative Analysis of Air. A number of different methods have been devised for the determination of the amounts of the constituents of the atmosphere. The most important of which are the following.

1. *Determination of Oxygen.*

a. The oxygen is withdrawn from a measured volume of air inclosed in a tube, by means of phosphorus. To make the determination, a graduated tube is filled with water and inverted in a vessel of water. Air is now introduced into the tube until it is partially filled with the gas. The volume of the inclosed air is carefully noted and reduced to standard conditions. A small piece of phosphorus is attached to a wire and brought within the tube as shown in Fig. 26. After a few hours the oxygen in the enclosed air will have combined with the phosphorus, the water rising to take its place. The volume is again noted and reduced to standard conditions. The contraction in the volume of the air is equal to the volume of oxygen absorbed.

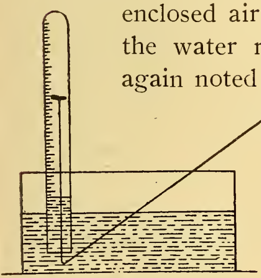


Fig. 62

b. The oxygen may also be removed from a measured volume of air by passing it through a tube containing copper heated to a high temperature. The oxygen in the air combines with the copper to form copper oxide, CuO. Hence the increase in the weight of the copper equals the weight of the oxygen in the volume of air taken.

c. A more accurate method is the following.

A eudiometer tube is filled with mercury and inverted in a vessel of the same liquid. A certain amount of air is then introduced into the tube and the volume accurately noted. There is then introduced more than sufficient hydrogen to combine with the oxygen present in the enclosed air, and the volume again accurately noted. The mixture is then exploded by an electric spark, and the volume is again taken. By subtracting this volume from the total volume of the air and hydrogen there is obtained the contraction in volume due to the union of the oxygen and hydrogen. The volume occupied by the water formed by the union of the two gases is so small in comparison with the volume of the gases which combined to form it that it may be disregarded altogether. It is evident then that the contraction in volume due to the combination is equal to the volume occupied by the oxygen in the air in the tube plus twice this volume of hydrogen; in other words one-third of the total contraction is equal to the volume occupied by the oxygen in the enclosed air. The following example will make this clear.

Volume of air in tube - - - - - - -	50 c.c.
Volume after introducing hydrogen - - - -	80 c.c.
Volume of hydrogen introduced=80—50 - - -	30 c.c.
Volume after combination of oxygen and hydrogen -	48.5 c.c.
Contraction in volume due to combination=80—48.5	31.5 c.c.
Volume of oxygen in 50 c.c. of air=$\frac{1}{3}$ of 31.5 - -	10.5 c.c.

The results obtained by these methods show that 100 volumes of air contain approximately 21 volumes of oxygen.

2. *Determination of Nitrogen.*

By passing the gas left after the removal of the oxygen over heated magnesium the nitrogen is withdrawn, argon and the other rare elements being left. It may thus be shown that of the 79 volumes of gas left after the removal of the oxygen from 100 volumes of air, approximately 78 are nitrogen and 0.93, argon, the other elements being present in such small quantities that they may be neglected.

3. *Determination of Carbon Dioxide.*

The amount of carbon dioxide present in the air may be determined by absorbing it with calcium hydroxide or some similar compound, the increase in weight being equal to the carbon dioxide absorbed. The amount present in the open normal air is from 3 to 4 parts in 10,000.

4. *Determination of Water Vapor.*

The water vapor may be determined by absorbing it with calcium chloride or some other good drying agent. The amount of it present varies not only with the locality but also varies greatly from day to day in the same locality, because of changes in temperature and the winds.

Air a Mechanical Mixture. The results of a great many such analyses have shown that the composition of the air, apart from water vapor, is very nearly constant. Even when collected from widely differing localities, and at all seasons of the year, it is almost exactly the same in composition, and would therefore appear to be a definite chemical compound. If it is a mechanical mixture, its composition should vary from place to place, and from season to season, for there are many processes going on in nature which would tend to change the proportion of its constituents.

That air is a mixture and not a compound can be shown in a number of ways among which are the following:

1. Water dissolves oxygen and nitrogen from the air in an entirely different proportion from that in which they are present in the air. This would not be the case if the two were combined.

2. A chemical compound in the form of a liquid has a definite boiling point. Water for example boils at 100°. Moreover the steam which is thus formed has the same composition as the water. The boiling point of liquid air on the other hand gradually rises as the liquid boils, the

nitrogen escaping first followed by the oxygen. If the two were combined, they would pass off together in the proportion in which they are found in the air.

The surprising constancy in the composition of the air is explained by several facts. The winds keep the air in constant motion, and so prevent local changes. The volume of the air is so vast that any changes which do occur are very small compared with the total amount of the air, and cannot be noticed. The changes occasioned by living organisms which are discussed in the next paragraph tend to balance each other to quite an extent.

Changes in the Atmosphere due to Respiration and Combustion. In the process of respiration, the oxygen in the inhaled air is absorbed by the blood and carried to all parts of the body, where it combines with the carbon of the worn out tissues. The products of oxidation are carried back to the lungs and exhaled in the form of carbon dioxide. All the ordinary forms of fuel contain large percentages of carbon. On burning, this carbon combines with the oxygen in the air forming carbon dioxide. Evidently in these two processes large amounts of oxygen are withdrawn from the atmosphere and returned to it in the form of carbon dioxide. This in itself would cause a diminution in the percentage of free oxygen present.

Plants however have the power, in the sunlight, of absorbing this carbon dioxide, retaining the carbon and returning the oxygen once more to the air, so that these two processes largely balance each other.

While air collected in the open fields shows a practically uniform composition, the case is different when it is collected from a closed or poorly ventilated room, occupied by a number of persons. Such air shows a rapid rise in the amount of carbon dioxide present. While this gas is not to be regarded as poisonous unless present in large amounts, nevertheless air containing more than 15 parts in 10,000, is not fit for respiration.

Along with the carbon dioxide a certain amount of organic matter is exhaled, which imparts to the respired air its foul odor. It is probable that this organic matter rather than the carbon dioxide is responsible for the injurious effects which follow the respiration of impure air. The extent of such impurities present may be judged however from the amount of carbon dioxide present, since the two are exhaled together.

The Properties of the Atmosphere. Inasmuch as the atmosphere is composed principally of a mixture of oxygen and nitrogen, which elements have already been discussed, its properties may largely be inferred from those of the two gases. 1 liter of it weighs 1.292 grams. It is thus 14.4 times as heavy as hydrogen. At the sea level it exerts an average pressure sufficient to sustain a column of mercury 760 mm. in height. This is taken as the standard pressure in determining the weights of gases as well as the boiling points of liquids. Water may be made to boil at any temperature between 0° and considerably above 100° by simply varying the pressure. It is only when the pressure upon it is equal to the normal pressure of the atmosphere at the sea level as indicated by a barometric reading of 760 mm. that it boils at 100°.

Liquid Air. Attention has already been called to the fact that both oxygen and nitrogen can be obtained in the liquid state by strongly cooling the gases and applying great pressure to them. Air being a mixture of these two gases can naturally be liquefied by the same methods.

Recently the methods for liquefying air have been much simplified in that artificial cooling is dispensed with, the temperature being reduced sufficiently by allowing a portion of the compressed air to expand. The expansion of a gas is always attended by the absorption of heat. In liquefying air the apparatus is so constructed that the heat absorbed is withdrawn from air already under great pressure. This process is continued until the temperature is lowered to the point of liquefaction.

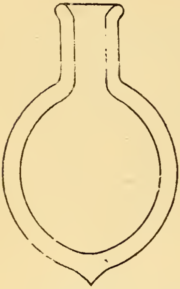


Fig. 27

It is not possible to preserve air in a liquid state by confining it, on account of the enormous pressure exerted by it in its tendency to pass into the gaseous state. It may be preserved for some hours or even days before it will completely evaporate, by simply placing it in an open vessel surrounded by a non-conducting material. The most efficient vessel for retaining it is the "Dewar bulb" shown in Fig. 27. The air is withdrawn from the space between the two walls thus making it non-conducting. One liter of liquid air placed in such a bulb may be preserved nearly two weeks before complete evaporation takes place.

When first prepared, liquid air is cloudy because of the presence of particles of solid carbon dioxide. These may be filtered off, leaving a liquid of slightly bluish color. It begins to boil at about —190°, the nitrogen passing off first gradually followed by the oxygen, the last portions being nearly pure oxygen. In this way oxygen is now prepared commercially.

Liquid air is also used as a cooling agent in the study of the properties of matter at low temperatures. It has thus been found that elements at extremely low temperatures largely lose their chemical activity.

The extremely low temperature of liquid air may be inferred from the fact that mercury when subjected to its action is frozen to a mass so hard that it may be used for driving nails.

CHAPTER IX.

SOLUTIONS.

It has been seen that when a substance disappears in a liquid in such a way as to thoroughly mix with it and be lost to sight as an individual body, the resulting product is called a solution. We shall frequently meet with two kinds of solutions and a brief study of them will be of advantage at this point.

I. Solution of Gases in Liquids. It has already been stated that oxygen, hydrogen and nitrogen are slightly soluble in water; accurate study has led to the conclusion that all gases are soluble to some extent not only in water, but in many other liquids. The amount of a gas which will dissolve in a liquid depends upon a number of conditions, and these can best be understood by supposing the gas to be confined over the liquid in such a way that it cannot escape or be displaced by another gas. Fig. 28 represents a gas confined in this way in a bell jar, which is inverted and placed over a liquid. The following conditions will determine how much of the gas will dissolve in the liquid.

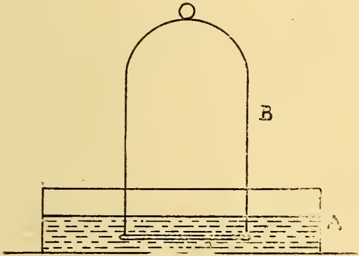


Fig. 28

(a) *Nature of the Gas.* Other conditions being equal some gases are much more soluble than others, so that each gas has its own peculiar solubility just as it has its own especial taste or odor. The solubility of gases varies between wide limits as will be seen from the following table, but as a rule a given volume of a liquid will not dissolve more than two or three times its own volume of a gas.

SOLUBILITY OF GASES IN WATER.

1,000 c.c. of water at 760 mm. pressure and at 0° will dissolve

Ammonia	1148.	liters
Hydrochloric acid	503.	liters
Sulphur dioxide	79.79	liters
Carbon dioxide	1.8	liters
Oxygen	41.14	c.c.
Hydrogen	21.15	c.c.
Nitrogen	20.03	c.c.

In the case of very soluble gases, such as the first three in the table, it is probable that feeble chemical combination between the liquid and the gas takes place.

(b) *Nature of the Liquid.* The character of the liquid has much influence upon the solubility of a gas. Water, alcohol, ether, each has its own peculiar solvent power. From the solubility of a gas in water, no prediction can be made as to its solubility in other liquids.

(c) *Influence of Pressure.* It is found that the amount of gas which dissolves in a given case is proportional to the pressure exerted upon the gas. If the pressure is doubled, the amount of gas going into solution is doubled; if the pressure is diminished to one-half of its original value, half of the dissolved gas will escape. Under high pressure, large quantities of gas can be dissolved in a liquid, and when the pressure is removed the gas escapes, causing the liquid to foam or effervesce. It is the sudden release of the pressure upon liquids containing carbon dioxide which causes the effervescence of soda water and similar substances.

(d) *Influence of Temperature.* In general, the lower the temperature of the liquid, the larger the amount of gas which it is able to dissolve. 1000 volumes of water at 0° will dissolve 41.14 volumes of oxygen; as the temperature rises, the amount of oxygen remaining in solution becomes less and less until at the boiling point all the oxygen is expelled.

II. Solutions of Solids in Liquids. *Physical and and Chemical Solutions.* The distinction between chemical and physical solutions must be carefully noted. We speak of dissolving zinc in sulphuric acid and likewise of dissolving salt in water, but these two acts are quite different. On evaporating the solution of salt, the salt is recovered entirely unchanged; by evaporating the solution of zinc in sulphuric acid it is impossible to regain the zinc. In its place is obtained a soft, white substance, bitter in taste, easily soluble in water — in short with properties entirely different from those of the original zinc.

The solution of the zinc was preceded by a chemical change which converted the zinc into another substance, zinc sulphate, which then dissolved in the water. Solutions of this kind are called chemical solutions, because accompanied by chemical changes in the substance dissolved. Solutions like that of salt in water, in which the dissolved substance can be recovered unchanged by evaporating the solvent, are called physical solutions, and it is with them that we are now concerned.

Circumstances Affecting the Solubility of a Solid.

(a) *Nature of the Solid.* Other conditions being the same, solids vary greatly in their solubility in liquids. Some are very soluble, others moderately so, while still others are said to be insoluble. Thus 100 parts of water at 18° will dissolve:

Calcium chloride	71.	parts
Sodium chloride	35.9	parts
Potassium nitrate	29.1	parts
Copper sulphate	21.4	parts
Calcium sulphate	0.207	parts

None are absolutely insoluble, but the amount dissolved may be so small as to be of no significance for most purposes. Thus barium sulphate, one of the most insoluble of common substance, dissolves in water to the extent of 1 part in 400,000.

(b) *Nature of Solvent.* Liquids vary much in their ability to dissolve solids. Some are said to be good solvents, since they dissolve a great variety of substances, and considerable quantities of them. Others have small solvent power, dissolving few substances, and those to but a slight extent. Broadly speaking, water is the most general solvent, and alcohol is perhaps second in solvent ability.

(c) *Temperature.* The amount of solid which a given liquid can dissolve varies with the temperature. Usually it increases rapidly as the temperature rises, so that the boiling liquid dissolves several times the amount which the cold liquid will dissolve. In some instances, as in the case of common salt dissolved in water, the temperature has little influence upon the solubility, and a few solids are more soluble in cold water than in hot. The following examples will serve as illustrations:

TABLE OF SOLUBILITY AT 0° AND AT 100°.

100 parts of water will dissolve

	at 0°		at 100°	
Calcium chloride	49.6	....	155.	parts
Sodium chloride	35.7	....	39.8	parts
Potassium nitrate ...	13.3	....	247.	parts
Copper sulphate	15.5	....	73.5	parts
Calcium sulphate	0.205	....	0.217	parts

Saturated Solutions. A liquid will not in general dissolve an unlimited amount of a solid. It becomes saturated, and when this point is reached no more of the solid will dissolve at that temperature. It is possible therefore to determine accurately the solubility of a substance for any given temperature. The liquid will however dissolve any quantity of the solid which is less than the amount required for saturation, and in this respect a solution differs very strikingly from a chemical compound in which, as we have seen, the constituents combine in certain definite proportions and in no others.

Crystallization. When a hot, saturated solution is allowed to cool, some of the dissolved solid must in general separate from the solution; for as we have seen, solids are usually more soluble in hot liquids than in cold. Usually the substance separates in the form of solid particles of definite geometric form, called crystals, and the process just described is called crystallization. Sometimes it separates as a powder which may consist of minute crystals, or may be without crystalline form. In the latter case it is said to be amorphous.

General Physical Properties. (*a*) *Distribution of the Solid in the Liquid.* A solid, when dissolved, tends to distribute itself uniformly through the liquid so that every part of the solution has the same strength or concentration. This process goes on very slowly unless hastened by stirring or shaking the solution. Thus if a few crystals of a highly colored substance such as potassium permanganate are placed in the bottom of a tall vessel full of water, it will be seen that it takes a long time for the solution to become uniformly colored.

(b) *Boiling Point of Solutions.* The boiling point of a liquid is raised by the presence of a substance dissolved in it. In general the amount of elevation of the boiling point of a liquid, caused by a given substance, is proportional to the amount of the solid dissolved. The extent of this elevation may be considerable when the solid is very soluble. A saturated solution of calcium chloride for example boils at 179.5°.

(c) *Freezing Point of Solutions.* A solution freezes at a lower temperature than the pure solvent. The lowering of the freezing point obeys the same law which holds for the raising of the boiling point — the amount of lowering is proportional to the amount of dissolved substance, that is to the concentration of the solution. The fact that sea water is usually free from ice when fresh water near by is frozen over is in part due to the large amount of salt which the sea water contains.

Electrolytic Dissociation. A large number of facts which can not be taken up in an elementary course have led chemists to believe that many substances when in solution undergo an important change. A portion of their molecules fall apart or dissociate into two or more parts which have been named ions. Sodium nitrate, $NaNO_3$, for example dissociates into the ions Na and NO_3. These ions differ widely in properties from the elements or groups of elements, in that they are heavily charged with electricity. Thus in the dissociation of $NaNO_3$, the Na ion carries a positive charge of electricity while the NO_3 ion carries a negative charge. Moreover the positive charge carried by the Na ion is exactly equal to the negative charge carried by the NO_3 ion so that the solution as a whole is electrically neutral. Certain molecules may dissociate into more than two ions. Thus sodium sulphate, Na_2SO_4, dissociates into two Na ions and one SO_4 ion. In this case the positive charges carried by the two Na ions are exactly equal to the negative charges carried by the SO_4 ion. In the dissociation of compounds of the metals it is always the metal ion which carries the positive charge.

The dissociation of compounds is sometimes represented in the form of equations like the following which represents the dissociation of sodium nitrate:

$$NaNO_3 = \overset{+}{Na} + \overset{-}{NO_3}$$

The marks + and — indicate the character of the charges carried by the ions.

These ions are free to move about in a solution independently of each other and for this reason were given the name "ion" which signifies "a wanderer."

Electrolytes. Solutions differ much in their ability to conduct the electrical current. Some, such as a solution of sugar in water, do not conduct the current appreciably, while others, as for example a solution of salt in water, conduct it with great ease. A substance whose solution will conduct the current is called an electrolyte, and a close study of these electrolytes has shown that they are all substances which dissociate into ions in solution. This fact has suggested that it is the ions which carry the current through a solution, and that consequently a solution containing no ions cannot conduct the current.

Electrolysis. When an electrical current is passed through the solution of an electrolyte, some chemical change always takes place in the electrolyte and often in the solvent. This change is called electrolysis. The dissociation theory offers a simple explanation of the facts of electrolysis which will be easily understood by reference to the following diagram:

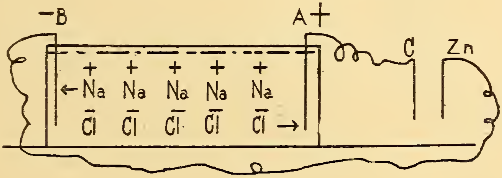


Fig. 29

When two electrodes, A and B in Fig. 29, are connected with the poles of a battery and placed in a solution of an electrolyte, the positive ions, called cations, are attracted to the negative electrode (cathode) and the negative ions, or anions, are attracted to the positive electrode (anode). On reaching the electrodes the ions are discharged and have then the properties of ordinary chemical substances. Thus if the electrolyte is sodium chloride dissolved in water, as represented in Fig. 29, the sodium ions on being discharged immediately attack the water, just as a bit of the metal sodium would do, and hydrogen is set free according to the equation $Na + H_2O = NaOH + H$

The chlorine ion, on being discharged, may either be given off as chlorine gas or may act upon the water as represented in the equation

$$2\ Cl + H_2O = 2\ HCl + O$$

In a similar way, sodium sulphate, Na_2SO_4, gives the ions $2Na$ and SO_4. On being discharged, the sodium atoms decompose water about the cathode as indicated above while the SO_4 ions when discharged at the anode decompose the water as represented in the equation

$$SO_4 + H_2O = H_2SO_4 + O$$

That NaOH is formed at the cathode and H_2SO_4 at the anode may be demonstrated in the following way: NaOH has the power to turn red litmus blue, while H_2SO_4 turns blue litmus red. A U-tube, such as is represented in Fig. 30, is partially filled with a solution of sodium sulphate, and the liquid in one arm is colored with red litmus, that in the other with blue litmus An electrode placed in the red solution is made to serve as cathode, while one in the blue solution is made the anode. On allowing the current to pass, the blue soturns red, indicating the formation of H_2SO_4 at the anode, while the red sotion turns blue, indicating the presence of NaOH at the cathode.

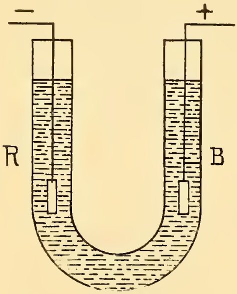


Fig. 30.

Electrolysis of Water. The reason for the addition of sulphuric acid to water in the preparation of oxygen and hydrogen by electrolysis will now be clear. Water itself is not an electrolyte, that is it does not form enough ions to carry a current. Sulphuric acid is an electrolyte, and in solution in water, dissociates into the ions 2 H and SO_4.

In the process of electrolysis of the solution, the hydrogen ions travel to the cathode and on being discharged escape as hydrogen gas. The SO_4 ions when discharged at the anode, act upon water, setting free oxygen and once more forming sulphuric acid.

$$SO_4 + H_2O = H_2SO_4 + O$$

The sulphuric acid can again dissociate, and the process repeat itself as long as any water is left. Hence the hydrogen and oxygen set free in the electrolysis of water really come directly from the acid, but indirectly from the water.

Although the theory of electrolytic dissociation may at first sight appear to be fanciful, it must be remembered that it is supported by a great many experimental facts, and it has very successfully stood the many tests which have been applied to it. The theory has been very useful in suggesting an explanation of many facts of chemistry which were formerly difficult to explain. It has also been of much value in leading to the discovery of new facts. In both respects therefore it has well served the purpose of a theory. We shall meet with many applications of the theory in subsequent pages.

CHAPTER X.

ACIDS, BASES, SALTS, VALENCE.

Acids. It is impossible to advance very far in the study of chemistry without meeting with substances called acids, and repeated mention has already been made of representatives of this class. The acids most frequently used in the laboratory are hydrochloric, nitric and sulphuric acids. These will be described in detail in subsequent chapters, but a few words concerning them are necessary at this place.

Hydrochloric acid is a gas composed of hydrogen and chlorine and has the formula HCl. It is very soluble in water, and it is this solution which is usually termed hydrochloric acid. Nitric acid is a substance composed of hydrogen, nitrogen and oxygen having the formula HNO_3. It is a heavy liquid, and as sold commercially contains about 32% of water. Sulphuric acid, whose composition is represented by the formula H_2SO_4, is an oily liquid nearly twice as heavy as water, and is commonly called oil of vitriol.

Properties Common to Acids. Acids have a number of properties in common. (1) They all contain hydrogen. (2) In dilute solution they have a sour taste recalling that of vinegar. (3) They have the property of changing the color of certain substances. Thus a solution of the blue coloring matter called litmus is turned red by even a trace of an acid; methyl orange is, in a similar way, changed from red to yellow. (4) The most important property of acids however, is their power to act chemically upon substances called bases. In this action the characteristic properties of both acid and base disappear, and substances with properties quite different from either of them are formed.

Bases. Among the members of this class commonly used in the laboratory are sodium hydroxide, $NaOH$, potassium hydroxide, KOH, and calcium hydroxide, $Ca(OH)_2$. These are white solids soluble in water, the calcium hydroxide being only sparingly so. Not all bases however are soluble in water. The strongest bases are sometimes called alkalies.

Properties Common to Bases. (1) Bases consist of a metallic element such as sodium, calcium, copper, iron, in combination with hydrogen and oxygen. (2) When soluble in water, they have a disagreeable, brackish taste. (3) They reverse the color change produced by acids, restoring the blue color to red litmus and the red color to methyl orange. (4) They have the power to act upon acids and in this reaction the peculiar properties of both acids and bases are lost.

Salts. When an acid acts upon a base, the hydrogen of the acid combines with the oxygen and hydrogen of the base to form water, while the remainder of the acid constituent combines with the metal of the base to form a substance called a salt. Thus sodium hydroxide acts with hydrochloric acid to form the salt sodium chloride, $NaCl$, and water as follows:

$$NaOH + HCl = NaCl + H_2O$$

Similarly calcium hydroxide acts with nitric acid to form the salt calcium nitrate, $Ca(NO_3)_2$ and water, the equation being,

$$Ca(OH)_2 + 2\ HNO_3 = Ca(NO_3)_2 + 2\ H_2O$$

This action of a base and an acid with each other is called neutralization. The products of neutralization are always a salt and water.

Properties Common to Salts. (1) A salt consists of a metal combined with the constituents of an acid other than its hydrogen. It may thus be regarded as derived from an acid by replacing the hydrogen of the acid with a metal. (2) They do not in general change the color of either red or blue litmus and for this reason are said to be neutral. (3) They have usually a salty or bitter taste quite different from the characteristic taste of acids and bases.

It is usually true that a base contains an equal number of atoms of oxygen and hydrogen and since these two elements nearly always act together in any chemical action which the base undergoes, the symbols of these elements are grouped together in writing the formula of the base. Thus the formula of calcium hydroxide is written $Ca(OH)_2$ rather than CaO_2H_2. Any group of elements which act together in this way is called a radical. Some of these radicals have been given names, the name signifying the elements present in the radical. Thus the group OH is called the hydroxyl radical.

Neutralization and the Dissociation Theory. The theory of electrolytic dissociation affords an interesting explanation of the facts of neutralization. Acids, bases and salts are all good electrolytes; that is their solutions are all good conductors of electricity. They are therefore substances which part, or dissociate, into ions when in solution in water. When acids dissociate the positive ion is always hydrogen, while the composition of the negative ion depends on the composition of the acid. Nitric, hydrochloric and sulphuric acids dissociate as indicated in the formulas;

$$\overset{+}{H},\ \overset{-}{NO_3} \qquad \overset{+}{H},\ \overset{-}{Cl} \qquad 2\overset{+}{H},\ \overset{--}{SO_4}$$

Bases dissociate into a positive metallic ion, and one or more negative hydroxyl ions as indicated in the formulas;

$$\overset{+}{Na},\ \overset{-}{OH} \qquad \overset{++}{Ca},\ 2(\overset{-}{OH})$$

In accordance with this view an acid may be defined as a substance which gives hydrogen ions in solution, while a base is a substance which gives hydroxyl ions in solution. Water is not appreciably dissociated, and whenever hydrogen and hydroxyl ions come together they unite to form undissociated water. Hence when solutions of an acid and base are mixed, the positive hydrogen ion of the acid and the negative hydroxyl ion of the base combine to form electrically neutral water, and the other ions remain unchanged. On driving off the water of the solution by evaporation, they gradually unite to form the neutral salt. The cause of the reaction is thus seen to be the formation of undissociated water from hydrogen and hydroxyl ions.

Metals. The elements fall naturally into two classes: (1) those which in combination with hydrogen and oxygen, form acids, and (2) those which, in combination with the same elements, form bases. The former are called non-metals; the latter, metals. Many of the metals are familiar substances, such as iron, copper, tin. They will be taken up for study after the non-metals have been considered. At present it need only be noted that they are a class of elements capable of forming bases when combined with hydrogen and oxygen, and of giving a positive ion when in solution.

Neutralization a Definite Act. The act of neutralization has been represented in a preceding paragraph by means of equations, and we have seen that equations should only be used to express a quantitative action between substances. The question therefore arises: Is neutralization a quantitative action between fixed amounts of acid and base? Many careful experiments have shown that it is. A definite amount of a base always requires exactly the same amount of a given acid for its neutralization. This can be demonstrated by weighing the substances which act upon each other; but it is more convenient to measure the volume of solutions of acid and base which are required for neutralization, having previously determined the strength of each solution. The experiment can be carried out as follows:

Prepare a solution of sodium hydroxide by diluting 20 c.c. of a 10% solution (the ordinary laboratory reagent) to 100 c.c.; also a solution of sulphuric acid by adding 1 c.c. of the strong acid to 100 c.c. of water. Fill two clean burettes with the two solutions, supporting them as shown in Fig. 31. By means of the stopcocks, draw off the solution in each burette until the level of the liquid is just at the zero mark. Now let exactly 15 c.c. of the acid flow into a small beaker, add a few drops of neutral solution of litmus, and then run in the alkali, drop by drop, stirring constantly with a glass rod. The instant the solution turns blue, stop adding the alkali, and note the amount which has been added. Repeat the experiment, using different amounts of the acid, say 10 c.c. and 20 c.c. Calculate in each case the amount of alkali required to neutralize 1 c.c. of the acid. It will be found that the same amount will be required in each case, showing that the act of neutralization is a definite one. If the strengths of the two solutions were accurately known, the amounts by weight of the acid and base could be readily calculated.

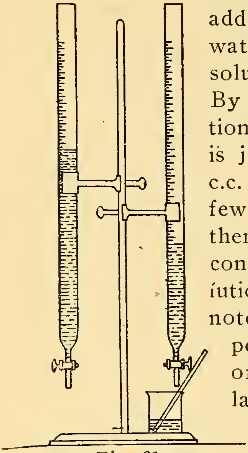


Fig. 31

Replacing Power of the Metals. The neutralization of some of the common acids by two of the most frequently used bases may be represented by the following equations:

$$NaOH + HCl = NaCl + H_2O$$
$$NaOH + HNO_3 = NaNO_3 + H_2O$$
$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$
$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$$
$$Ca(OH)_2 + 2\,HNO_3 = Ca(NO_3)_2 + 2\,H_2O.$$
$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2\,H_2O$$

A study of these reactions will show a singular fact. It appears that one atom of sodium can replace but a single atom of hydrogen in an acid, while an atom of calcium can replace two. A study of the metallic elements shows that they differ much in the number of hydrogen atoms which they are able to displace in an acid. Some are like sodium and can take the place of but a single hydrogen atom; some, like calcium, can replace two; still others can replace three. This peculiar property of the metals is called their replacing power. We have no knowledge as to why the atoms differ in this respect, and there is no way to tell how many hydrogen atoms a given metal will replace save by experiment.

Replacing Power of Metals and the Formulas of Salts. When the replacing power of a metal and the formula of an acid are known it is easy to predict the probable formula of the salt which the metal will form with the acid. Thus sodium can replace but a single hydrogen atom; consequently with the acids HCl, H_2SO_4, H_3PO_4, it gives the salts $NaCl$, Na_2SO_4, Na_3PO_4. Calcium can replace two hydrogen atoms, and the formulas of the calcium salts of the same acids will be $CaCl_2$, $CaSO_4$, $Ca_3(PO_4)_2$.

In writing the equation expressing the neutralization of an acid by a base, it is therefore necessary to take the two in such proportions that the replacing power of the metal atoms of the base will equal the hydrogen atoms of the acid. The correct formula of the salt will then be easily obtained.

Valence. Elements differ not only in the number of hydrogen atoms which they can displace from an acid, but also in the number of atoms of other elements which they are able to hold in combination. Thus we have the compounds represented by the formulas:

HCl, H_2O, H_3N, H_4C.

H_2O, CaO, Al_2O_3, CO_2, N_2O_5, SO_3.

It will be noticed that elements differ much in respect to the number of hydrogen atoms which they can hold in combination, and the same difference appears in regard to the oxygen atoms, as is seen in the formulas of the oxides.

That property of an element which determines the number of atoms of another element which it can hold in combination, is called its valence. Valence is strictly a numerical relation between the elements, and does not tell anything about the strength of the attraction between them. Thus oxygen has a far stronger attraction for hydrogen than does nitrogen, but it can only combine with two atoms of hydrogen whereas nitrogen can combine with three.

Measure of Valence. In expressing the valence of an element we must select some standard of value just as in the measure of any other numerical quantity. If we select the oxygen atom as a standard of valence, a glance at the formulas of the oxides given above will show that hydrogen will have a valence of $\frac{1}{2}$, calcium of 1, aluminium of $1\frac{1}{2}$. The atom of hydrogen never combines with more than one atom of another element, and therefore serves as a better standard. It is called a univalent element. That property of the metals which we have called their replacing power is thus seen to be their valence as indicated by the number of hydrogen atoms which an atom of the metal can replace in an acid.

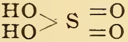
Elements like chlorine which combine with hydrogen to form compounds consisting of a single atom of each, such as HCl, are likewise said to be univalent. Elements such as oxygen, which combine with two hydrogen atoms, forming such compounds as H_2O, are said to be divalent; and in like manner there are elements which are trivalent, tetravalent, pentavalent. None have a valence of more than eight.

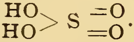
Many elements, especially among the metals, do not readily form compounds with hydrogen, and their valence is not easy to determine directly. They will, however, combine with other univalent elements, and their valence can be determined from these compounds.

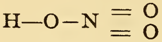
It will not do to assume that because the molecule of a compound is made up of a single atom of each of two elements, that each of these is univalent. Thus we have the compound CaO; but the formulas of the substances $CaCl_2$ and H_2O show that both calcium and oxygen are divalent.

Variable Valence. Many elements are able to exert different valences depending on circumstances. Thus we have the compounds Cu_2O and CuO; CO and CO_2; $FeCl_2$ and $FeCl_3$. It is not always possible therefore to assign a fixed valence to an element; but each element tends to exert some normal valence, and compounds in which it has a valence different from this are apt to be unstable and easily changed into the compounds of normal valence.

Structure of Compounds. It often happens that we cannot decide upon the valence of an element in a compound until we know how the atoms are arranged in the molecule. Thus in the compounds water and hydrogen dioxide, H_2O and H_2O_2, the oxygen appears to have the valences 2 and 1. If we know that the atoms are arranged as represented in the formulas H-O-H and H-O-O-H, it is evident that the oxygen has in each case a valence of two.

In such a compound as sulphuric acid, H_2SO_4, we must know much more than the mere formula tells us before we can draw conclusions as to the valence of the elements in it. If it is known that the atoms are arranged as represented in the formula  $\begin{matrix}HO\\HO\end{matrix}\!>S\begin{matrix}=O\\=O\end{matrix}$, the valence of the oxygen being two and that of the hydrogen one, the valence of the sulphur will be six.

It is quite possible to gain such information about compounds, and the formulas which express this knowledge are called *structural formulas.* The structural formula for sulphuric acid has been shown by many careful experiments to be  $\begin{matrix}HO\\HO\end{matrix}\!>S\begin{matrix}=O\\=O\end{matrix}$. The elements whose symbols are joined by lines are supposed to be directly combined with each other, and the number of lines leaving the symbol of an element, indicates the valence of the element. In a similar way calcium oxide may be represented by the formula $Ca = O$; sodium hydroxide by the formula $Na\text{-}O\text{-}H$; nitric acid by the formula



$$H{-}O{-}N\begin{smallmatrix}=O\\=O\end{smallmatrix}$$

It must constantly be remembered that such formulas have value only as they represent facts which have been established by experiment. It should be carefully noted also that valence itself is not a force or an attraction, and that two lines between two atoms, as in the formula $Ca{=}O$, does not mean that they are held together with double the attraction which unites the elements in the compound $H\text{-}Cl$, but merely that each of the elements is divalent.

Nomenclature of Acids, Bases and Salts. Acids, bases and salts are named in accordance with a few simple principles, the names being suggested by the characteristic elements in the compounds. The acids and salts are, for the purpose of naming, grouped in two classes; binary, or those containing but two elements, and ternary, or those containing three. Some contain more than three, but we shall meet very few of them.

Nomenclature of Binary Acids. A binary acid is named by combining the names of the elements composing it, so as to form a euphonious word, the termination "ic" being used. The word hydrogen is always abbreviated to "hydro," which is used as a prefix. Thus we have HCl, hydrochloric acid; H_2S, hydrosulphuric acid.

Nomenclature of Ternary Acids. In addition to the hydrogen present in all acids, nearly all of the ternary acids which we shall study also contain oxygen. In addition to the hydrogen and oxygen, each ternary acid contains a third element which gives its name to the acid, the termination "ic" being used. Thus HNO_3 is called nitric acid; H_2SO_4 is called sulphuric acid; $HClO_3$ is called chloric acid.

There may be more than one acid, however, composed of the same elements, but differing in the amounts of oxygen present. If two such acids are known, the one containing the smaller amount of oxygen has the termination "ous." Thus we have:

H_2SO_4.....sulphuric acid. HNO_3...........nitric acid.
H_2SO_3. . .sulphurous acid. HNO_2..........nitrous acid.

In some cases more than two acids are known differing only in the amount of oxygen present. In such cases the one containing less oxygen than the "ous" acid, takes the name of the "ous" acid with the prefix "hypo," while the one containing more oxygen than the "ic" acid, takes the name of the "ic" acid with the prefix "per." Thus the names and formulas of the four acids containing hydrogen, chlorine and oxygen are

$HClO$ . .hypochlorous acid. $HClO_3$ ......chloric acid.
$HClO_2$ .....chlorous acid. $HClO_4$ ....perchloric acid.

Nomenclature of Binary Salts. A binary salt is named from the elements composing it, the name of the non-metal receiving the termination "ide." Thus we have

$NaCl$ .....sodium chloride. Ag_2S .....silver sulphide.
KI .....potassium iodide. CaF_2 .....calcium fluoride.

Nomenclature of Ternary Salts. It has been stated that a salt may be regarded as derived from an acid by substituting a metal for its hydrogen. Ternary salts receive their names from the acids from which they may be regarded as derived, by changing the termination "ic" of the acid to "ate;" or in case it is derived from an "ous" acid, the "ous" is changed to "ite," the name of the metal being prefixed in either case. This method is illustrated in the following table, which gives the names and formulas of the ternary chlorine acids as well as the names and formulas of their corresponding sodium salts:

$HClO$ hypochlorous acid	$NaClO$ sodium hypochlorite
$HClO_2$ chlorous acid	$NaClO_2$ sodium chlorite
$HClO_3$ chloric acid	$NaClO_3$ sodium chlorate
$HClO_4$ perchloric acid	$NaClO_4$ sodium perchlorate

Nomenclature of Bases. The naming of bases or hydroxides, presents few difficulties, the name being made up of the name of the metal and the word hydroxide, e. g. sodium hydroxide, ($NaOH$). Some metals are able to form more than one hydroxide, since they can exercise two different valences. The base with the smaller number of hydroxyl groups adds the suffix -ous to the name of the metal, while the one with the larger number of hydroxyl groups adds -ic. Thus we have cuprous hydroxide, $Cu(OH)$, and cupric hydroxide, $Cu(OH)_2$; ferrous hydroxide, $Fe(OH)_2$, and ferric hydroxide, $Fe(OH)_3$.

Compounds of the metals, other than the hydroxides, are named in the same way, the suffix -ous indicating a smaller valence than the suffix -ic. Thus we have cuprous chloride, $CuCl$, and cupric chloride, $CuCl_2$; cuprous oxide, Cu_2O, and cupric oxide, CuO.

Acid, Basic and Normal Salts. It has been seen that in neutralization the hydrogen of an acid is replaced by a metal. When an acid has more than one hydrogen atom in it however, it is possible with proper care to replace only a part of the hydrogen. Thus sodium may replace only one of the hydrogen atoms of sulphuric acid, forming a compound of the formula $NaHSO_4$.

$$NaOH + H_2SO_4 = NaHSO_4 + H_2O$$

Such a substance is called an acid salt. It still contains hydrogen which is capable of forming an ion in solution, and is therefore an acid; part of the hydrogen of the acid has been replaced by a metal, and the substance formed is therefore a salt.

In a similar way, part of the hydroxyl groups of a base may be neutralized by an acid, and part remain unchanged. Thus we could have the reaction

$$Ca(OH)_2 + HCl = Ca(OH)Cl + H_2O$$

Such a substance is called a basic salt.

When all of the hydrogen of the acid is replaced by a metal, the product is called a normal salt. Examples of these are sodium sulphate, Na_2SO_4, potassium chloride, KCl, calcium nitrate, $Ca(NO_3)_2$. Normal salts are in general neutral in reaction. A few, however, are acid while others are basic.

CHAPTER XI.

COMPOUNDS OF NITROGEN.

Introduction. As has been already stated, nitrogen constitutes a large portion of the atmosphere. The compounds of nitrogen, however, can not readily be obtained from this source, since nitrogen does not combine directly with many of the elements except at high temperatures.

Combined with certain other elements, nitrogen occurs in the soil from which it is taken up by the plants and built into complex compounds composed chiefly of carbon, hydrogen, oxygen and nitrogen. Animals feeding on these plants assimilate the nitrogen, so that this element is an essential constituent of both plants and animals.

Decomposition of Organic Matter by Bacteria. All plants and animals then contain nitrogen as an essential element of their living matter. When the living matter dies, and undergoes decay, the carbon, hydrogen and oxygen are converted for the most part into carbon dioxide and water, while the nitrogen may appear either as free nitrogen or as ammonia, NH_3, or as oxides of nitrogen. In the latter case, the oxides of nitrogen are subsequently converted into nitrites or nitrates, which are respectively salts of nitrous and nitric acids.

It has been shown that all such processes of decay are due to the action of different kinds of bacteria, each particular kind effecting a definite change. The vast deposits of sodium nitrate which are found in warm, dry regions, especially in Chili and some parts of California, are thought to owe their origin to the decay of animal matter under the influence of these bacteria.

Decomposition of Organic Matter by Heat. When organic matter is strongly heated decomposition into simpler substances takes place, much as in the case of bacterial decomposition. If air is excluded, the nitrogen is liberated largely in the form of free nitrogen, although a considerable portion of it is combined with hydrogen to form ammonia. In the presence of plenty of air, oxides of nitrogen or nitric acid are formed. When coal, which is a complex substance of vegetable origin consisting largely of carbon, but also containing hydrogen, oxygen and nitrogen, is heated in a closed vessel, a part of the nitrogen present is changed into ammonia, and this is the chief source from which ammonia and its compounds are obtained.

I. Compounds of Nitrogen with Hydrogen. — Ammonia. Several compounds consisting exclusively of nitrogen and hydrogen are known, but only one, ammonia, need be considered here.

Preparation of Ammonia.

a. *Laboratory Method.* In the laboratory ammonia is prepared from ammonium chloride obtained in the manufacture of coal gas. When this substance is warmed with sodium hydroxide the reaction expressed in the following equation takes place:

$$NH_4Cl + NaOH = NaCl + NH_4OH$$

The ammonium hydroxide, NH_4OH, so formed is unstable, and breaks down into water and ammonia.

$$NH_4OH = NH_3 + H_2O$$

The two equations can be combined into one as follows:

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O$$

The cheaper calcium hydroxide, $Ca(OH)_2$, is frequently used in place of sodium hydroxide, the equation being

$$2\ NH_4Cl + Ca(OH)_2 = CaCl_2 + 2\ H_2O + 2\ NH_3$$

The ammonium chloride and calcium hydroxide are mixed together and placed in a flask arranged as shown in Fig. 32. The mixture is gently warmed, when ammonia gas is evolved, and being lighter than air, it is collected by upward displacement.

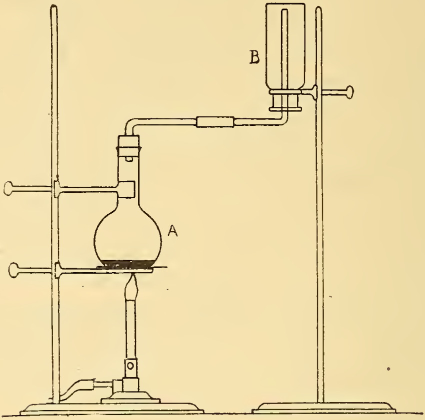


Fig. 32

Small amounts of ammonia can be made by passing electrical sparks through a mixture of hydrogen and nitrogen. The two elements combine directly. The action ceases however when a very small fraction of the two gases has combined, so that the method is not a practical one.

b. *Commercial Method.* Nearly all the ammonia of commerce comes from the gas works. Ordinary illuminating gas is made by heating coal in the absence of air. The product at first obtained contains a large number of compounds, solids, liquids and gases. The solids and liquids are removed by cooling the product. Among the gaseous products is ammonia. This is very soluble in cold water, while the gases valuable for illuminating purposes are not. The ammonia can therefore be separated from the other gases by passing the mixture through a vessel in which a spray of cold water plays upon the mixture, the ammonia being absorbed in the water. The liquid so obtained, called gas liquor, contains not only ammonia but other soluble substances. Most of these combine chemically with lime, while ammonia does not: if then lime is added to the gas liquor and the liquor is heated, the ammonia is driven out from it, being little soluble in hot water. It may be absorbed again in pure cold water forming the *aqua ammonia,* or ammonia water of commerce. More frequently it is absorbed in water containing sulphuric or hydrochloric acids; under these circumstances the ammonia combines with the acid to form respectively ammonium sulphate and ammonium chloride. These are solid compounds and can be obtained by evaporating the water and crystallizing out the salt.

Physical Properties. Under ordinary conditions ammonia is a gas whose weight compared with that of an equal volume of air is 0.59 — that is, it is little more than half as heavy as air. It is easily condensed into a colorless liquid, and can now be purchased in liquid form in stout vessels. The gas is colorless and has a strong, suffocating odor. It is extremely soluble in water, one liter of water at 0° and 760 mm. pressure dissolving 1,148 liters of the gas. In dissolving this large amount of gas the water expands considerably, so that the density of the solution is less than that of water, the strongest solutions having a density of 0.88. The solution is called aqua ammonia.

Chemical Properties. Ammonia will not support combustion, nor will it burn under ordinary conditions. In an atmosphere of oxygen it readily burns with a yellowish flame. When quite dry it is not a very active substance.

Ammonium Hydroxide. The solution of ammonia in water is found to have strong basic properties. It turns red litmus blue; it has a soapy feel; it neutralizes acids forming salts with them. We have seen that a study of bases has led to the conclusion that their chief characteristic is that they contain one or more hydroxyl groups which act as ions in solution. It seems probable therefore that when ammonia dissolves in water it combines chemically with it according to the equation

$$NH_3 + H_2O = NH_4OH$$

and that it is the substance NH_4OH, called ammonium hydroxide, which has the basic properties, dissociating into the ions NH_4 and OH.

The group of atoms or radical NH_4 plays the part of a metal and is called ammonium, since the names of metals generally have the ending -ium. The salts formed by the action of the base ammonium hydroxide on acids are called ammonium salts. Thus with hydrochloric acid there is formed ammonium chloride in accordance with the equation

$$NH_4OH + HCl = NH_4Cl + H_2O$$

Similarly with nitric acid there is formed ammonium nitrate, NH_4NO_3, and with sulphuric acid, ammonium sulphate, $(NH_4)_2SO_4$.

Ammonium hydroxide has never been obtained in a pure state. At every attempt to isolate it, the substance breaks up into water and ammonia.

$$NH_4OH = NH_3 + H_2O.$$

It will be noticed that in the neutralization of ammonium hydroxide by acids the group NH_4 replaces one hydrogen atom of the acid, just as sodium does. The group therefore acts as a univalent metal.

Volume Relations of Combining Gases. It has been found that when two volumes of ammonia are decomposed, three volumes of hydrogen are formed and one of nitrogen. If the two elements were to combine directly therefore, one volume of nitrogen would combine with three volumes of hydrogen to form two volumes of ammonia. In a former chapter we have seen that two volumes of hydrogen combine with one volume of oxygen to form two volumes of water vapor. The compound hydrochloric acid which has been frequently mentioned, can be made by the direct union of the gas chlorine and hydrogen, and it has been found that in this reaction one volume of chlorine combines with one volume of hydrogen to form two volumes of hydrochloric acid gas.

These results may be represented graphically thus:

$$\boxed{\mathrm{H}} + \boxed{\mathrm{Cl}} = \boxed{\mathrm{HCl}} + \boxed{\mathrm{HCl}}$$

$$\boxed{\mathrm{H}}\ \boxed{\mathrm{H}} + \boxed{\mathrm{O}} = \boxed{\mathrm{H_2O}} + \boxed{\mathrm{H_2O}}$$

$$\boxed{\mathrm{H}}\ \boxed{\mathrm{H}}\ \boxed{\mathrm{H}} + \boxed{\mathrm{N}} = \boxed{\mathrm{NH_3}} + \boxed{\mathrm{NH_3}}$$

In the early part of the past century, Gay-Lussac, a distinguished French chemist, studied the volume relations of many combining gases, and concluded that similar relations always hold. His observations are summed up in the following:

Law of Gay-Lussac. When two gases combine chemically, there is always a simple ratio between the volumes of the combining gases, and between the volume of either one of them and that of the product, provided it is a gas. By a simple ratio is of course meant the ratio of small whole numbers as 1 : 2, 2 : 3.

II. Compounds of Nitrogen with Oxygen and Hydrogen. Nitrogen forms several compounds with hydrogen and oxygen, of which nitric acid, HNO_3, and nitrous acid, HNO_2, are the most familiar.

a. **Nitric Acid.** Nitric acid is not found to any extent in nature, but some of its salts, especially sodium nitrate, $NaNO_3$, and potassium nitrate, KNO_3, are found in large quantities. From these salts nitric acid can be obtained.

Preparation of Nitric Acid. When sodium nitrate is treated with strong, cold sulphuric acid, no chemical action seems to take place. If however the mixture is heated in a retort, nitric acid is given off as a vapor and may be easily condensed to a liquid, by passing the vapor into a tube surrounded by cold water as shown in Fig. 33.

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

The reason that this reaction takes place is not that the sodium has a stronger affinity for the SO_4 group than for the NO_3 group; for if sodium sulphate and nitric acid are brought together the reaction goes the other way to quite an extent.

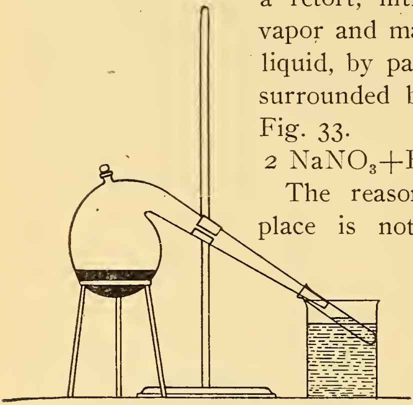


Fig. 33

$$(1)\quad Na_2SO_4 + 2HNO_3 = H_2SO_4 + 2NaNO_3$$

A reaction of this kind is said to be reversible, that is it can go in either way, depending upon the conditions. Under ordinary conditions the reaction

$$(2)\quad 2\ NaNO_3 + H_2SO_4 = Na_2SO_4 + 2\ HNO_3$$

goes on till a part of the sodium nitrate is changed into sulphate, and then apparently ceases, the change in the one way being at the same rate as the change in the other. There is thus a kind of balance or equilibrium set up between the tendency to go as in equation (1) and as in (2).

If, when a state of balance has been reached, the amount of one of the four substances is changed, the equilibrium is disturbed. Thus if the nitric acid escapes from the mixture, more nitric acid will be formed to take its place. If the temperature rises above the boiling point of nitric acid, the nitric acid escapes as fast as formed and the reaction will go on until all the sodium nitrate has been decomposed.

Law of Mass Action. In a reaction which is capable of going in either way, that is in a reversible reaction, it is therefore the relative amounts of the various substances present which determines in a large measure to what extent the reaction will proceed, and when it will reach an equilibrium. The amounts of the substances which are available for the reaction are called the active masses of the substances. The general statement can therefore be made: The extent to which a reversible reaction will take place depends upon the relative active masses of the substances taking part in the reaction. This is called the law of mass action.

When we desire to have the reaction between sodium nitrate and sulphuric acid go on until it is complete, we must work under such conditions that the active mass of the nitric acid keeps very small. This will be the case when the temperature of the mixture is kept above the boiling point of nitric acid, for the acid will then boil away as fast as formed, and never accumulate in the mixture.

To prepare an acid therefore we need only treat one of its salts with some other acid which has a higher boiling point, and heat the mixture (if necessary) above the boiling point of the lower boiling acid.

Physical Properties of Nitric Acid. Pure nitric acid is a colorless liquid which boils at about 86° and has a density of 1.56. The strong acid of commerce contains about 68% of HNO_3, the remainder being water. Such a mixture has a density of 1.4. The strong acid fumes somewhat in moist air, and has a sharp choking odor.

Chemical Properties. 1. *Acid Properties.* As the name indicates, this substance is an acid, and has all the properties of that class of substances. It changes blue litmus red, has a sour taste in dilute solutions, and neutralizes bases forming salts. With potassium hydroxide and sodium hydroxide the reactions are represented by the equations:

$$HNO_3 + KOH = KNO_3 + H_2O$$
$$HNO_3 + NaOH = NaNO_3 + H_2O$$

It also acts upon the oxides of most metals, forming a salt and water as in equations:

$$PbO + 2\ HNO_3 = Pb(NO_3)_2 + H_2O$$
$$CuO + 2\ HNO_3 = Cu(NO_3)_2 + H_2O$$

It is one of the strongest acids, by which is meant that it is largely broken up into its ions H and NO_3 in solution.

2. *Decomposition on Heating.* When boiled, or exposed for some time to sunlight, it suffers a partial decomposition according to the equation

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

The substance NO_2, called nitrogen peroxide, is a brownish gas which is readily soluble in water and in nitric acid. It therefore dissolves in the undecomposed acid, and imparts a yellowish color to it. Strong nitric acid highly charged with this substance is called fuming nitric acid.

3. *Nitric Acid as an Oxidizing Agent.* As is shown by its formula, nitric acid contains a large amount of oxygen, and the reaction just mentioned shows that the compound is not a very stable one, easily undergoing decomposition. These properties should make it a good oxidizing agent, and we find that this is the case. Under ordinary circumstances, when acting as an oxidizing agent, it is decomposed according to the equation

$$2\ HNO_3 = H_2O + 2\ NO + 3\ O$$

the oxygen being taken up by the substance oxidized, and not set free as is indicated in the equation. Thus if sulphur is oxidized by nitric acid, the oxygen will combine with sulphur, forming the substance SO_3 and we will have

$$3\ O + S = SO_3$$

The two equations combined will be

$$2\ HNO_3 + S = H_2O + 2\ NO + SO_3$$

Copper is oxidized by nitric acid, which converts it first of all into copper oxide.

$$Cu + O = CuO.$$

But copper oxide is very easily acted on by nitric acid, as are most metallic oxides, forming a nitrate.

$$CuO + 2\ HNO_3 = Cu(NO_3)_2 + H_2O$$

So the complete action of nitric acid upon copper may be represented by the three equations:

(1) $2\ HNO_3 = H_2O + 2\ NO + 3\ O$

(2) $3\ O + 3\ Cu = 3\ CuO$

(3) $3\ CuO + 6\ HNO_3 = 3\ Cu(NO_3)_2 + 3H_2O$

These three equations may be combined into one by simply adding them together and canceling the equal quantities on each side the equation.

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

This reaction is not peculiar to copper, but represents the usual action of nitric acid upon metals. The stages in it should be carefully noted.

Salts of Nitric Acid — Nitrates. The salts of nitric acid are called nitrates. When heated to a high temperature nitrates undergo decomposition. In a few cases part of the oxygen is given off and a nitrite is left behind.

$$NaNO_3 = NaNO_2 + O$$

In other cases the decomposition goes further, and the metal is left as oxide

$$Cu(NO_3)_2 = CuO + 2\ NO_2 + O.$$

All nitrates are soluble in water.

b. Nitrous Acid. It is not difficult to obtain sodium nitrite, as the reaction given above indicates. Instead of merely heating the nitrate, it is better to heat it together with lead, when the reaction

$$NaNO_3 + Pb = PbO + NaNO_2$$

easily takes place.

When sodium nitrite is treated with an acid such as sulphuric acid it is decomposed and nitrous acid is set free:

$$2\ NaNO_2 + H_2SO_4 = Na_2SO_4 + 2\ HNO_2$$

The acid is very unstable however, and breaks up readily into water and an oxide of nitrogen:

$$2\ HNO_2 = H_2O + N_2O_3$$

Dilute solutions of the acid can, however, be obtained.

III. Compounds of Nitrogen with Oxygen. Nitrogen combines with oxygen to form five different oxides. The formulas and names of these are as follows:

N_2O, nitrous oxide.
NO, nitric oxide.
N_2O_3, nitrogen trioxide or nitrous anhydride.
NO_2, nitrogen peroxide.
N_2O_5, nitrogen pentoxide or nitric anhydride.

These will now be briefly discussed.

1. **Nitrous Oxide — Laughing Gas.** Ammonium nitrate, like all nitrates, when heated undergoes decomposition; but owing to the fact that it contains no metal the reaction is a peculiar one.

$$NH_4NO_3 = 2\ H_2O + N_2O$$

The oxide of nitrogen so formed is called nitrous oxide or laughing gas.

Properties. It is a colorless gas having a slight odor. It is somewhat soluble in water, and in solution has a slightly sweetish taste. It is easily converted into a liquid and can be purchased in this form. When inhaled it produces a kind of hysteria, (hence the name "laughing gas") and in larger amounts unconsciousness and insensibility to pain. It has long been used as an anæsthetic for minor surgical operations such as those of dentistry, but owing to its unpleasant after effects it is not so much used as it formerly was.

Chemically, nitrous oxide is remarkable for the fact that it is a very energetic oxidizing agent. Substances such as carbon, sulphur, iron and phosphorus burn in it almost as brilliantly as in oxygen, forming oxides and setting free nitrogen. Evidently the oxygen in nitrous oxide cannot be held in very firm combination by the nitrogen.

2. **Nitric Oxide.** We have seen that when nitric acid acts upon metals such as copper, the reaction represented by the following equation takes place:

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

Nitric oxide, NO, is most conveniently prepared in this way. The metal is placed in the flask A (Fig. 34) and the acid added slowly through the funnel tube B. The gas escapes through C and is collected over water. Pure nitric oxide is a colorless gas, slightly heavier than air, and is practically insoluble in water. It is a difficult gas to liquefy. Unlike nitrous oxide, nitric oxide does not part with its oxygen easily, and burning substances introduced into this gas are usually extinguished. A few substances like phosphorus which have a very strong affinity for oxygen and which are burning energetically in the air, will continue to burn in an atmosphere of nitric oxide. In this case the nitric oxide loses all of its oxygen and the nitrogen is set free as gas.

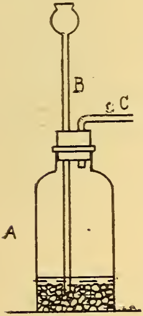


Fig. 34

It seems strange that nitrous oxide, though containing so much less oxygen than nitric oxide should give it up so much more readily. The explanation of this conduct seems to be that the molecules of nitrous oxide consist of a more unstable grouping of atoms than in the case of nitric oxide. The stability of a molecule seems to depend partly upon the character and number of atoms in it, and partly upon the way in which they are arranged. So even with the same kind of atoms we may have one arrangement which is stable and one which is easily decomposed.

When nitric oxide comes into contact with oxygen or with the air, it at once combines with oxygen even at ordinary temperatures, forming a reddish yellow gas of the formula NO_2 which is called nitrogen peroxide. This action is not energetic enough to produce a flame, but considerable heat is set free in it. Owing to the ease with which this action takes place it is impossible to say whether nitric oxide has a taste or odor of its own, for what we taste or smell will not be nitric oxide, but nitrogen peroxide.

3. **Nitrogen Peroxide, NO_2.** This gas as we have just seen is prepared by allowing nitric oxide to come in contact with oxygen. It can also be made by heating a nitrate such as lead nitrate:

$$Pb(NO_3)_2 = PbO + 2\ NO_2 + O$$

It is a reddish yellow gas of unpleasant odor, which is quite poisonous when inhaled. It is heavier than air and is easily condensed to a liquid. It dissolves in water, but this solution is not a mere physical solution; the nitrogen peroxide is decomposed, forming a mixture of nitric and nitrous acids.

$$2\ NO_2 + H_2O = HNO_2 + HNO_3$$

Nitrogen peroxide will not combine with more oxygen; it will however give up a part of its oxygen to burning substances, acting as an oxidizing agent.

$$NO_2 = NO + O$$

In this case the nitrogen peroxide is usually reduced to nitric oxide, which on exposure to the air will change once more to nitrogen peroxide. This substance can therefore be used to transfer the oxygen from the air to substances which will not burn in the air, but will burn in nitrogen peroxide. We shall see that a large industry depends upon this reaction.

Anhydrides. The oxides N_2O_3 or nitrogen trioxide, and N_2O_5 or nitrogen pentoxide, bear a very interesting relation to the acids of nitrogen. When dissolved in water, they combine with the water forming acids.

$$N_2O_5 + H_2O = 2\ HNO_3$$
$$N_2O_3 + H_2O = 2\ HNO_2$$

On the other hand nitrous acid very easily decomposes yielding water and nitrogen trioxide, and by suitable means nitric acid likewise may be decomposed into water and nitric acid.

$$2\ HNO_2 = H_2O + N_2O_3$$
$$2\ HNO_3 = H_2O + N_2O_5$$

In view of the close relation between these oxides and the corresponding acids they are called anhydrides of the acids; N_2O_3 being nitrous anhydride and N_2O_5, nitric anhydride. In general any oxide which will combine with water to form an acid, or which, together with water, is formed by the decomposition of an acid, is called an anhydride of that acid. We shall meet with many examples of such oxides.

CHAPTER XII.

SULPHUR.

Occurrence. The element sulphur has been known from the earliest times, since it is widely distributed in nature and occurs in large quantities in the elementary form, especially in the neighborhood of volcanoes. Sicily has long been famous for its sulphur mines, and smaller deposits are found in other localities in Italy, Iceland, Mexico and Louisiana. In combination, sulphur occurs in the form of sulphides, especially as sulphide of iron, copper, zinc and lead; it also occurs as sulphates, particularly as calcium sulphate or gypsum, $CaSO_4, 2\,H_2O$ and as barium sulphate or heavy spar, $BaSO_4$. In smaller amounts it is found in a great variety of mineral forms, and is a constituent of many animal and vegetable substances.

Extraction of Sulphur. The separation of crude sulphur from the rock and earthy materials with which it is mixed is a very simple process. The ore from the mines is merely heated until the sulphur melts and drains away from the earthy impurities. The crude sulphur obtained in this way is purified by distillation. It is heated to boiling in a retort-shaped vessel made of iron, the exit tube of which opens into a cooling chamber of brickwork. When the sulphur vapor first enters the cooling chamber it condenses upon the walls as a fine crystalline powder called flowers of sulphur. As the condensing chamber becomes warm, the sulphur collects as a liquid in it, and is drawn off into cylindrical moulds, the product being called roll sulphur or brimstone.

Physical Properties. Roll sulphur is a pale yellow, crystalline solid without marked taste and with but a faint odor. It is insoluble in water but is freely soluble in a few liquids as for example in carbon disulphide.

From solution in these solvents it may be obtained in crystals which have the same color as roll sulphur and, like the latter substance, melt at 114.8°. Just above the melting point, sulphur forms a rather thin, straw-colored liquid; as the temperature is raised, this liquid turns darker in color and becomes thicker until at about 235° it is almost black and so thick that the vessel containing it can be inverted without danger of the liquid running out. At higher temperatures it becomes thin once more, the color remaining dark, and boils at 448°, forming a yellowish vapor. On cooling the same changes take place in reverse order.

When melted sulphur is allowed to cool until a part of the liquid has solidified, and the remaining liquid is then poured off, it is found that the solid sulphur remaining in the vessel has assumed the form of fine needle-shaped crystals which differ much in appearance from those which are obtained by crystallizing sulphur from solutions, and which are rhombic in form. The needle-shaped form is called monoclinic sulphur. The two varieties differ also in density and in melting point, the monoclinic sulphur melting at 120°. In a few days the needles become opaque and crumble into fragments which are found to have the rhombic form, and to melt at 114.8° like the other variety. Heat is set free in this transformation.

Crystallography. In order to understand the difference between these two kinds of crystals, it is necessary to know something about crystals in general and the forms which they may assume. An examination of a large number of crystals has shown that although they may differ much in geometric form, they can all be considered as modifications of a few simple plans. The best way to understand the relation of one crystal to another is to look upon every crystal as having its faces and angles arranged in definite fashion about certain imaginary lines drawn through the crystal. These lines are called axes, and bear much the same relation to a crystal as do the axis and parallels of latitude and longitude to the earth and a geographical study of it. All crystals can be referred to one of six simple plans or systems which have their axes as shown in the following drawings.

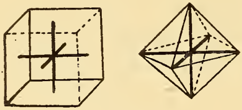


Fig. 35

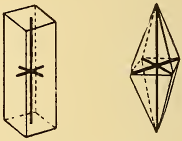


Fig. 36

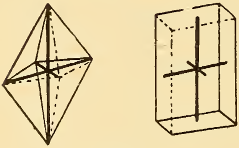


Fig. 37

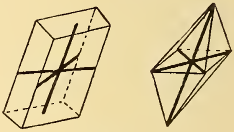


Fig. 38

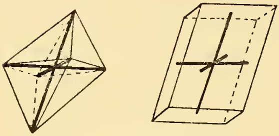


Fig. 39

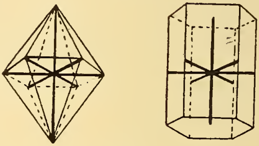


Fig. 40

The names and characteristics of these systems are as follows:

1. Isometric or regular system (Fig. 35). Three equal axes all at right angles.

2. Tetragonal system (Fig. 36). Two equal axes and one of different length, all at right angles to each other.

3. Orthorombic system (Fig. 37). Three unequal axes, all at right angles to each other.

4. Monoclinic system (Fig. 38). Two axes at right angles, and a third at right angles to one of these, but inclined to the other.

5. Triclinic system (Fig. 39). Three axes all inclined to each other.

6. Hexagonal system (Fig. 40). Three equal axes in the same plane intersecting at angles of 60°, and a fourth at right angles to all of these.

Every crystal can be imagined to have its faces and angles arranged in definite way around one of these systems of axes. A cube for instance is referred to plan 1, an axis ending in the center of each face; while in a regular octohedron, an axis ends in each solid angle. These forms are shown in Fig. 35. It will be seen that both of these figures belong to the same system, though they are very different in appearance. In the same way many geometric forms may be derived from each of the systems, and the light lines about the axes in the drawings show two of the simplest forms of each of the systems.

In general, a given substance always crystallizes in the same system, and two corresponding faces of each crystal of it always make the same angle with each other. A few substances, of which sulphur is an example, crystallize in two different systems, and the crystals differ in such physical properties as melting point and density. Such substances are said to be dimorphus.

Amorphous Sulphur. Sulphur also exists in a third physical form called amorphous sulphur. Flowers of sulphur always contains some of this modification, and when the crystalline part of the flowers is dissolved away by carbon disulphide, the amorphous sulphur is left undissolved as a nearly white powder, it being insoluble in carbon disulphide.

Plastic Sulphur. When highly heated liquid sulphur is poured into cold water it assumes a gummy, dough-like form which is quite elastic. This can be seen in a very striking manner by distilling sulphur from a small, short necked retort such as is represented in Fig. 41 and allowing the liquid to run directly into water.

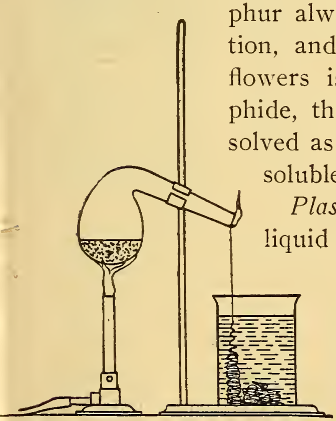


Fig. 41

In a few days it becomes quite brittle and passes over into ordinary rhombic sulphur.

Allotropic Forms. In the study of oxygen it was explained that the gas ozone is an allotropic form of oxygen. The modifications of sulphur just described are good examples of allotropic forms of a solid element. These forms differ not only in appearance, but also in their energy content. The amount of heat liberated by burning a gram of rhombic sulphur, for example, is different from that which is set free in the combustion of a gram of monoclinic sulphur.

Chemical Properties of Sulphur. When any of the forms of sulphur are sufficiently heated in oxygen or in the air, the sulphur burns with a pale blue flame forming sulphur dioxide, SO_2. Small quantities of sulphur trioxide, SO_3, may also be formed. Most metals when heated with sulphur, combine directly with it forming metallic sulphides. In some cases the action is so energetic that the mass becomes incandescent as has been seen in the case of iron uniting with sulphur. This property recalls the action of oxygen upon metals, and in general the metals which combine readily with oxygen are apt to combine quite readily with sulphur.

Large quantities of sulphur are used in the manufacture of gunpowder, matches, vulcanized rubber and pure sulphuric acid; smaller quantities are used in a great variety of ways.

Compounds of Sulphur with Hydrogen. Hydrosulphuric Acid, H_2S. A gas having the composition expressed by the formula H_2S is found in the vapors issuing from volcanoes, and in solution in the waters of many springs. It is also formed when organic matter containing sulphur undergoes decay, just as ammonia is formed under similar circumstances from nitrogenous matter. This gas is commonly called hydrogen sulphide.

Preparation. Hydrosulphuric acid is prepared in the laboratory by treating some sulphide — usually iron sulphide — with an acid.

$$FeS + 2\ HCl = FeCl_2 + H_2S$$

A convenient apparatus is shown in Fig. 42. A few lumps of iron sulphide are placed in the bottle A and diluted acid is poured upon it in small quantities at a time through the funnel tube B, the gas escaping through the tube C. Iron sulphide is a salt of hydrosulphuric acid, and this reaction is therefore similar to the one which takes place when sulphuric acid acts upon a nitrate.

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

In both cases when the salt and an acid are brought together, there is a tendency for the reaction to go on until a state of balance is reached between all four of the substances represented in the equation. This balance is constantly disturbed by the escape of the gaseous acid set free, so that the reaction goes on until all of the original salt has been decomposed. The two reactions differ in that the first one is complete at ordinary temperatures, while in the case of sulphuric acid acting upon sodium nitrate, the reacting substances must be heated so as to secure a temperature at which nitric acid will be a gas.

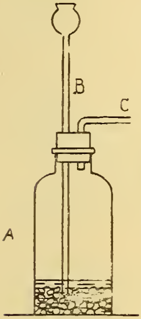


Fig. 42

Physical Properties. Hydrosulphuric acid is a colorless gas having a weak, disagreeable taste and an exceedingly offensive odor. It is rather sparingly soluble in water at ordinary temperatures, about 3 volumes dissolving in 100 of water. In boiling water it is not soluble at all. In pure form it acts as a violent poison and even when diluted largely with air produces poison symptoms such as headache, dizziness and nausea. It is a little heavier than air, having a density of 1.18.

Chemical Properties. The elements in the hydrosulphuric acid are not very firmly held together and in consequence the compound is easily decomposed. It readily burns in the air, both of the elements in it forming oxides.

$$H_2S + 3\ O = H_2O + SO_2$$

When there is not enough oxygen for both the sulphur and the hydrogen, the hydrogen takes the oxygen and the sulphur is set free.

$$H_2S + O = H_2O + S$$

On account of the ease with which the compound breaks down, and the strong affinity of both sulphur and hydrogen for oxygen, hydrosulphuric acid is a strong reducing agent, taking the oxygen away from substances containing it.

We have seen, that when water vapor is passed over hot iron, an oxide of iron is formed and hydrogen is set free. The equation is

$$4\ H_2O + 3\ Fe = Fe_3O_4 + 8\ H$$

A very similar action takes place when hydrosulphuric acid is passed over hot iron:

$$4\ H_2S + 3\ Fe = Fe_3S_4 + 8\ H$$

Hydrosulphuric acid is a weak acid. In solution in water it turns blue litmus red and neutralizes bases forming salts called sulphides. Many of these are insoluble in water and in acids, so that when hydrosulphuric acid is passed into solutions of certain metallic salts an insoluble sulphide is precipitated:

$$CuCl_2 + H_2S = CuS + 2\ HCl$$

In this case, as in all others where a salt and an acid are brought together in solution, there is a tendency to an interchange of the metal between the acids until a state of balance is reached. But copper sulphide is insoluble in the liquid in which the reaction occurs, and consequently is precipitated, so that the amount in solution, that is the active mass of the sulphide, is kept very small. As a result a balance can not be reached, and the reaction goes on until all the copper has been precipitated.

Because of the fact that some metals are precipitated as sulphides in this way, while some are not under similar circumstances, hydrosulphuric acid finds a practical use in the problem of separating the metals from each other in chemical analysis, and is much used in the laboratory for this purpose.

Oxides of Sulphur. Sulphur forms two well known oxides; sulphur dioxide, SO_2, and sulphur trioxide, sometimes called sulphuric anhydride, SO_3.

Sulphur Dioxide. SO_2. This substance is the chief product of the combustion of sulphur in air or in oxygen:

$$S + 2\ O = SO_2$$

It is also formed when substances containing sulphur are burned. Thus when metallic sulphides are heated in a current of air, both the metal and the sulphur are changed into oxides

$$ZnS + 3\ O = ZnO + SO_2$$
$$2\ FeS_2 + 11\ O = Fe_2O_3 + 4\ SO_2.$$

It is not surprising therefore that this substance is one of the gases which issues abundantly from volcanoes.

Laboratory Preparation. In the laboratory sulphur dioxide is usually made by one of two methods.

1. When a sulphite, which is a salt of sulphurous acid H_2SO_3, is treated with an acid, sulphurous acid is set free, and being very unstable, decomposes into water and sulphur dioxide. These reactions are expressed in the equations

$$Na_2SO_3 + 2\ HCl = 2\ NaCl + H_2SO_3$$
$$H_2SO_3 = H_2O + SO_2$$

In this case we have two reversible reactions depending on each other. In the first reaction

$$Na_2SO_3 + 2\ HCl = 2\ NaCl + H_2SO_3$$

we should expect a balanced state to result, for none of the four substances in the equation are insoluble or volatile when water is present to hold them in solution. But the active mass of the H_2SO_3 is constantly diminishing owing to the fact that it decomposes as represented in the equation

$$H_2SO_3 = H_2O + SO_2$$

and the SO_2 being a volatile gas, escapes. No stable balance can therefore result, since the active mass of the sulphurous acid is constantly being diminished because of the escape of SO_2.

2. Under some circumstances strong sulphuric acid acts as an oxidizing agent and is itself reduced to sulphurous acid, the sulphurous acid so formed decomposing as represented in the last equation. Thus when copper is heated with the strong sulphuric acid the reactions expressed in the following equations take place:

$$Cu + H_2SO_4 = CuO + H_2SO_3$$
$$H_2SO_3 = H_2O + SO_2$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

The three equations may be combined into one:

$$Cu + 2\ H_2SO_4 = CuSO_4 + SO_2 + 2\ H_2O$$

Physical Properties. Sulphur dioxide is a colorless gas, which at ordinary temperatures is about 2.2 times as heavy as air. It has a peculiar irritating odor which is familiar to every one since it is perceived when a sulphur match is burning. The gas is very soluble in water, one volume of water dissolving about 80 of the gas at 0°. It is easily condensed to a colorless liquid and can be purchased in this condition stored in strong glass bottles, such as the one represented in Fig. 43.

Chemical Properties. 1. When sulphur dioxide is dissolved in water, the solution acquires acid properties, and is found to contain an acid of the formula H_2SO_3, called

Fig. 43

sulphurous acid. Like nitrous acid, sulphurous acid is very unstable, and cannot be isolated in pure form; on warming a solution containing it, the acid is decomposed into water and the anhydride, as is the case with most acids whose anhydrides are gases. Salts of sulphurous acid can readily be made by treating a solution of the acid with a solution containing a soluble base,

$$2\ NaOH + H_2SO_3 = Na_2SO_3 + 2\ H_2O$$

2. Solutions of sulphur dioxide act as good reducing agents; that is sulpurous acid has the power to take up oxygen from the air or from substances rich in oxygen, and is by this reaction changed into sulphuric acid.

$$H_2SO_3 + O = H_2SO_4$$
$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O$$

The sulphites, i. e., the salts of sulphurous acid, likewise have the power to take up oxygen, and are thereby changed into the corresponding sulphates. For this reason commercial sulphites are often contaminated with sulphates.

3. Moist sulphur dioxide has strong bleaching properties, acting upon many colored substances in such a way as to destroy their color. This is in part due to the reducing properties of the sulphurous acid. The action for the most part consists in partially reducing the color substance, and in many cases it happens that the substance into which it is changed is colorless. The gas is much used to bleach paper, straw goods and even such foods as canned corn.

4. Sulphur dioxide also possesses marked antiseptic properties, and has the power to arrest fermentation. It is therefore used as a preservative. Enormous quantities are used in the manufacture of sulphuric acid.

Sulphur Trioxide. When sulphur dioxide and oxygen are heated together at a rather high temperature a small amount of sulphur trioxide, SO_3, is formed, but the reaction is slow and incomplete. If however the heating takes place in the presence of very fine platinum dust the reaction is rapid and nearly complete.

The experiment can be easily performed by the use of the apparatus shown in Fig. 44, the fine platinum being secured by moistening asbestos fiber with a solution of platinum chloride and igniting it in a flame. The fiber, covered with fine platinum, is placed in a tube of hard glass which is then heated with a burner, while sulphur dioxide and air are passed into the tube. Union takes place at once, and the strongly fuming sulphur trioxide escapes from the jet at the end of the tube, and may be condensed by surrounding the receiving tube with a freezing mixture.

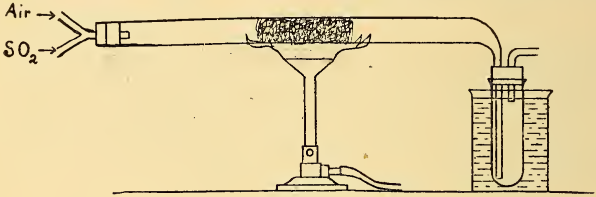


Fig. 44.

Catalysis. It has been found that many chemical reactions are, like this one, much influenced by the presence of substances which do not themselves seem to take a part in the reaction, and are left apparently unchanged after it has ceased. In most cases these reactions are ones which go on very slowly under ordinary circumstances, but are much hastened by the presence of the foreign substance. Substances which bring about reactions in this way, or hasten very slow reactions, are said to act as catalytic agents, and the whole action is called catalysis. Just how the action is brought about is not well understood. We have already had several instances of such action. Oxygen and hydrogen combine with each other at ordinary temperatures in the presence of platinum sponge, though their ordinary kindling temperature is rather high. Potassium chlorate, when heated with manganese dioxide, gives up its oxygen at a much lower temperature than when heated alone. Manganese dioxide dropped into a strong solution of hydrogen dioxide causes it to decompose very rapidly into water and oxygen. On the other hand the catalytic agent sometimes retards chemical action. A solution of hydrogen dioxide decomposes more slowly when it contains a little phosphoric acid, than when perfectly pure.

Properties. Sulphur trioxide is a colorless liquid which solidifies at about 15° and boils at 46°. A trace of moisture causes it to solidify into a mass of silky white crystals, somewhat resembling asbestos fiber in appearance. In contact with the air it fumes strongly, and thrown upon water it dissolves with a hissing sound and the liberation of a great deal of heat. The product of this reaction is sulphuric acid, so that sulphur trioxide is an anhydride.

$$SO_3 + H_2O = H_2SO_4$$

Manufacture of Sulphuric Acid.

1. *Contact Method.* Advantage is taken of the reactions just described, in the preparation of sulphuric acid on the large scale. Large iron tubes are packed with some porous material, such as calcium and magnesium sulphates, which contains a suitable catalytic substance scattered through it. The catalizers most used are platinum powder and iron oxide. Purified sulphur dioxide and air are passed through the tubes which are kept at a temperature of about 400°. Sulphur trioxide is formed, and as it issues from the tube it is absorbed in water or dilute sulphuric acid. The process is continued until all the water in the absorbing vessel has been changed into sulphuric acid, so that a very concentrated acid is made in this way. Sulphuric acid has the power to dissolve sulphur trioxide, and such a solution is called fuming sulphuric acid.

2. *Chamber Process.* The method of manufacture exclusively used until recent years, and still in very extensive use, is much more complicated, but it is exceedingly interesting as showing the way in which difficult chemical problems can be solved. As has been stated, sulphur dioxide combines very slowly with oxygen to form sulphur trioxide, and this is the practical difficulty in the manufacture of sulphuric acid. Indirectly this combination can be brought about in the following way.

Sulphur dioxide is conducted into a very large lead lined chamber containing the gas NO_2; steam and air are at the same time blown into the chamber. Reaction takes place according to the equation

$$2\ SO_2 + 2\ NO_2 + H_2O + O = 2\ SO_2(OH)(NO_2).$$

The product formed in this reaction is called nitro- sulphuric acid. This substance is immediately acted upon by an additional amount of steam, sulphur dioxide and air, decomposition taking place according to the equation

$$SO_2 + 2\ SO_2(OH)(NO_2) + 2\ H_2O + 2\ O = 3\ H_2SO_4 + 2\ NO_2$$

The nitrogen peroxide formed in this last reaction can now enter into combination with a new amount of sulphur dioxide, steam and oxygen and the series of reactions go on indefinitely. It takes a great deal of careful watching to keep the substances present in just the right proportions. Although the equations do not indicate it, there is a constant loss of nitrogen peroxide through leakage, and through its solubility in the liquids formed; hence it must be replaced from time to time.

The nitrogen peroxide is obtained by the action of sulphuric acid upon sodium nitrate, the nitric acid so obtained decomposing in the lead chamber to form the necessary oxide of nitrogen. Two or three parts of nitrate are used up for every 100 parts of sulphuric acid produced. The sulphur dioxide is made by burning iron pyrite, FeS_2, or is obtained as a by-product in the treatment of sulphide ores. Occasionally sulphur itself is burned to furnish it.

The sulphuric acid so formed, together with the excess of condensed steam, collects upon the floor of the lead chamber, the acid liquid so obtained containing about 55% sulphuric acid. The product is called chamber acid, and is quite impure; but for many purposes such as the manufacture of fertilizers it needs no further treatment. It can be concentrated by boiling it in vessels made of iron or platinum which resist the action of the acid, nearly all of the water boiling off and leaving the high boiling acid behind. Pure concentrated acid can best be made by the contact process while the chamber process is cheaper for dilute, impure acid.

Properties of Sulphuric Acid. Sulphuric acid is a colorless, oily liquid nearly twice as heavy as water. The ordinary concentrated acid contains about 2% of water, has a density of 1.84 and boils at 338°. It is sometimes called oil of vitriol, since it was formerly made by distilling green vitriol. It possesses chemical properties which make it one of the most important of chemical substances.

1. *Action on Water.* Sulphuric acid has a very great affinity for water, and is therefore an effective dehydrating agent. Gases which have no chemical action upon sulphuric acid can be freed from water vapor by bubbling them through the strong acid. When the acid is diluted with water much heat is set free, and care must be taken to keep the liquid thoroughly stirred during the mixing, and to pour the acid into the water — never the reverse.

Not only can sulphuric acid absorb water, but it will often withdraw the elements hydrogen and oxygen from a compound containing them, decomposing the compound, and combining with the water so formed. For this reason most organic substances such as sugar, wood, cotton and wool fiber, and even flesh, all of which contain much oxygen and hydrogen, are charred or burned by the action of the strong acid.

2. *Action on Salts.* We have repeatedly seen that an acid of high boiling point heated with the salt of some acid of lower boiling point will drive out the low boiling acid. The boiling point of sulphuric acid (338°) is higher than that of almost any common acid, so that this acid is much used to decompose salts in the preparation of acids from them.

3. *Oxidizing Action.* Sulphuric acid contains a large percentage of oxygen and like most substances rich in oxygen it loses a part of it when heated with substances having a strong affinity for the element. When the strong acid is heated with carbon, sulphur, metals and many other substances this kind of action takes place, as is shown in the equations following:

$$C + 2\,H_2SO_4 = CO_2 + 2\,H_2SO_3$$
$$S + 2\,H_2SO_4 = SO_2 + 2\,H_2SO_3$$
$$Cu + H_2SO_4 = CuO + H_2SO_3$$

In each case the sulphurous acid formed in the reaction breaks down into sulphur dioxide and water. When a metallic oxide is produced by the oxidizing power of sulphuric acid, it dissolves in an additional amount of the acid forming a sulphate. Thus with copper the complete reaction is

$$Cu + 2\,H_2SO_4 = CuSO_4 + H_2O + SO_2$$

In some cases sulphuric acid may lose all of its oxygen and be reduced to hydrosulphuric acid, H_2S. With the substance HI we have such a reaction under some conditions.

$$H_2SO_4 + 8\,HI = H_2S + 4\,H_2O + 8\,I$$

4. *Action as an Acid.* In dilute solutions sulphuric acid acts as any other acid, neutralizing bases, forming salts with metallic oxides and liberating hydrogen when acted upon by metals such as zinc and iron.

Salts of Sulphuric Acid — Sulphates. The salts of sulphuric acid are among the most familiar of all the salts, and many of them have familiar uses. Copperas, (iron sulphate), blue vitriol (copper sulphate), Epsom salt (magnesium sulphate) are good examples of this. Many sulphates are important minerals, prominent among these being gypsum (calcium sulphate) and barytes (barium sulphate).

Thiosulphuric Acid — Thiosulphates. Many other acids of sulphur containing oxygen are known, but none of them are of great importance. Most of them cannot be prepared in a pure state, and are known only through their salts.

When sodium sulphite is boiled with sulphur the two substances combine forming a salt which has the composition represented in the formula $Na_2S_2O_3$ to which the name sodium thiosulphate has been given.

$$Na_2SO_3 + S = Na_2S_2O_3$$

This reaction is quite similar to the action of oxygen upon sulphites.

$$Na_2SO_3 + O = Na_2SO_4$$

More commonly the salt is called sodium hyposulphite, or "hypo." It is extensively used in photography, and since it has the power to absorb large amounts of chlorine, it is used in the bleaching industry to remove the chlorine left upon cotton cloth after it has been bleached by chlorine. It is also used as a disinfecting agent.

Monobasic and Dibasic Acids. Such acids as hydrochloric acid, which can yield only one hydrogen ion, are called monobasic acids, while those giving more than one are called di-, tri-, or tetrabasic acids, according as they give two, three of four hydrogen ions. The three acids of sulphur are dibasic acids. It is therefore possible for them to form both normal and acid salts.

The acid salts can be made in two ways: the acid may be treated with only half enough base to neutralize it:

$NaOH + H_2SO_4 = NaHSO_4 + H_2O$

or a normal salt may be treated with the free acid:

$Na_2SO_4 + H_2SO_4 = 2\ NaHSO_4$

Acid sulphites and sulphides may be made in the same ways.

Carbon Disulphide. CS_2. When sulphur vapor is passed over highly heated carbon, the two elements combine forming carbon disulphide, CS_2, just as oxygen and carbon unite to form carbon dioxide, CO_2. The operation is carried out in such a way that the sulphur and carbon are heated together by means of a strong electrical current passed through the carbon, heating it to a high temperature. The substance is a heavy, colorless liquid, possessing when pure a pleasant ethereal odor. On standing for some time, especially when exposed to sunlight, it undergoes a slight decomposition and acquires a most disagreeable, rancid odor. It has the power of dissolving many substances such as gums, resins and waxes which are not soluble in most liquids, and its chief use is as a solvent for such substances.

It boils at a low temperature (46°) and its vapor is very inflammable, burning in the air to form carbon dioxide and sulphur dioxide.

$$CS_2 + 6\ O = CO_2 + 2\ SO_2$$

Comparison of Sulphur and Oxygen. A comparison of the formulas and the chemical properties of corresponding compounds of oxygen and sulphur brings to light many striking similarities. The conduct of H_2S and H_2O toward many substances has been seen to be very similar; the oxides and sulphides of the metals have similar formulas and undergo many similar reactions. Carbon dioxide and disulphide are prepared in similar ways and have many analogous reactions. It is clear therefore that these two elements are far more closely related to each other than to any of the other elements so far studied.

Selenium and Tellurium. These two very uncommon elements are still more closely related to sulphur than is oxygen. They occur in very small quantities and are usually found associated with sulphur and sulphides, either as the free elements, or more commonly in combination with metals. They form compounds with hydrogen of the formulas H_2Se and H_2Te; these bodies are gases with properties very similar to those of H_2S. They also form oxides and oxygen acids which resemble the corresponding sulphur compounds. The elements even have allotropic forms corresponding very closely to those of sulphur, selenium corresponding more perfectly, while tellurium is in appearance more metallic.

Tellurium is sometimes found in combination with gold and copper, and occasions some difficulties in the refining of these metals. The elements have very few practical applications.

CHAPTER XIII.

PERIODIC LAW.

A number of the elements have now been studied somewhat closely. The first three of these, oxygen, hydrogen and nitrogen, while having some physical properties in common with each other, have almost no point of similarity as regards their chemical conduct. We have seen that oxygen and sulphur, on the other hand, while quite different physically have much in common in their chemical properties.

About 80 elements are now known, and if all of these should have properties as diverse as do oxygen, hydrogen and nitrogen, the study of chemistry would plainly be a very difficult and complicated one. If, however, the elements can be classified in groups the members of which have very similar properties, the study will be a much more simple matter.

Natural Grouping of Elements. Efforts have been made for a long time to find some natural principle in accordance with which the elements can be satisfactorily classified. Of course with such a large number of elements, many chance resemblances will necessarily occur. But it was felt that there must be some real cause in the nature of the elements sulphur and oxygen which occasions their similarity; and that the same cause should group other elements together in families of similar properties.

Metals and Non-Metals. The division of the elements which most readily suggests itself, and which was first made, was into metals and non-metals. This division was founded largely upon physical properties, a metal being an element of high density, bright luster, opaque towards light, a good conductor of electricity, at least somewhat malleable and ductile; and since elements possessing these properties were usually base forming in character, the ability to form bases came to be regarded as a characteristic property of metals. The non-metals were acid forming with physical properties opposite to those of the metals.

This division is unsatisfactory for two reasons. There are so many elements in each group that little is gained by a division. It is not based on a fundamental property, and the properties of some of the elements make it difficult to assign them to either of the divisions. Potassium is undoubtedly a metal, yet it is one of the lightest of solids. Iodine, a typical non-metal, has a high metallic luster. Many elements can form either an acid or a base depending on the circumstances.

Triad Families. It was pointed out by Doebereiner in 1825 that there is an interesting relation existing between the atomic weights of chemically similar elements. Lithium, sodium and potassium resemble each other in much the same way as do sulphur and oxygen. The atomic weight of sodium is almost an arithmetical mean between those of the other two $\frac{7+39}{2}=23$. In many chemical and physical properties sodium stands midway between the other two. Barium, strontium and calcium form a similar group, with strontium a mean between the others, both in atomic weight, and in most other properties. A number of other triad groups have been found. But among 80 elements whose atomic weights range all the way from 1 to 240, such agreements might be mere chance, and many such arithmetical groups can be found where there is no chemical similarity.

Periodic Law. In 1869 the Russian chemist Mendelejeff devised an arrangement of the elements based on their atomic weights, which has proved to be of great service in the comparative study of the elements. A few months later, the German, Lothar Meyer, independently suggested the same ideas. Since this arrangement has brought to light a great generalization in respect to the elements, the generalization is known as a law — the periodic law. The arrangement suggested by Mendelejeff, modified somewhat by other workers and more recent investigations, is as follows.

Arrangement of the Periodic Table. Beginning with lithium which has an atomic weight of 7, the elements are arranged in a horizontal row in order of their atomic weights. Thus:

Li (7), Gl (9), B (10.9), C (11.9), N (13.9), O (15.8), F (18.9)

These seven elements all differ markedly from each other. The eighth element, sodium, is very similar to lithium. It is placed just under lithium and a new row follows:

Na (22.9). Mg (24.2), Al (26.9), Si (28.2), P (30.8), S (31.8), Cl (35.2)

When the sixteenth element, potassium, is reached, it is placed under sodium, to which it is very similar, and serves to begin a third row:

K (38.9), Ca (39.8), Sc (43.8), Ti (47.7), V (50.8), Cr (51.7), Mn (54.6).

Not only is there a strong similarity between sodium, lithium and potassium, which have been placed in a vertical row because of this resemblance to each other, but the elements in the other vertical rows exhibit much of the same kind of similarity among themselves, and evidently form little natural groups.

The three elements following manganese, namely, iron, nickel and cobalt, have atomic weights near together, and are very similar chemically. They do not strongly resemble any of the elements so far considered, and are accordingly placed in a group by themselves, following manganese. A new row is begun with copper, which somewhat resembles the elements of the first vertical column. Following the fifth and seventh rows are groups of three closely related elements so that the completed arrangement has the appearance represented in the table on page 148.

A single horizontal row is called a short period. A group of elements in the eighth column, together with the short period just before the three, and the one just after—17 elements in all—is called a long period. A short period just preceding a group of three in the eighth column is called an even period; one just following is called an odd period. It will be noticed that the elements of the even periods are placed at one side (at the left) of the vertical column in which they fall while the elements of the odd periods are placed at the other side (at the right). This divides each group into two families. Arranging the elements in this way, certain very striking facts appear.

Properties of Elements Vary with Atomic Weight. There is evidently a close relation between the properties of an element and its atomic weight. Lithium, at the beginning of the first period, is a very strong base-forming element, with pronounced metallic properties. Glucinum, following lithium, is less metallic, while boron has some metallic and some acid-forming properties. In carbon, all metallic properties have disappeared, and the acid forming properties are more marked than in boron. These become still more emphasized as we pass through nitrogen and oxygen, until on reaching fluorine, we have one of the strongest acid-forming elements. The properties of these seven elements therefore vary regulary with their atomic weights, or in mathematical language, are functions of them.

Periodic Variation of Properties. The properties of the first seven elements vary *continuously* — that is steadily — away from metallic, and toward acid-forming properties. If lithium were the lightest of all elements in atomic weight, and fluorine the heaviest, so that in passing from one to the other we had gone over all the elements, we could say

THE PERIODIC ARRANGEMENT OF THE ELEMENTS.

Periods.	Group O.		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	A	B	
1 2	H = 1 He = 4		Li = 7		Gl = 9		B = 10.9		C = 11.9		N = 13.9		O = 15.9		F = 18.9		
3		Ne = 19.9	Na = 22.9			Mg = 24.2		Al = 26.9		Si = 28.2		P = 30.8		S = 31.8		Cl = 35.2	
4	A = 39.6		K = 38.9		Ca = 39.7		Sc = 43.8		Ti = 47.7		V = 50.8		Cr 51.7		Mn = 54.6		Fe = 55.6 Ni = 58.3 Co = 58.6
5				Cu = 63.1		Zn = 64.9		Ga = 69.5		Ge = 71.5		As = 74.4		Se = 78.5		Br = 79.4	
6	Kr = 81.2		Rb = 84.8		Sr = 86.9		Y = 88.3		Zr = 90.		Cb = 93.3		Mo = 95.3				Ru = 100.9 Rh = 102.2 Pd = 105.2
7				Ag = 107.1		Cd = 111.6		In = 113.1		Sn = 117.6		Sb = 119.1		Te = 126		I = 125.9	
8	X = 127.		Cs = 132.		Ba = 136.4		La = 137		Ce — Yb* 139 — 172		Ta = 181.6		W = 182.6				Os = 189.6 Ir = 191.5 Pt = 193.3
9				Au = 195.7		Hg = 198.8		Tl = 202.6		Pb = 205.4		Bi = 206.9					
10					Ra = 225				Th = 230.8		U = 237.7						
			R_2O RH		RO RH_2		R_2O_3 RH_3		RO_2 RH_4		R_2O_5 RH_3		RO_3 RH_2		R_2O_7 RH		RO_4

*This includes a number of elements whose weights lie between 140 and 173, but which have not been accurately studied, so that their proper arrangement is uncertain.

that the properties of elements are a continuous function of their atomic weights. But fluorine is an element of small atomic weight, and the one following it, sodium, breaks the regular order, for in it reappear all the characteristic properties of lithium. Magnesium, following sodium, bears much the same relation to glucinum that sodium does to lithium, and the properties of the elements in the second row keep varying much as in the first row, until potassium is reached, when another repetition begins. The properties of the elements do not vary continuously, therefore, with atomic weight, but at regular intervals there is a repetition, or period. The periodic law may be thus stated: The properties of an element are a periodic function of its atomic weight.

The two Families in a Group. While all the elements in a given vertical column bear a general resemblance to each other, the ones belonging to an even period, and placed to the left in a group column, are very strikingly similar to each other, and the same is true of the elements at the right, in the odd periods. Thus lithium, sodium and potassium are very much alike; so too are copper, silver and gold. The resemblance between lithium and copper, or sodium and silver, is much less marked. The periodic arrangement therefore divides the elements into a number of families, each containing three or four members between which there is a great similarity.

Family Resemblances. Let us now inquire more closely in what respects the elements of a family resemble each other.

1. *Valence.* In general the valence of the elements in a family is the same, and the formulas of their compounds are therefore similar. If we know that the formula of sodium chloride is $NaCl$, it is pretty certain that the formula of potassium chloride will be KCl—not KCl_2 or KCl_3. The for-

mulas R_2O, RO, etc., placed below the columns show the formulas of the oxides of the elements in the column, while the formulas RH, RH_2, etc., show the composition of the compounds formed with hydrogen or chlorine.

2. *Chemical Properties.* The chemical properties of the members of a family are quite similar. If one member is a metal, the others usually are: if one is a non-metal, so too are the others. The families in the first two columns consist of metals, while the elements found in the last two columns form acids. There is in addition a certain regularity in properties of the elements in one family. If the element at the head of the family is a strong acid-forming element, this property is likely to diminish gradually, as we pass to the members of the family with higher atomic weight. Thus phosphorus is strongly acid-forming, arsenic less so, antimony still less so, while bismuth has almost no acid forming properties. We shall meet with many illustrations of this fact.

3. *Physical Properties.* In the same way, the physical properties of the members of a family are in general somewhat similar, and show a regular gradation as we pass from element to element in the family.

Value of the Periodic Law. It is at once evident that such regularities very much simplify the study of chemistry. A thorough study of one element of a family makes the study of the other members a much easier task, since so many of the properties and chemical reactions of the elements are so similar. If an element with atomic weight 100 should be discovered, it would be possible to predict many of its chief characteristics from the position it would occupy in the periodic table.

When the periodic law was first formulated, there were a number of gaps in it, as there still are, which evidently belonged to elements at that time unknown. From their position in the table, Mendelejeff predicted with great minuteness, the properties of the elements which he felt sure would one day be discovered to fill these places. Three of them, scandium, germanium and gallium, were found within fifteen years and their properties agreed in a remarkable way with the predictions of Mendelejeff.

The physical constants of many of the elements did not at first agree with those demanded by the law, and a further study of many of such cases showed that errors had been made, so that the law has done much service in indicating probable error.

Imperfections of the Law. There still remain a good many features which must be regarded as imperfections in the law. Most conspicuous is the fact that the element hydrogen has no place in the table. At first there seemed to be no place for argon, but when the other inactive elements were found, it was seen that they together formed a group just preceding the first group, as shown in the table.

In some of the groups, elements appear in one of the families, while all of their properties show that they belong in the other. Thus sodium belongs with lithium and not with copper; fluorine belongs with chlorine and not with manganese. There are two instances where the elements are transposed in order to make them fit into their proper group. Tellurium should precede iodine, and argon should precede potassium. The table separates some elements altogether, which in many respects have closely agreeing properties. Iron, chromium and manganese are all in different groups, although they are similar in many respects.

The system is therefore to be regarded as but a partial and imperfect expression of some very important and fundamental relation between the substances which we know as elements, the exact nature of this relation being not as yet completely clear to us.

CHAPTER XIV.

CHLORINE FAMILY.

General. The four elements fluorine, chlorine, bromine and iodine form a strongly marked family of elements and illustrate very clearly the way in which the members of a family in the periodic group resemble each other and the character of the differences which we may expect to find between the individual members. The compounds of the last three elements are found extensively in sea salt, and on this account the name *halogens,* signifying "producers of sea salt," is sometimes applied to this family. It is more frequently called the chlorine family.

FLUORINE.

Occurrence. The element fluorine occurs in nature most abundantly as the mineral fluorspar, CaF_2, as cryolite, Na_3AlF_6 and in the complex mineral apatite, $Ca_3(PO_4)_2$, CaF_2.

Preparation. All attempts to isolate the element resulted in failure until recent years. Methods similar to those which succeed in the preparation of the other elements of the family cannot be used for the reason that the fluorine as soon as liberated, instantly combines with hydrogen of the water always present or with the materials of which the apparatus is made. The preparation of fluorine was finally accomplished by the French chemist Moissan in the following way. Perfectly dry hydrofluoric acid was condensed to a liquid and placed in a U-shaped tube made of platinum (or copper), which was furnished with electrodes and delivery tubes as shown in Fig. 45. A current will not pass through this liquid any more than through pure water; but if an electrolyte such as potassium fluoride is added the current will then pass. Hydrogen is set free at one electrode and fluorine at the other.

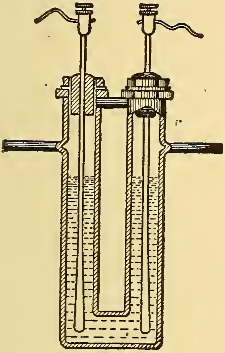


Fig. 45.

Properties. Fluorine is a gas of slightly yellowish color, which can be liquefied by cold and pressure, the liquid boiling at —187° under atmospheric pressure. It is extremely active chemically, being at ordinary temperatures the most active of any of the elements.

It combines with all the common elements save oxygen, very often with incandescence, and the liberation of much heat. It has a great affinity for hydrogen and is able to withdraw it from its compounds with other elements. Because of its great activity it is extremely poisonous.

Hydrofluoric Acid. Hydrofluoric acid is readily obtained from fluorspar by the action of strong sulphuric acid. The equation is

$$CaF_2 + H_2SO_4 = CaSO_4 + 2\ HF$$

In its physical properties it resembles the hydrogen acids of the other elements of this family, being however, more easily condensed to a liquid. The anhydrous acid boils at 19° and can therefore be prepared at ordinary pressures. It is freely soluble in water, and a strong solution — about 50% — is prepared for the market. Its fumes are exceedingly irritating to the respiratory organs and several chemists have met their death by accidently breathing them.

Chemical Properties. Hydrofluoric acid resembles hydrochloric acid in many particulars, only that it is more energetic, acting upon substances which are not attacked by the latter acid. It acts very vigorously upon organic matter even a drop of the strong acid making a sore on the skin which is very painful and slow in healing. Its most characteristic property is its action upon silicon dioxide SiO_2, with which it forms the gas silicon tetrafluoride, SiF_4, and water, as shown in the equation

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

Glass consists of certain compounds of silicon, which are likewise acted on by the acid so that it cannot be kept in glass bottles. It is preserved in flasks made of wax or gutta percha.

Etching. Advantage is taken of this reaction in etching designs upon glass. The glass vessel is painted over with a protective paint upon which the acid will not act, the parts which it is desired to make opaque being unprotected. A mixture of fluorspar and sulphuric acid is then painted over the vessel and after a few minutes the vessel is washed clean. Wherever the hydrofluoric acid comes in contact with the glass, it acts upon it, destroying its luster and making it opaque, so that the exposed design will be etched upon the clear glass. Frosted glass globes are often made in this way.

Fluorides. The fluorides have formulas similar to the chlorides, bromides and iodides, but their properties are usually very different. This is seen in the solubility of the salts. Those metals whose chlorides are insoluble form soluble fluorides, while many of the metals forming soluble chlorides form insoluble fluorides. Most of the soluble fluorides are poisonous. Fluorine does not form any oxides, or any acids containing oxygen.

CHLORINE.

Historical. While studying the action of hydrochloric acid upon the mineral pyrolusite in 1774, Scheele, a Swedish chemist, obtained a yellowish gaseous substance to which he gave a name in keeping with the phlogiston theory then current. It was supposed to be a compound containing oxygen until the English chemist, Sir Humphrey Davy, in 1810 proved it to be an element and renamed it chlorine, the term signifying yellowish green which is the color of the gas.

Occurrence. Chlorine does not occur free in nature but its compounds are widely distributed. For the most part it occurs in combination with the metals in the form of chlorides, those of sodium, potassium and magnesium being the most abundant. Nearly all salt water contains these substances, particularly sodium chloride, and very large salt beds of similar composition are found in many countries.

Preparation.

a. *Laboratory Method.* In the laboratory chlorine is made by warming the mineral pyrolusite, (manganese dioxide, MnO_2), with strong hydrochloric acid. The first reaction seems to be similar to the action of acids upon oxides in general.

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$

The manganese compound so formed is very unstable however and breaks down according to the equation

$$MnCl_4 = MnCl_2 + 2\ Cl$$

The manganese dioxide and the hydrochloric acid are brought together in a flask as represented in Fig. 46, and gentle heat is applied. The rate of evolution of the gas is regulated by the amount of heat applied, and the gas is collected by downward displacement. As the equations show, only half of the chlorine present in the hydrochloric acid is liberated. Instead of using hydrochloric acid in the preparation of chlorine, it will serve just

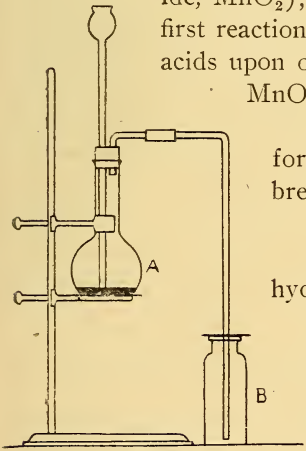


Fig. 46.

as well to use a mixture of sodium chloride and sulphuric acid, since these two react to form hydrochloric acid. The following equations then express the changes.

$$4\ NaCl + 2\ H_2SO_4 = 4\ HCl + 2\ Na_2SO_4$$
$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

The manganese chloride is further acted on by the sulphuric acid present as follows:

$$MnCl_2 + H_2SO_4 = MnSO_4 + 2\ HCl.$$

The hydrochloric acid liberated in this reaction is then free to act on more of the manganese dioxide, so that all the chlorine present in the sodium chloride is set free.

b. *Electrolytic Methods.* Chlorine is readily prepared by the electrolysis of a solution of hydrochloric acid in water. The action is very similar to the electrolysis of water, and can be carried out in the same apparatus. It can likewise be obtained by the electrolysis of a solution of a chloride. In the case of sodium chloride for example, the equation representing the reaction is $NaCl = Na + Cl$. The sodium however at once reacts with the water present in the following way: $Na + H_2O = NaOH + H$. The final products of the electrolysis of a solution of sodium chloride are therefore, chlorine which escapes at the anode, hydrogen, which escapes at the cathode and sodium hydroxide which remains in solution.

Properties. Chlorine is a greenish yellow gas which has a peculiar suffocating odor and a very violent effect upon the throat and lungs. Even when inhaled in small quantities it often produces all the symptoms of a hard cold, and in larger quantities may have serious and even fatal action. It is quite heavy (density=2.45) and can therefore be collected by downward displacement. It is somewhat soluble in water, one volume of water under ordinary conditions dissolving about three volumes of chlorine gas. The gas is readily liquefied, a pressure of six atmospheres serving to liquefy it at 0°. It forms a yellowish liquid which solidifies to a yellow solid at —102°.

Chemical Properties. Chlorine is far more active chemically at ordinary temperatures than any of the elements we have so far met with, with the exception of fluorine; indeed it is one of the most active of all elements.

(1) *Action on Metals.* A great many metals combine directly with chlorine, especially when hot. A strip of copper foil, heated in a burner flame and then dropped into chlorine, burns with incandescence. Sodium burns brilliantly when heated strongly in slightly moist chlorine. Gold and silver are quickly tarnished by the gas.

(2) *Action on Non-metals.* Chlorine has likewise a strong affinity for many of the non-metals. Thus phosphorus burns in a current of the gas while antimony and arsenic in the form of a fine powder at once burst into flame when dropped into jars of the gas. The products formed in all cases where chlorine combines with another element are called chlorides.

(3) *Combination with Hydrogen.* Like oxygen, chlorine has a strong affinity for hydrogen uniting with it to form hydrochloric acid. A jet of hydrogen burning in the air, continues to burn when introduced into a jar of chlorine, giving a somewhat luminous flame. The two gases when mixed together, explode violently when a spark is passed through the mixture or when exposed to bright sunlight. In the latter case it is the light and not the heat which starts the action.

(4) *Action on Substances Containing Hydrogen.* Not only will chlorine combine directly with hydrogen, but it will often abstract hydrogen from chemical compounds which contain it. Thus when chlorine is passed into a solution

containing hydrosulphuric acid, sulphur is precipitated, and hydrochloric acid formed.

$$H_2S + 2\ Cl = 2\ HCl + S$$

With ammonia the action is similar.

$$NH_3 + 3\ Cl = 3\ HCl + N$$

The same tendency is very strikingly seen in the action of chlorine upon turpentine. The latter substance has the composition represented by the formula $C_{10}H_{16}$. When a strip of paper moistened with warm turpentine is placed in a jar of chlorine, dense fumes of hydrochloric acid appear, and a black deposit of carbon is formed. Even water, which is a very stable compound, can be decomposed by chlorine, the oxygen being liberated.

If a long tube of rather large diameter is filled with a strong solution of chlorine in water and inverted in a vessel of the same solution as shown in Fig. 47, and the apparatus is placed in bright sunlight, very soon bubbles of a gas will be observed to rise through the solution and collect in the tube. An examination of this gas shows it to be oxygen, while the chlorine has disappeared from the solution and in its place hydrochloric acid is found to be present.

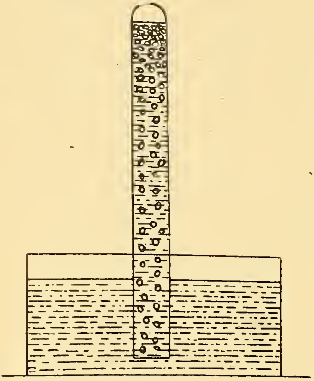


Fig. 47.

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

Bleaching Action of Chlorine If strips of brightly colored cloth, or some highly colored flowers are placed in quite dry chlorine, no marked change in color is noticed as a rule. If however the cloth and flowers are first moistened, the color rapidly disappears, that is the objects are bleached. Evidently the moisture as well as the chlorine is concerned in the action, and a study of the case shows that the chlorine has combined with the hydrogen of the water. The oxygen set free oxidizes the color substance converting it into a colorless compound. It is evident from this explanation that chlorine will not bleach all colors. Chlorine has also marked germicidal properties, and the free element, as well as compounds from which it is easily liberated, are used as disinfectants.

Nascent State. It will be noticed that oxygen set free under these circumstances is able to do what ordinary oxygen cannot do, for both the cloth and the flowers are unchanged in the air which contains oxygen. It is generally true that elements at the instant of liberation from their compounds are more active than they are after standing for a time in the free state. To express this difference elements at the instant of liberation are said to be in the nascent state. It is nascent oxygen which does the bleaching.

Hydrochloric Acid. The product formed by the burning of hydrogen in chlorine is the gas hydrochloric acid. This substance is much more easily obtained by treating common salt (sodium chloride) with sulphuric acid.

$$2\ NaCl + H_2SO_4 = Na_2SO_4 + 2\ HCl$$

Dry salt is placed in a flask furnished with a funnel tube and an exit tube, the sulphuric acid is added, and the flask gently warmed. The hydrochloric acid gas is rapidly given off and can be collected by downward displacement of air. The same apparatus can be used as was employed in the preparation of chlorine. (Fig. 46.)

When a *solution* of salt is treated with sulphuric acid there is no very marked action. The hydrochloric acid formed is very soluble in water, and so does not escape from the solution; hence a state of balance is soon reached with all four of the substances represented in the equation present. Only when strong sulphuric acid, in which hydrochloric acid is not soluble is poured upon dry salt is the reaction complete.

Physical Properties. Hydrochloric acid is a colorless gas which has an irritating effect when inhaled, and a sour, biting taste, but no marked odor. It is heavier than air (density = 1.26) and is very soluble in water. One volume of water at 0° and 760 mm. dissolves about 500 volumes of the gas. On warming such a solution, the gas escapes until at the boiling point the solution contains about 20% by weight of HCl. Further boiling will not drive out any more acid, but the solution will distill with unchanged concentration. A weaker solution than this will lose water on boiling until it has reached the same concentration — 20% — and will then distill unchanged. Under high pressure the gas can be liquefied, 40 atmospheres being required at 10°. It forms a colorless liquid which is not very active chemically. Owing to its great attraction for water hydrochloric acid fumes strongly in the air. The fumes are really minute particles of water which the acid has condensed from the air and in which it dissolves.

Chemical Properties. (1) As the name indicates, the substance is an acid, and indeed it is one of the strongest of acids; by this is meant that a large percentage of the acid is dissociated into its ions in solutions. It acts upon oxides and hydroxides, converting them into salts.

$$NaOH + HCl = NaCl + H_2O$$
$$CuO + 2\ HCl = CuCl_2 + H_2O$$

It acts upon many metals, forming chlorides and liberating hydrogen.

$$Zn + 2\ HCl = ZnCl_2 + 2\ H$$
$$Al + 3\ HCl = AlCl_3 + 3\ H$$

Unlike nitric and sulphuric acid it cannot oxidize metals, so that when it acts at all on them, hydrogen is always given off.

(2) Hydrochloric acid is neither combustible nor a supporter of combustion and is therefore not readily decomposed.

(3) Though hydrochloric acid is incombustible it can be oxidized under some circumstances, in which case the hydrogen combines with oxygen, while the chlorine is set free. Thus when hydrochloric acid acts upon manganese dioxide part of the chlorine is set free.

$$MnO_2 + 4\ HCl = MnCl_2 + 2\ H_2O + 2\ Cl$$

Aqua Regia. It has been seen that when nitric acid acts as an oxidizing agent it usually decomposes as represented in the equation

$$2\ HNO_3 = H_2O + 2\ NO + 3\ O$$

The oxygen so set free is able to oxidize hydrochloric acid:

$$6\ HCl + 3O = 3\ H_2O + 6\ Cl.$$

The complete equation therefore is

$$2\ HNO_3 + 6\ HCl = 4\ H_2O + 2\ NO + 6\ Cl$$

When strong nitric and hydrochloric acids are mixed this reaction goes on slowly, chlorine and some other substances not represented in the equation being formed. The mixture is known as aqua regia; it acts more powerfully upon metals and other substances than either of the acids separately, and owes its strength not to acid properties, but to the action of the nascent chlorine which it liberates. Consequently when it acts upon metals such as gold, they are converted into chlorides, and the reaction can be represented by such equations as

$$Au + 3\ Cl = AuCl_3$$

Composition of Hydrochloric Acid. When a solution of hydrochloric acid is electrolyzed in an apparatus similiar to the one in which water was electrolyzed (Fig. 19), chlorine collects at one pole and hydrogen at the other. At first the chlorine dissolves in the water, but soon the water in the one tube becomes saturated with it, and if the stopcocks are left open until this is the case, and are then closed, it will be seen that the two gases are set free in equal volumes. When measured volumes of the two gases are collected over a strong salt solution, which does not dissolve either one of them, and a spark is passed through the mixture, combination takes place, and it is found that one volume of hydrogen combines with one of chlorine. Other experiments show that the volume of hydrochloric acid formed is just equal to the sum of the volumes of hydrogen and chlorine. One volume of hydrogen therefore combines with one volume of chlorine to form two volumes of hydrochloric acid gas. Since chlorine is 35.18 times as heavy as hydrogen, it follows that 1 part of hydrogen combines with 35.18 parts of chlorine to form 36.18 parts of hydrochloric acid.

Manufacture of Hydrochloric Acid. Hydrochloric acid is prepared commercially in connection with the manufacture of sodium sulphate, which is largely used in the preparation of sodium carbonate. Common salt is heated with strong sulphuric acid, and the hydrochloric acid as it escapes in the form of gas, is passed into water in which it dissolves, the solution being the hydrochloric acid of commerce. When the materials are pure, a pure, colorless solution is obtained, the strongest solution having a density of 1.2 and containing 40% HCl; the commercial acid, often called muriatic acid, is usually colored yellow with impurities.

Compounds of Chlorine with Oxygen and Hydrogen. Chlorine combines with oxygen and hydrogen to form no less than four different substances, all of which have the properties of acids. They are all quite unstable, and most of them cannot be prepared in pure form. Their salts can easily be made however, and some of them will be met with in the study of the metals. The names and formulas of these acids are as follows:

$HClO$, ...hypochlorous acid
$HClO_2$, ...chlorous acid.
$HClO_3$, ...chloric acid
$HClO_4$, ...perchloric acid

Oxides of Chlorine. Two oxides are known, having the formulas Cl_2O and ClO_2. They decompose very easily, and are good oxidizing agents.

BROMINE.

Historical. Bromine was discovered in 1826 by the French chemist Ballard, who isolated it from sea salt. He named it bromine (stench), because of its unbearable fumes.

Occurrence. Bromine occurs almost entirely in the form of bromides, especially as sodium bromide and magnesium bromide which are found in many salt springs and salt deposits. The Stassfurt deposits in Germany, and the salt waters of Michigan and Ohio are especially rich in bromides.

Preparation of Bromine.

1. *Laboratory Method.* As in the case of chlorine, bromine can be prepared by the action of hydrobromic acid, HBr, on manganese dioxide. Since the hydrobromic acid is not an article of commerce, a mixture of sulphuric acid and a bromide is commonly substituted for it. The materials are placed in a retort like the one used in the preparation of nitric acid (Fig. 33). On heating the bromine distills over and is collected in the cold receiver.

2. *Commercial Method.* Bromine is prepared commercially from the waters from salt wells, those being taken which are rich in bromides. On passing a current of elec-

tricity through such waters, the bromine is first liberated. Any chlorine liberated however will assist in the reaction, since free chlorine decomposes bromides as shown in the equation

$$NaBr + Cl = NaCl + Br$$

Properties. Bromine is a dark red liquid, about three times as heavy as water. Its vapor has a very offensive odor, and is most irritating to the eyes and throat. The liquid boils at 59° and solidifies at —7°; but at ordinary temperatures it evaporates rapidly, forming a reddish brown gas, very similar to nitrogen peroxide in appearance. Bromine is somewhat soluble in water, 100 volumes of water under ordinary conditions dissolving 1 volume of the liquid.

In chemical action bromine is very similar to chlorine. It combines directly with many of the same elements with which chlorine unites, but with less energy. It combines with hydrogen and takes away the latter element from its compounds, but not so readily as does chlorine. Its bleaching properties are also less marked.

Hydrobromic Acid. HBr. When sulphuric acid acts upon a bromide, hydrobromic acid is set free.

$$2\ NaBr + H_2SO_4 = Na_2SO_4 + 2\ HBr$$

At the same time some bromine is set free, as can be seen from the red fumes which appear, and from the odor. The explanation of this is found in the fact that hydrobromic acid is much less stable than hydrochloric acid, and is therefore more easily oxidized. Sulphuric acid is a good oxidizing agent. So the strong sulphuric acid oxidizes a part of the hydrobromic acid, forming bromine from it.

$$H_2SO_4 + 2\ HBr = 2\ H_2O + SO_2 + 2\ Br$$

A convenient way to make pure hydrobromic acid is by the action of bromine upon moist red phosphorus. This can be done with the apparatus shown in Fig. 48. Bromine is put into the dropping funnel A, and red phosphorous, together with enough water to cover it, into the flask B. By means of the stopcock, the bromine is allowed to flow drop by drop into the flask, the reaction taking place without the application of heat. The equations are:

$$P + 3\,Br = PBr_3$$
$$PBr_3 + 3\,H_2O = P(OH)_3 + 3\,HBr$$

The U-tube C contains glass beads which have been moistened with water and rubbed in red phosphorus. Any bromine escaping action in the flask acts upon the phosphorus in the U-tube. The hydrobromic acid is collected in the same way as hydrochloric acid.

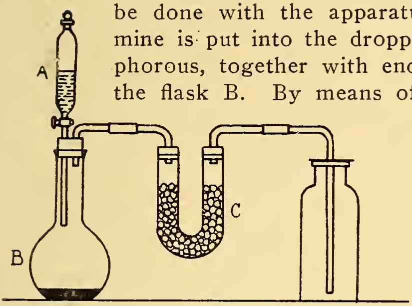


Fig. 48.

Properties. Hydrobromic acid very strikingly resembles hydrochloric acid in physical and chemical properties. It is a colorless, strongly fuming gas, heavier than hydrochloric acid, and like it, very soluble in water. One volume of water under standard conditions dissolves 610 volumes of the gas. Chemically, the chief point in which it differs from hydrochloric acid is in the fact that it is much more easily oxidized, so that bromine is more easily set free from it than chlorine is from hydrochloric acid.

The bromides are very similar to the chlorides in their properties. Chlorine acts upon both bromides and free hydrobromic acid, liberating bromine from them.

$$KBr + Cl = KCl + Br$$
$$HBr + Cl = HCl + Br$$

Bromine finds many uses in the manufacture of organic drugs and dye stuffs. Some of the bromides are used in photography and as drugs.

Oxygen Compounds. No oxides of bromine are surely known, and bromine does not form so many oxygen acids as chlorine does. Salts of hypobromous acid, $HBrO$, and bromic acid, $HBrO_3$, are known.

IODINE.

Historical. Iodine was discovered by Courtois (1812) in the ashes of certain sea plants. Its presence was revealed by its beautful violet vapor, and this suggested the name iodine (from the Greek for violet appearance).

Occurrence. In the combined state iodine occurs in very small quantity in sea water, from which it is absorbed by certain sea plants, so that it is found in their ashes. It occurs along with bromine in salt springs and beds, and is also found in small amounts in Chili saltpetre.

Preparation. Iodine can readily be prepared in the laboratory from an iodide by the same method as is used in preparing bromine, only that in place of sodium bromide, sodium iodide is substituted. It can also be made by passing chlorine into a solution of an iodide.

Commercially, iodine was formerly prepared from seaweed (kelp) but is now obtained almost entirely from the mother liquors from which Chili saltpetre has been crystallized. The iodine is present in the liquors in the form of sodium iodate, and the chemical reaction by which it is prepared is a complicated one. It depends on the fact that sulphurous acid acts upon iodic acid setting iodine free.

$$2\ HIO_3 + 5\ H_2SO_3 = 5\ H_2SO_4 + H_2O + 2\ I$$

Physical Properties. Iodine is a purplish-black, shining, heavy solid which crystallizes in brilliant plates. Even at ordinary temperatures it gives off a beautiful violet vapor, which increases in amount as the iodine is heated. It melts at 107° and boils at 175°. It is slightly soluble in water, but readily dissolves in alcohol, forming a brown solution (tincture of iodine), and in carbon disulphide, forming a violet solution. When even minute traces of it are added to thin starch paste, a very intense blue color developes and this reaction forms a delicate test for iodine. The element has a strong, unpleasant odor, though by no means so irritating as that of chlorine and bromine.

Chemical Properties. Chemically, it is quite similar to chlorine and bromine but is still less active than bromine. It combines directly with many elements, and at elevated temperatures with hydrogen; but the latter reaction is incomplete and the compound formed is quite easily decomposed. Both chlorine and bromine displace it from its salts.

$$KI + Br = KBr + I$$
$$KI + Cl = KCl + I$$

Hydriodic Acid. Hydriodic acid cannot be prepared in pure form by treating an iodide with sulphuric acid, since under these conditions iodine and not hydriodic acid is set free. The explanation of this is the same as in the case of bromine. Hydriodic acid is a strong reducing agent, and when set free, acts upon the sulphuric acid.

$$2\ NaI + H_2SO_4 = Na_2SO_4 + 2\ HI$$
$$2\ HI + H_2SO_4 = 2\ H_2O + SO_2 + 2\ I$$

It is most easily prepared in the way described for the preparation of hydrobromic acid. Red phosphorus and iodine are rubbed together and placed in a small flask. The mixture is warmed gently, and water is slowly dropped upon the mixture.

$$P + 3\ I = PI_3$$
$$PI_3 + 3\ H_2O = 3\ HI + P(OH)_3$$

Physical Properties. Hydriodic acid is a strongly fuming colorless gas which might be easily mistaken for either hydrochloric or hydrobromic acids. It is very soluble in water, 1 volume of water under standard conditions dissolving about 460 volumes of the gas. It is easily condensed to a colorless liquid by a pressure of four atmospheres at 0°.

Chemical Properties. A solution of hydriodic acid has strong acid properties, acting very much like the corresponding solutions of hydrochloric and hydrobromic acids. It is however much more unstable. On standing exposed to the air, the solution turns brown from the separation of iodine;

$$2\ HI + O = H_2O + 2\ I$$

Owing to the small affinity between the iodine and the hydrogen, the compound gives up its hydrogen very easily, and is therefore a very strong reducing agent. Of the salts of this acid, potassium iodide is the most familiar.

Iodine has a much greater affinity for oxygen than has either chlorine or bromine. It forms a stable oxide I_2O_5 which is made by boiling iodine with nitric acid. Salts of iodic acid, HIO_3 and periodic acid, HIO_4, are easily prepared, and the free acids are much more stable than those of the other members of this family.

Uses of Iodine. Iodine is extensively used in medicine, especially in the form of a tincture, and it is also much used in the preparation of dyes and organic drugs. Iodoform, a substance with the composition CHI_3, is much used in surgery as an antiseptic.

CHAPTER XV.

CARBON AND SOME OF ITS SIMPLER COMPOUNDS.

Occurrence. Carbon is found in nature in the uncombined state in several forms. The diamond is practically pure carbon, while graphite and coal are largely carbon, but contain small amounts of other substances mixed with it. Its natural compounds are exceedingly numerous, and occur as gases, liquids and solids. Carbon dioxide is its most familiar gaseous compound. Natural gas and petroleum are largely compounds of carbon with hydrogen. The carbonates, especially calcium carbonate, constitute great strata of rocks, and are found in almost every locality. All living organisms, both plant and animals, contain a large percentage of this element, and the number of its compounds which go to make up all the vast variety of animate nature is almost limitless.

Allotropic Forms. Carbon occurs in three distinct forms, two of which are crystalline and one amorphous.

1. *Crystalline Forms.*

a. Diamond. Diamonds are found in considerable quantities in several localities, especially in the East Indies, South Africa and Brazil. The crystals belong to the regular system, but the natural stones do not show this very clearly. When found they are usually covered with a rough coating which is removed in the process of cutting.

The pure diamond is perfectly transparent and colorless, but many are tinted a variety of colors by traces of metallic substances. In some instances the color adds to the value; thus the famous Hope diamond is a beautiful blue. Usually the colorless ones are the most highly prized. Light passing through a diamond is very much refracted, and to this fact the stone owes its brilliancy and sparkle.

The density of the diamond is 3.5 and though brittle, it is one of the hardest of substances. Black diamonds, as well as broken and imperfect stones, which are valueless as gems are used for grinding hard substances. Few chemical reagents have any action on the diamond; but when heated strongly in oxygen or the air, it blackens and burns forming carbon dioxide.

Lavoisier first showed that carbon dioxide is formed by the combustion of the diamond; and Sir Humphrey Davy in 1814 showed that this is the only product of combustion, and that the diamond is therefore pure carbon.

Many attempts have been made to produce diamonds artificially, but for a long time these always ended in failure, graphite and not diamonds being the product obtained. In his extended study of chemistry at high temperatures, the French chemist Moissan finally succeeded (1893) in making some small ones. He accomplished this by dissolving carbon in boiling iron and suddenly plunging the crucible containing the iron into water. Under these conditions the carbon was crystallized in the iron in the form of the diamond.

b. Graphite. Graphite is found in large quantities especially in Ceylon, Siberia and in some localities of the United States and Canada. It is a shining black substance, very soft and greasy to the touch. Its density is about 2.15. It varies somewhat in properties according to the locality in which it is found, and is more easily attacked by reagents than is the diamond. It is manufactured by heating carbon with a small amount of iron (3%) in an electric furnace. It is used in the manufacture of lead pencils and crucibles, as a lubricant where oil cannot be used, and as a protective covering for iron in the form of a polish, such as stove polish, or as a paint.

2. *Amorphous Carbon.* There are many varieties of amorphous carbon known, and these substances are of the greatest importance, owing to their many uses in the arts

and industries. As they occur in nature, or are made artificially, they are nearly all impure carbon, the impurity depending on the particular substance in question.

a. Pure amorphous carbon is best prepared by charring sugar. This is a substance consisting of carbon, hydrogen and oxygen, the latter two elements being present in the ratio of one oxygen atom to two of hydrogen. When sugar is strongly heated, the oxygen and hydrogen are driven off in the form of water, and pure carbon is left behind. Prepared in this way it is a soft, lustrous, very bulky, black powder.

b. Coals of various kinds were probably formed from vast accumulations of vegetable matter in former ages, which became covered over with earthy material and protected from rapid decay. Under various natural agencies the organic matter was slowly changed into coal. In anthracite, these changes have gone the farthest, and this variety of coal is nearly pure carbon. Soft, or bituminous, coals contain considerable organic matter besides carbon and mineral substances. When distilled, (heated strongly out of contact with air), the organic matter is driven off in the form of gases and vapors, and only the mineral matter and carbon remain behind. The gaseous product is chiefly illuminating gas, and the solid residue is coke. Some of the coke is found as a dense cake on the sides and roof of the retort. This is called retort carbon and is quite pure.

c. Charcoal is prepared from wood in the same way that coke is made from coal. When the process is carried on in retorts, the products expelled by the heat are saved. Among these are many valuable substances such as wood alcohol and acetic acid. Where timber is abundant, the process is carried out in a wasteful way, by merely covering piles of wood with sod, and setting the wood on fire. Some wood burns, and the heat from this decomposes the wood not burned, forming charcoal from it. The charcoal of course contains the mineral part of the wood from which it is formed.

d. Bone-black or animal charcoal is made by charring bones and animal refuse. The organic part of the materials is thus decomposed, and carbon is left in very finely divided state, scattered through the mineral part, which consists largely of calcium phosphate. For some uses this mineral part is removed by treatment with hydrochloric acid, and prolonged washing.

e. Lampblack and soot are products of imperfect combustion of oil and coal, and are deposited from a smoky flame on a cold surface. The carbon in this form is very finely divided, and usually contains various oily materials.

Properties. Carbon in any of its forms is characterized by its great stability towards heat. Only in the intense heat of the electric arc does it volatilize, passing directly from the solid state into a vapor. It is not acted on at ordinary temperatures by very many reagents, but at a higher temperature combines with many of the elements. Its compounds with the metals are called carbides.

Uses of Carbon. The chief use of amorphous carbon is for fuel to furnish heat and power for all the uses of civilization. Enormous quantities of the purer coals, coke and charcoal are used as a reducing agent in the manufacture of the various metals, especially in the metallurgy of iron. Thus iron is found in nature chiefly in the form of an oxide. When heated with carbon, this oxide is reduced to metallic iron.

This use can be readily illustrated by heating in a hard glass test tube an intimate mixture of 2 or 3 grams of copper oxide with an equal bulk of powdered charcoal. The mixture turns reddish and if the evolved gases are passed through clear lime water, the presence of carbon dioxide can be demonstrated.

Retort carbon and coke are used to make electric light carbons and battery plates, while lampblack is used for indelible inks, printer's ink and black varnishes. Boneblack and charcoal have the property of absorbing large volumes of certain gases, as well as smaller amounts of organic matter; hence they are used in filters to remove noxious gases and objectionable colors and odors from water. Boneblack is used extensively in the sugar refineries to remove coloring matter from the impure sugars.

Fuels. A variety of substances are used as fuels, the most important of them being coal, wood and gas. These are composed of carbon, hydrogen and, in the case of the first two, oxygen. When the fuel burns in a free supply of air, the carbon is converted into carbon dioxide, and the hydrogen into water. In the case of gas, which often contains a large percentage of hydrogen, the amount of water vapor formed is very great, and rooms heated by gas fires are often very damp because of faulty ventilation for the products of combustion of the gas.

Chemistry of Carbon Compounds. Carbon is remarkable for the very large number of compounds which it forms with the other elements, especially with oxygen and hydrogen. Compounds containing carbon are more numerous than all others put together, and the chemistry of these substances presents peculiarities not met with in the study of other substances. For these reasons the systematic study of carbon compounds or of organic chemistry as it is usually called, must be deferred until the student has gained some knowledge of the chemistry of other elements. An acquaintance with a few of the most familiar carbon compounds is, however, essential for the understanding of the general principles of chemistry.

Compounds of Carbon with Hydrogen. Carbon forms a very large number of compounds with hydrogen, and when no other element is present, such substances are called hydrocarbons. Petroleum and natural gas are essentially mixtures of a great variety of hydrocarbons. Many are found in living plants, and the decay of organic matter in the absence of air always produces them.

Marsh Gas — Methane. Marsh gas, CH_4 is one of the most important of these hydrocarbons. As its name suggests it is formed in marshes by the decay of vegetable matter under water, and bubbles of it are often seen to rise when the dead leaves on the bottom of pools are stirred. It also collects in mines, and is called fire damp by the miners, because of its great inflammability—damp being an old name for a gas. It is formed when organic matter, such as coal or wood, is heated in closed vessels, and is therefore a principal constiuent of coal gas.

Methane is prepared in the laboratory by heating a mixture of sodium or calcium acetate and soda-lime. Equal weights of fused sodium acetate and soda-lime are thoroughly mixed, and placed in a good-sized, hard-glass test tube, fitted with a one-holed stopper and delivery tube. The mixture is gradually heated, and when the air has been displaced from the tube, the gas is collected in bottles by displacement of water. Soda lime is a mixture of sodium and calcium hydroxides. Regarding it as sodium hydroxide alone, the equation is

$$NaC_2H_3O_2+NaOH=Na_2CO_3+CH_4.$$

Properties. Methane is a colorless, odorless gas, whose density is 0.55. It is difficult to liquefy, boiling at — 155° under standard pressure, and is almost insoluble in water. It burns with a pale blue flame, liberating much heat, and mixed with oxygen it forms a very explosive mixture.

Davy's Safety Lamp. In 1815 Sir Humphrey Davy invented a lamp for the use of miners to prevent the dreadful mine explosions then common, due to methane mixed with the oxygen of the air. The invention consisted in surrounding the common miner's lamp with a mantle of wire gauze.

It has been seen that two gases will not combine until raised to their kindling temperature, and if, while combining, they are cooled below this point, the combination ceases. A flame will not pass through a wire gauze because the metal, being a good conductor of heat, takes away so much heat from the flame that the gases are cooled below the kindling temperature. When a lamp so protected is brought into an explosive mixture, the gases inside the wire mantle burn in a series of little explosions, giving warning to the miner that the air is unsafe.

Acetylene, C_2H_2, is a colorless gas usually possessed of a disagreeable odor due to impurities. It is formed in many processes, and is one of the most important constituents of illuminating gas. It is now made in large quantities from calcium carbide, CaC_2. This substance is formed when coal and lime are heated together in an electric furnace. When treated with water, the carbide is decomposed yielding acetylene.

$$CaC_2 + 2\ H_2O = C_2H_2 + Ca(OH)_2.$$

The gas can be readily liquefied, but it is not used in this way, because it has been found that the liquid sometimes explodes especially when exposed to a sudden shock. Under ordinary conditions it burns with a very smoky flame; in burners constructed so as to secure a large amount of oxygen, it burns with a very brilliant white light, and hence is used as an illuminant. The gas can be readily prepared in a generator such as is shown in Fig. 49. The inner tube contains fragments of calcium carbide, the outer, water. The gas can be lighted as it issues from the burner.

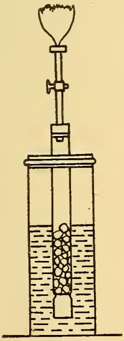


Fig. 49.

Other Hydrocarbons. At first thought the law of multiple proportion would seem to indicate that there must be a limit to the number of compounds which two elements can form with each other, and our experience so far has shown that in general the number is a small one. Yet hundreds of hydrocarbons are known. The ability of carbon to form such a surprising number of compounds with hydrogen appears to be due to the fact that carbon atoms have the peculiar power of combining with each other to form long chains and this makes possible a great variety of compounds. Thus we have the hydrocarbons

Ethane........................$H_3C — CH_3$
Propane ....$H_3C — CH_2 — CH_3$
Butane ....$H_3C — CH_2 — CH_2 — CH_3$

Oxides of Carbon. Carbon forms two oxides, viz., carbon dioxide, CO_2, and carbon monoxide, CO.

1. *Carbon Dioxide* CO_2. Occurrence. Carbon dioxide is present in the air to the extent of about 4 parts in 10,000, and this apparently small amount is of fundamental importance in nature. It escapes from the earth in some localities in great quantities, and many spring waters carry large amounts of it in solution. When these highly charged spring waters reach the surface of the earth, and the pressure on them is removed, the carbon dioxide escapes with effervescence. It is a product of the oxidation of all organic matter and is therefore formed in fires, as well is in the process of decay. It is thrown off from the lungs of all animals in respiration. It is a product of many fermentation processes such as vinegar making and brewing. Combined with metallic oxides, it forms vast deposits of carbonates in nature.

Preparation. In the laboratory, carbon dioxide is always prepared by the action of an acid upon a carbonate, usually calcium carbonate, the apparatus shown in Fig 42 serving the purpose very well. This reaction might be expected to produce carbonic acid, thus:

$$CaCO_3 + 2\ HCl = CaCl_2 + H_2CO_3$$

Carbonic acid is very unstable however, and decomposes into its anhydride, CO_2, and water.

$$H_2CO_3 = H_2O + CO_2.$$

The complete reaction is therefore represented by the equation:

$$CaCO_3 + 2\ HCl = CaCl_2 + CO_2 + H_2O.$$

The reaction is therefore quite similar to the one in which sulphur dioxide is prepared by the action of an acid on a sulphite:

$$Na_2SO_3 + 2\ HCl = 2\ NaCl + SO_2 + H_2O.$$

Physical Properties. Carbon dioxide is a colorless, practically odorless gas whose density is 1.5. Its weight can be inferred from the fact that it can be siphoned or poured like water from one vessel downward into another vessel. It is somewhat soluble in water. At 15° and under ordinary pressure, it dissolves in its own volume of water, and imparts a somewhat biting, pungent taste to it. It is easily condensed and is prepared now commercially in this form, by pumping the gas into steel cylinders (see Fig. 6), which are kept cold during the process. When the liquid is permitted to escape into the air, part of it instantly evaporates and in so doing, absorbs so much heat that another portion is solidified, the solid form strikingly resembling snow in appearance. This snow is very cold, and mercury can easily be frozen with it.

Such cylinders of carbon dioxide are inexpensive, and should be available in every school. To demonstrate the properties of solid carbon dioxide, the cylinder should be placed across the table and supported in such a way that the stopcock end is several inches lower than the bottom of the cylinder. A loose bag is made by holding the corners of a handkerchief around the neck of the stopcock, and the cock is then turned on so that the gas rushes out in large quantities. In a few minutes a considerable quantity of the snow collects in the handkerchief. To freeze mercury, press a piece of filter paper into a small evaporating dish, and pour the mercury upon it. Coil a flat spiral upon the end of a wire, and dip the spiral into the mercury. Place a quantity of solid carbon dioxide upon the mercury and pour 10-15 c.c. of ether over it. In a minute or two the mercury will solidify, and can be removed from the dish by the wire serving as a handle. The filter paper is to prevent the mercury sticking to the dish; the ether dissolves the solid carbon dioxide and promotes its rapid conversion into gas.

In the liquid form carbon dioxide is sold for charging water with the gas — such highly charged water being used in soda water and similar drinks.

Chemical Properties. Carbon dioxide is incombustible, since it is like water a product of combustion. It does not support combustion, as does nitrogen peroxide because the oxygen in it is held in very firm chemical union with the carbon. Very strong reducing agents such as highly heated carbon, can take away half of its oxygen:

$$CO_2 + C = 2\ CO.$$

Carbon dioxide and water are therefore both of them good fire extinguishers. Chemical fire extinguishers are simply devices for rapidly generating a large amount of carbon dioxide. The gas is directed upon the burning substance and smothers the fire just as water would.

It is not necessary that all the oxygen should be kept away from the fire to smother it. A burning candle is extinguished in air which has been mixed with only 2.5% carbon dioxide, and this fact adds very much to the effectiveness of fire extinguishers which make use of carbon dioxide.

When passed into clear lime water, carbon dioxide forms an insoluble substance, calcium carbonate, and this is the easiest way of testing for the gas.

Carbonic Acid and the Carbonates. Like most of the oxides of the non-metallic elements, carbon dioxide is an acid anhydride. It combines with water to form an acid of the formula H_2CO_3, called carbonic acid.

$$H_2O + CO_2 = H_2CO_3.$$

The acid is, however, very unstable, and cannot be isolated. Only a very small amount of it is actually formed when carbon dioxide is passed into water, as is evident from the small solubility of the gas. If, however, a base is present in water, salts of carbonic acid are formed, and these are quite stable.

$$2\ NaOH + H_2O + CO_2 = Na_2CO_3 + 2\ H_2O.$$

This conduct is best explained by the law of mass action already referred to. The equation $H_2O+CO_2=H_2CO_3$, is a reversible equation, and the extent to which the reaction progresses depends upon the relative amounts—that is, upon the active masses, of each of the three factors in it. Equilibrium is ordinarily reached when very little H_2CO_3 is formed. If the quantity of CO_2 is increased by pressure, more of the acid is formed; and when the pressure is removed the reaction is reversed, and the CO_2 is given off. If a base is present in the water to take up the H_2CO_3 as fast as it is formed, that is to keep the active mass of the acid very small, all of the CO_2 is converted into H_2CO_3, and thence into a carbonate. When an acid which contains a gaseous anhydride, such as H_2CO_3, H_2SO_3, HNO_2, is set free, it is apt to decompose, and if its anhydride is insoluble or nearly so, the decomposition is complete, because one of the factors in the reaction is constantly escaping, and this reduces its active mass below the point of equilibrium.

The carbonates form a very important class of salts. They are found in large quantities in nature, and are often used in chemical processes. Only the carbonates of sodium, potassium and ammonium are soluble, and these can be made by the action of carbon dioxide on solutions of the bases as just explained.

The insoluble carbonates are formed as precipitates, when a soluble metallic compound is treated with a solution of a soluble carbonate. Thus the insoluble calcium carbonate can be made by bringing together solutions of calcium chloride and sodium carbonate:

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2\ NaCl$$

Most of the carbonates are decomposed by heat, yielding an oxide of the metal and carbon dioxide. Lime (calcium oxide) is made by strongly heating calcium carbonate:

$$CaCO_3 = CaO + CO_2.$$

Acid Carbonates. Like all acids containing two acid hydrogen atoms, carbonic acid can form both normal and acid salts. The acid carbonates are made by treating a normal carbonate with an excess of carbonic acid. They are all very unstable, and decompose even when their solutions are heated.

If carbon dioxide is passed into clear lime water, calcium carbonate is at first precipitated: $Ca(OH)_2+CO_2=CaCO_3+H_2O$. The precipitate soon dissolves, because the excess of carbonic acid forms calcium acid carbonate: $CaCO_3+H_2CO_3=Ca(HCO_3)_2$. If now the solution is heated, the acid carbonate will be decomposed, and calcium carbonate once more precipitated. $Ca(HCO_3)_2=CaCO_3+H_2CO_3$.

Carbon Dioxide and Plant Life. Although large amounts of carbon dioxide are constantly being formed in nature, the amount in the air remains almost constant. The reason for this is that plant life is dependent upon carbon dioxide for food, and that growing plants absorb it from the air. Although it is a very stable substance, it is decomposed in the plant under the influence of the sunlight. Water also undergoes decomposition at the same time. Part of the oxygen of these two substances is restored to the air from the leaves of the plants, while the carbon and hydrogen and a part of the oxygen are built up into the complex structure of the plant. The plants are therefore laboratories where carbon dioxide and water are made over into more complex substances, while the oxygen is in part returned to the air.

Since much heat is liberated when wood is burned, that is when the process of its formation is reversed, the oxygen being taken again from the air and the wood being converted into carbon dioxide and water, it is evident that much energy is absorbed when the carbon dioxide and water are decomposed and built up into the woody structure. This energy is supplied by the sun acting on the growing plant. Thus the plants serve as reservoirs to store up for a time the energy of the sun in the form of complex chemical substances, and this energy is again liberated when the plant is burned.

2. *Carbon Monoxide.* Carbon monoxide can be made in two general ways: (1) by partial oxidation of carbon, (2) by partial reduction of carbon dioxide. If a slow current of air is conducted over highly heated carbon, the monoxide is formed: $C + O = CO$. It is therefore often formed in stoves when the air draught is insufficient. Water gas, which contains large amounts of carbon monoxide, is made by partially oxidizing carbon with steam:

$$C + H_2O = CO + H_2$$

When CO_2 is conducted over highly heated carbon, it is reduced to CO by the excess of carbon: $CO_2 + C = 2\ CO$. When coal is burning in a stove or grate, carbon dioxide is at first formed in the free supply of air; as the hot gas rises through the glowing coal, it is reduced to carbon monoxide. When the carbon monoxide reaches the free air above the coal, it takes up oxygen to form carbon dioxide, burning with the blue flame so familiar above a bed of coals, especially in the case of hard coal. In the laboratory carbon monoxide is usually prepared by the action of sulphuric acid upon oxalic acid. The latter substance has the formula $C_2H_2O_4$. The sulphuric acid owing to its affinity for water causes it to decompose as represented in the equation

$$C_2H_2O_4 + (H_2SO_4) = (H_2SO_4) + H_2O + CO_2 + CO$$

Properties. Carbon monoxide is a light, colorless, almost odorless gas, very difficult to liquefy. Chemically it is very active, combining directly with a great many substances. It has a great affinity for oxygen, and is therefore combustible, and a good reducing agent. Thus if carbon monoxide is passed over hot copper oxide, the copper is reduced to the metallic state: $CuO + CO = Cu + CO_2$. When inhaled, it combines with the red coloring matter of the blood, and even a very small amount of the gas will cause death.

Carbon Disulphide. Just as carbon combines with oxygen to form carbon dioxide, so it combines with sulphur to form carbon disulphide, CS_2. This compound has already been described in the chapter on sulphur.

Hydrocyanic Acid — Cyanides. Carbon unites with nitrogen and hydrogen to form the acid HCN, called hydrocyanic acid. It is a weak volatile acid, and is therefore easily prepared by treating its salts with sulphuric acid.

$$KCN + H_2SO_4 = KHSO_4 + HCN.$$

It is most familiar as a gas, though it condenses to a colorless liquid, boiling at 26°. It has a peculiar odor suggesting bitter almond, and is extremely poisonous. A single drop may cause death. It dissolves readily in water, its solution being commonly called prussic acid. Its salts are called cyanides, the cyanides of sodium and potassium being the best known. These are white solids and extremely poisonous.

CHAPTER XVI.

FLAMES — ILLUMINANTS.

It has been seen that when two substances unite chemically, with the production of light and heat, the act of union is called combustion. When one of the substances undergoing combustion remains solid at the temperature occasioned by the combustion, light may be given off, but there is no flame. Thus, iron wire burning in oxygen throws off a shower of sparks, and is brilliantly incandescent, but no flame is seen. When however both of the substances are gases or vapors at the temperature reached in the combustion, the act of union is accompanied by a flame.

Many substances which are liquids or solids at ordinary temperatures burn with a flame because the heat of combustion vaporizes them slowly, and the flame is due to the union of this vapor with the gas supporting the combustion. Thus the oil in a lamp is drawn up through the wick by capillary attraction and is vaporized by the heat of the flame. Again in the burning of a candle the heat of combustion is sufficient to slowly melt the solid wax at the end of the candle. The resulting liquid is drawn up in the wick by capillary attraction and is vaporized, the flame being due to the union of this vapor with oxygen in the air. Solid substances like wood burn with a flame because the heat of combustion expels volatile combustible matter from the wood. If the wood is first heated strongly in the absence of the air, the volatile matter is all expelled and the resulting substance, charcoal, simply glows when it burns, there being no flame.

Supporter of Combustion. That gas which surrounds the flame and constitutes the atmosphere in which the combustion occurs is said to support the combustion. The other gas which issues into this atmosphere is said to be the combustible gas. Thus in the ordinary combustion of coal gas in the air, the coal gas is said to be combustible while the air is the supporter of combustion. These terms are entirely relative however for a jet of air issuing into an atmosphere of coal gas will burn when ignited, the coal gas supporting the combustion. Ordinarily when we say that a gas is combustible, we mean that it is combustible in an atmosphere of air.

That the terms "combustible" and "supporter of combustion" are merely relative may be shown in the following way. A lamp chimney is fitted with a cork and glass tubes as shown in Fig. 50. The tube C should have a diameter of from 12 to 15 mm. A thin sheet of asbestos in which is cut a circular opening about 2 cm. in diameter, is placed over the top of the chimney. The opening in the asbestos is closed with the palm of the hand and gas is admitted to the chimney through the tube B. The air in the chimney is soon expelled through the tube C and the gas itself is then lighted at the end of this tube. The hand is now removed from the opening in the asbestos, when the flame at the end of the tube at once rises and appears at the end of the tube within the chimney as shown in the figure. The coal gas now escapes from the opening in the asbestos and may be lighted. The flame at the top of the chimney is due to the combustion of coal gas in air while the flame within the chimney is due to the combustion of air in coal gas, the air being drawn up through the tube by the escaping coal gas.

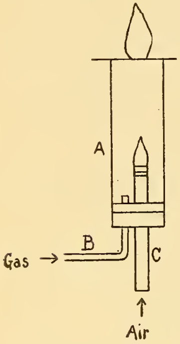


Fig. 50.

Appearance of Flames. The flame caused by the union of hydrogen and oxygen is almost colorless and invisible. Chlorine and hydrogen combine with a pale violet flame; carbon monoxide burns in oxygen with a blue flame, ammonia with a deep yellow flame. The color and appearance of flames are therefore often quite characteristic of the particular combustion which occasions them.

Structure of Flames. When the gas undergoing combustion issues from a round opening into an atmosphere of the gas supporting the combustion, as is the case with the burning Bunsen burner shown in Fig. 51, the flame is in general conical in outline. It consists of several distinct cones, one within the other, the boundary between them being marked by differences of color or luminosity. In the simplest flame, of which hydrogen burning in oxygen is a good example, these cones are two in number; an inner one, formed by unburned gas, and an outer one, usually more or less luminous, consisting of the combining gases. This outer one is in turn surrounded by a third envelope of the products of combustion, and this is sometimes invisible, as in the present case, but is sometimes faintly luminous. The lower part of the inner cone of the flame is quite cool, and consists of unburned gas. Toward the top of the inner cone the gas has become heated to a high temperature by the burning envelope surrounding it. On reaching the supporter of combustion on the outside it is far above its kindling temperature, and combustion follows with evolution of much heat. The region of combustion just outside the inner cone is therefore the hottest part of the flame.

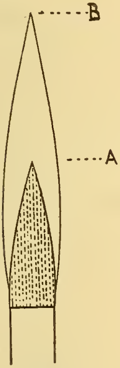


Fig. 51.

When the combustible gas is a compound substance, and undergoes decomposition before burning, or burns in several stages, the number of the cones may be increased, a new cone appearing for each chemical reaction taking place. In the case of ammonia burning in oxygen, the heated ammonia decomposes, thus $2NH_3 = N_2 + 3H_2$. The hydrogen then burns to form water, and the nitrogen escapes for the most part unchanged. There is in this case a double cone surrounding the inner cone of unburned gas. When a gaseous hydrocarbon, such as methane, is burned there are several cones to the flame, for the methane does not burn as represented in the simple equation $CH_4 + 2O_2 = CO_2 + 2H_2O$, but in a series of stages. Acetylene is one of the intermediate products and part of the luminosity of the gas flame is due to its formation and subsequent combustion.

Oxidizing and Reducing Flames. Since the tip of the outside cone consists of very hot products of combustion, mixed with oxygen from the air, a substance capable of oxidation placed in this part of the flame is easily oxidized. The hot gases raise it to a high temperature, and under these circumstances it combines with the oxygen abundant near the tip of the flame. The oxygen with which it combines comes, of course, from the atmosphere, and not from the products of combustion. This outer tip of the flame is called the oxidizing flame.

At the tip of the inner cone the conditions are quite different. This region consists of a highly heated combustible gas, which has not yet reached a supply of oxygen. If a substance, rich in oxygen, such as a metallic oxide, is placed in this region of the flame, the heated gases combine with its oxygen, instead of that of the air, and the substance is reduced. This part of the flame is called the reducing flame.

Luminosity of Flames. Much careful study has shown that the luminosity of flames is due to a number of distinct causes, and that it may therefore be increased or diminished in several ways. (1) The most obvious of these factors is the presence in the flame of incandescent solid matter. Thus chalk dust sifted into a non-luminous flame renders it luminous. When hydrocarbons form a part of the combustible gas, as they do in nearly all illuminating gases and oils, some carbon is usually set free in the process of combustion. This is made very hot by the flame, and becomes incandescent, giving out light. In a well regulated flame it is afterward burned up, and when the supply of oxygen is insufficient, it escapes from the flame as lampblack or soot. That it is temporarily present in a well burning luminous flame may be demonstrated by holding a cold substance, as a small evaporating dish, in the flame for a few seconds. The cold object cools the carbon below its kindling temperature, and it is deposited on the object as soot.

Substances differ much in the ease with which they become incandescent in a flame, and in the amount of light which they give off when heated to incandescence. The various kinds of mantles for gas lights now so commonly used, are made of substances which become incandescent at a low temperature, and which then give off an unusual amount of light. These mantles are suspended around a non-luminous flame, and it is the incandescent substance in the flame which gives the light.

(2) A second factor in the luminosity of flames is the pressure under which the gases are burning. Under increased pressure there is more matter in a given volume of a gas, and the chemical action is more energetic than when the gases are rarified. Consequently there is more heat and light. A candle burning on a high mountain gives less light than when it burns at the sea level.

If the gas is diluted with a non-combustible gas, the effect is the same as to rarify it. There is less combustible gas in a given volume. The difference observed between burning in air and burning in oxygen is due to the presence of so much incombustible nitrogen which serves to dilute the oxygen of the air.

(3) The luminosity also depends upon the temperature attained in the combustion. In general the hotter the flame the greater the luminosity. Hence cooling the gases before combustion diminishes the luminosity of the flame they will make, because it diminishes the temperature attained in the combustion.

With these principles in mind, the several kinds of flames in common use are readily understood.

Bunsen Flame. The luminous Bunsen flame is produced by hydrocarbons and other gases burning in air. It is very hot, and owes its luminosity to its high temperature and to the plentiful supply of incandescent carbon in it. When air is admitted at the base of the burner, the luminosity disappears. The cause of this is in part that oxygen is drawn up with the gas, and the hot carbon compounds do not have to wait for complete combustion until they reach the outer cone of the flame. Much less carbon is actually set free in any stage of the combustion. The burning gas is also diluted and cooled by the air drawn in, which tends to diminish luminosity.

Blowpipe Flame. This is made by blowing into a small, luminous Bunsen flame from one side, through a blowpipe. This is a tube of the shape shown in Fig. 52. The flame is easily directed in any desired way, and has the oxidizing and reducing regions very clearly marked (Fig. 53). It is non-luminous from the same causes as render the open Bunsen burner non-luminous, the gases from the lungs serving to furnish oxygen, and to dilute the combustible gas.


Fig. 52.

Illuminating and Fuel Gases. A number of mixtures of combustible gases consisting largely of carbon compounds and hydrogen, find extensive use for the production of light and heat. The three chief varieties are (1) coal gas, (2) water gas, (3) natural gas. The use of acetylene gas has already been referred to.

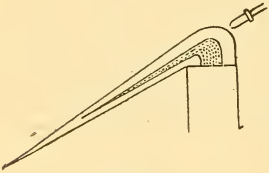


Fig. 53.

Coal Gas is made by heating bituminous coal in large retorts out of contact with the air. Such a process is called dry distillation.

Soft or bituminous coal contains, in addition to large amounts of carbon, considerable quantities of compounds of hydrogen, oxygen, nitrogen and sulphur. When distilled, the nitrogen is liberated partly in the form of ammonia and partly as free nitrogen gas; the sulphur is converted into hydrogen sulphide; the oxygen into water, and oxides of carbon. The remaining hydrogen is partly set free as hydrogen, and partly in combination with carbon in the form of hydrocarbons, chiefly as methane, with smaller quantities of many others, some of which are liquids and solids at ordinary temperatures. The great bulk of the carbon remains behind as coke and retort carbon.

The mixture of gases is freed from tarry and solid materials by being passed through condensing chambers, and from soluble gases such as hydrogen sulphide and ammonia, in towers called scrubbers, in which sprays of water are played upon the gas. It is then passed over beds of lime or iron oxide to absorb carbon dioxide and remaining traces of sulphur compounds, and thence into holders for distribution. The scrubbers furnish all the ammonia of commerce, while from the tarry products, known as coal tar or pitch, many valuable products are obtained. Among these are benzene, toluene, carbolic acid, naphthalene.

Water Gas is essentially a mixture of carbon monoxide and hydrogen. It is made by passing steam over very hot anthracite coal, when the reaction shown in the following equation takes place: $C + H_2O = CO + H_2$. When required merely for fuel gas, to produce heat, the gas is at once ready for use. When made for illuminating purposes it must be enriched, that is illuminants must be added. This is accomplished by passing it as it comes from the producer into heaters, containing highly heated petroleum oils. The gas takes up hydrocarbon gases formed in the decomposition of the petroleum oils, which make it burn with a luminous flame, whereas the original water gas burns with a nonluminous flame of burning carbon monoxide and hydrogen. The final composition of enriched water gas does not differ very much from that of coal gas, excepting that it has much more carbon monoxide in it.

Natural Gas. This substance, so abundant in many localities, varies much in composition, but in a general way it resembles coal gas. It contains much more methane, and its luminosity is not so great. When used for lighting purposes, it is usually burned in a burner resembling an open Bunsen, the illumination being furnished by an incandescent mantle. Contrary to statements frequently made, natural gas contains no free hydrogen.

Table Showing Composition of Gases.

	Pennsylvania Natural Gas.	Coal Gas.	Water Gas.	Enriched Water Gas.
Hydrogen	.....	41.3	52.88	30.00
Methane	90.64	43.6	2.16	24.00
Illuminants (C_2H_4).....	.....	3.9	....	12.05
Carbon monoxide	.....	6.4	36.80	29.00
Carbon dioxide	0.30	2.0	3.47	0.30
Nitrogen	9.06	1.2	4.69	2.50
Oxygen	.....	0.3	.....	1.50
Hydrocarbon vapors ..	.....	1.5	.....	1.50

These are analyses of actual samples, and may be taken as about the average for the various kinds of gases. Any one of these may vary considerably. The nitrogen and oxygen in most cases is due to a slight admixture of air which is difficult to exclude entirely in the manufacture and handling of gases.

The Electric Furnace. Until recent years about the only source of heat for practical purposes has been the combustion of such substances as coal, the gases just described, and hydrogen. When a very intense heat was desired the oxyhydrogen

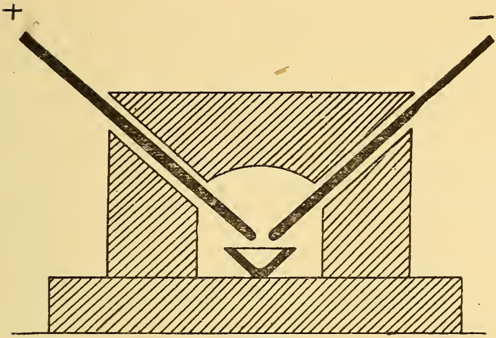


Fig. 54.

blow-pipe was used. With the development of the cheap production of the electric current, a new source of heat, namely, the electric furnace, is rapidly becoming an important factor in the production of very high temperatures.

In the simplest type of the electric furnace, the source of heat is the arc formed when a strong current passes between carbon poles separated a little from each other. The substance to be heated is placed in a graphite crucible, and this crucible is put just below the arc in a cavity in some difficultly fusible material such as a block of lime. Over this block is placed a similar one with a corresponding cavity. The arc is therefore formed in a small open space, the walls of which consist of difficultly fusible material, which confine the heat to a small space and reflect it downward upon the open crucible placed below the arc. (See Fig. 54.)

In some more recent types, the current is passed through very infusible material which is packed around the crucible containing the substance to be heated, and which becomes intensely hot when the current is passing through it. This furnace has the advantage that the temperature reached can be more easily controlled. Temperatures estimated to be as high as 3500° can be reached in the electric furnace.

CHAPTER XVII.

MOLECULAR WEIGHTS, ATOMIC WEIGHTS, FORMULAS.

Introduction. In the chapter on the Atomic Theory, it was pointed out that if it were true that an atom of one element always united with a single atom of every element with which it forms a compound, and in no other ratio, it would be a very easy matter to decide upon figures which would represent the relative weights of the different atoms. It would only be necessary to select some one element as a standard, and determine the weight of every element which combines with a unit amount (one gram) of the standard element. The figures so obtained would evidently represent the relative weights of the atoms.

For example, if hydrogen is selected as the standard element, it will be found that 1 gram of hydrogen combines with 7.94 grams of oxygen, forming 8.94 grams of water. Any weight of water no matter how small will contain oxygen and hydrogen in the ratio 1 : 7.94. Consequently the molecule of water will contain the elements in this ratio, and if a single atom of each is present, these figures must represent their relative weights.

But the law of multiple proportion at once reminds us that two elements may unite in several proportions; and there is no simple way to decide in which one of the compounds so formed the molecules consist of a single atom of each of the elements present. Consequently the problem of deciding upon the relative atomic weights is not an easy one. To the solution of this problem we must now turn.

When Dalton first advanced the atomic theory he attempted to solve this problem by very simple methods. He thought that when only one compound of two elements is known, it is reasonable to suppose that it contains one atom of each element. He therefore gave the formula HO to water, and HN to ammonia, CH to ethylene gas (C_2H_4). When more than two compounds were known he assumed that the most familiar or the most stable compound had the simple formula. He then determined the atomic weight as explained above. The results he obtained were contradictory, and very far from satisfactory, and it was soon seen that some other way, resting on much more scientific grounds, must be found to decide what compounds have a single atom of each element present.

Three distinct steps are involved in the selection of the proper number to express the atomic weight of an element:

1. Determination of the Equivalent.

Definition. By the equivalent of an element is meant the mass of the element which will combine with a fixed mass of some other element chosen as a standard. Since hydrogen has the smallest equivalent, it is chosen as the standard; the equivalent of an element is therefore the amount of it which combines with a gram of hydrogen, or displaces a gram of hydrogen from an acid. Thus, 1 gram of hydrogen combines with 7.94 grams of oxygen, 15.92 grams of sulphur, 35.18 grams of chlorine. 32.45 grams of zinc and 31.92 grams of copper displace a gram of hydrogen from acids. These figures therefore represent the equivalent weights of these elements.

Indirect Determination of the Equivalents. Many of the elements do not form compounds with hydrogen which can be easily obtained and analyzed, nor do they all displace hydrogen from acids in such a way that the hydrogen can be collected and measured. Nearly all the elements do, however, combine with oxygen, and since the equivalent of oxygen is 7.94 the equivalent of an element can often be determined by finding out how much of it combines with 7.94 grams of oxygen.

Relation of Equivalents to Atomic Weights. According to the atomic theory combination always takes place between whole numbers of atoms. One atom unites with one other, or with two or three; or two atoms may unite with three, or three with five. When oxygen combines with hydrogen the combination must be between definite numbers of the two kinds of atoms. If one atom of hydrogen combines with one of oxygen, and we find by experiment that the ratio by weight is 1 gram of hydrogen to 7.94 grams of oxygen, then the atom of oxygen must be 7.94 times the weight of the hydrogen atom. If two atoms of hydrogen combine with one of oxygen, the oxygen atom is 15.88 times as heavy as the hydrogen atom.

It is evident that the equivalent must bear a simple relation to the real atomic weight; it is either some multiple or aliquot part of it. And since the equivalents can be very accurately determined, we can in this way obtain a value for each element which stands in this very simple relation to its atomic weight.

Combining Weights. The equivalent of an element denotes not only the amount of it which will combine with a gram of hydrogen, but also the amount which will combine with the equivalent weight of another element. We have seen that the figures 7.94, 15.92 and 35 18 are the equivalents respectively of oxygen, sulphur and chlorine, and that 32.45 is the equivalent of zinc. Now it has been found by experiment that 32.45 grams of zinc will combine with 7.94 grams of oxygen, 15.92 grams of sulphur and 35.18 grams of chlorine. These figures may therefore be called the combining weights of the elements named. It is important to notice that the fact that a number can be found for each element which indicates the proportion in which the element combines with other elements is not a part of a theory, but is a fact of nature, just as the fact expressed by the law of multiple proportion is a fact and not a theory.

Elements with more than one Equivalent. It will be remembered that oxygen combines with hydrogen in two ratios. In the one case 1 gram of hydrogen combines with 7.94 grams of oxygen to form water; in the other 1 gram of hydrogen combines with 15.88 grams of oxygen to form hydrogen dioxide. The equivalents of oxygen are therefore 7.94 and 15.88. Barium combines with oxygen in two proportions: in barium oxide the proportion is 7.94 grams of oxygen to 68.72 grams of barium; in barium dioxide the proportion is 7.94 grams of oxygen to 34.36 grams of barium.

In each case the one equivalent is a simple multiple of the other, so the fact that there may be two equivalents does not add uncertainty to the case; for all we knew before was that the true atomic weight is some multiple of the equivalent.

2. The Determination of Molecular Weights. To decide the question as to which multiple of the equivalent correctly represents the atomic weight of an element, it has been found necessary to devise a method of determining the molecular weights of compounds containing the element in question. Since the molecular weight of a compound is merely the sum of all the weights of all the atoms present in it, it would seem to be impossible to determine the molecular weight of a compound without first knowing the atomic weights of the constituent atoms, and how many atoms of each element are present in the molecule. But certain facts have been discovered which suggest a way in which this can be done.

Simplicity of the Gas Laws. We have already found that the laws which govern the conduct of gases are very simple and seem to apply to all gases whatever their chemical properties may be. *Boyle's Law* tells us that a given volume of any gas under standard conditions is affected in the same degree by a given change in pressure. *Dalton's Law* states the fact that a given volume of any gas under standard conditions is affected in the same degree by a given change in temperature. *Gay-Lussac's Law* shows that very simple relations hold between the volumes of combining gases, as well as between them and the volume of the gaseous product formed. It is evident therefore that the structure of gases must be very simple, and that it is much the same in all gases.

Avogadro's Hypothesis. In 1811, Avogadro, an Italian physicist, suggested that if we assume that all gases, under the same conditions of temperature and pressure, have the same number of molecules in a given volume, we will have a probable explanation of these simple relations. Plainly we cannot prove such an hypothesis, but there are a great many facts known which make it seem probable that it expresses the truth. Avogadro's hypothesis then is: — Equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules.

Avogadro's Hypothesis and Molecular Weights. Assuming that Avogadro's hypothesis is correct, we have a very simple means for deciding upon the relative weights of molecules. For if equal volumes of two gases contain the same number of molecules, the weights of the two volumes must be in the same ratio as the weights of the indivdual molecules which they contain. If we adopt some one gas as a standard we can express the weights of all other gases as compared with this one, and the same figures will express the relative weights of the molecules of which the gases are composed.

Hydrogen as Standard. Hydrogen, being the lightest of all gases, is a suitable standard. On comparing the weights of equal volumes of hydrogen and other gases, it is found that oxygen is 15.88 times as heavy as hydrogen: nitrogen 14 times as heavy; chlorine 35.18 and hydrochloric acid 18.09 times as heavy. Since these equal volumes have the same number of molecules in them, it follows that these figures express the weights of the molecules of the substances named, compared with the hydrogen molecule as unity.

The relative weights of equal volumes of two gases can be easily determined. A small flask such as is shown in the Fig. 55 is filled with one of the gases, and after the temperature and pressure have been noted, the flask is sealed up and weighed. The top is then broken off of the sealed end, the flask filled with the second gas, and its weight determined. If the weight of the empty flask is subtracted from these two weighings, the relative weights of the gases is readily found.

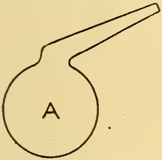


Fig. 55.

The Hydrogen Molecule Contains Two Atoms. It has already been shown that when hydrogen and chlorine combine, one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid gas. Let us suppose that the equal volumes of hydrogen and chlorine contained 1,000 molecules; then by Avogadro's law, the double volume of hydrochloric acid formed will contain 2,000 molecules. But each of these 2,000 molecules must contain at least one atom of hydrogen, or 2,000 atoms in all, and the 2,000 hydrogen atoms came from 1,000 molecules of hydrogen. It follows therefore that the hydrogen molecule consists of at least two atoms. Evidently this reasoning only proves that there are *at least* two atoms in the hydrogen molecule; there may be more than that, but as there is no evidence of any kind that this is the case we assume that the molecule contains only two atoms.

We have just seen that the oxygen molecule is 16 times as heavy as the hydrogen molecule; and if the hydrogen molecule contains two atoms, the oxygen molecule is evidently 32 times as heavy as the hydrogen atom. For many reasons the hydrogen atom is a more convenient standard than the hydrogen molecule with which to measure the relative weights of other molecules. Consequently to determine the molecular weight of a gas we find its weight compared with the weight of an equal volume of hydrogen gas, and multiply this value by two; hence molecular weight = 2 × density (compared with hydrogen). In determining the density of gases it is customary to use air as a standard rather than hydrogen. Since air is 14.44 times as heavy as hydrogen, we can substitute the density compared with air in the above equation instead of the density compared with hydrogen, if at the same time we multiply by 14.44. We have then the formula; molecular weight = 2 × 14.44 × density (referred to air) or in brief: $M = d \times 28.88$.

3. **Deduction of Atomic Weights from Molecular Weights and Equivalents.** We have now seen how the equivalent of an element, which is some aliquot part of the atomic weight, and the molecular weight of compounds containing the element, can be obtained. Let us see how it is possible to decide which multiple of the equivalent really is the true atomic weight. An example will make the reasoning clear, so let us suppose that the equivalent of oxygen has been found to be 7.94 and that it is desired to obtain its atomic weight. The next step is to obtain the molecular weights of a large number of compounds containing oxygen. The following will serve:

	Molecular weight (in round numbers).	Part due to oxygen (in round numbers).
Water	18	16
Hydrogen dioxide	34	32
Carbon monoxide	28	16
Carbon dioxide	44	32
Nitrogen peroxide	46	32
Phosphorus pentoxide ..	142	80

The figures under molecular weight gives the weight of the molecules compared with the hydrogen atom, and have been determined as just described. The figures in the second column show what part of this total weight is due to the oxygen in the compound, and have been found by analysis of the substances. Now if the molecular weights represent the sum of the atomic weights, then the figures in the second column must also represent the sum of the weights of the oxygen atoms in the molecules; and since the molecule is composed of whole atoms, the figures representing the weights of the atoms must be the sum of the weights of whole atoms of oxygen. Now among all the compounds containing oxygen, there will doubtless be some containing only one atom of oxygen, and so we should find some small figure in the column expressing the weights of the sum of the oxygen atoms which is the weight of a single oxygen atom, and all the other weights should be multiples of this least weight. No compound has ever been found which contains less than 16 parts of oxygen in the molecular weight of a compound, and all other weights are multiples of 16. We therefore assume that 16 is the atomic weight of oxygen.

Accurate Determination of Atomic Weights. Molecular weights cannot be determined very accurately, and consequently the part in the molecular weights due to oxygen is a little uncertain. All we can tell by this method is that the true weight is very near 16. The equivalent can however be determined very accurately, and we have seen that it is some aliquot part of the true atomic weight. Since molecular weight determination has shown that in the case of oxygen the atomic weight is near 16, and we have found the equivalent to be 7.94, it is evident that the true atomic weight is twice the equivalent, or $7.94 \times 2 = 15.88$.

These then are the steps necessary to establish the atomic weight of an element:

1. Determine the equivalent accurately by analysis.

2. Determine the molecular weight of a large number of compounds of the element, and by analysis the part of the molecular weight due to the element. The smallest number so obtained will be approximately the atomic weight.

3. Multiply the equivalent by the small whole number (usually 1, 2 or 3), which will make a number very close to the approximate atomic weight. The figure so obtained will be the true atomic weight.

Other Methods of Determining Molecular Weights. It will be noticed that the reason Avogadro's Law furnishes us with a method by which we can determine the relative weights of the molecules of two gases is that it enables us to tell when we are dealing with an equal number of the two kinds of molecules. If by any other means we can get this information, we can make use of the knowledge so gained to determine the molecular weights of the two substances.

Raoult's Laws. Two laws have been discovered which give us just such information. They are known as Raoult's Laws, and can be stated as follows:

1. When weights of substances which are proportional to their molecular weights are dissolved in the same weight of solvent, the rise of the boiling point is the same in each case.

2. When weights of substances which are proportional to their molecular weights are dissolved in the same weight of solvent, the lowering of the freezing point is the same in each case.

By taking advantage of these laws it is possible to determine when two solutions contain the same number of molecules of two dissolved substances, and consequently the relative molecular weights of the two substances.

Direct Method of Determining Atomic Weights. In 1819 Dulong and Petit discovered a very interesting relation between the atomic weight of an element and its specific heat, which holds true for elements in solid state. If equal weights of two solids, say lead and silver, are heated through the same range of temperature, as from 10°—20°, it is found that very different amounts of heat are required. The amount of heat required to change the temperature of a solid or a liquid by a definite amount compared with the amount required to change the temperature of an equal weight of water by the same amount is called its specific heat. Dulong and Petit found that the specific heat of an element in the solid form multiplied by its atomic weight is the same in all cases, and is equal to a nearly constant value of 6.25. That is $\text{atomic weight} \times \text{specific heat} = 6.25$ and consequently $\text{atomic weight} = \frac{6.25}{\text{specific heat}}$ This law is not very accurate, but it is often found possible by means of it to decide upon what multiple of the equivalent is the real atomic weight. Thus the specific heat of iron is found to be 0.112 and its equivalent is 28. $6.25 \div 0.112 = 55.8$. We see therefore that the atomic weight is twice the equivalent or 56.

How Formulas are Determined. It will be well in connection with molecular weights to consider how the formula of a compound is decided upon, for the two subjects are very closely associated. Some examples will make the method followed clear.

The molecular weight of a substance containing hydrogen and chlorine was 36.4. By analysis 36.4 parts of the substance was found to contain 1 part of hydrogen and 35.4 parts of chlorine. As these are the simple atomic weights of the two elements, the formula and the compound must be HCl.

A substance consisting of oxygen and hydrogen was found to have a molecular weight of 34. Analysis showed that in 34 parts of the substance there are 2 parts of hydrogen and 32 parts of oxygen. Dividing these figures by the atomic weights of the two elements we get $2 \div 1 = 2$ for H: $32 \div 16 = 2$ for O. The formula is therefore H_2O_2.

A substance containing 2.04% H, 32.6% S and 65.3% O was found to have a molecular weight of 98. In this 98 parts of the substance there are $98 \times 2.04\% = 2$ parts of H, $98 \times 32.6\% = 32$, S and $98 \times 65.3\% = 64$, O. If the molecule weighs 98, the hydrogen atoms present must together weigh 2, the sulphur atoms 32, and the oxygen atoms 64. Dividing these figures by the respective atomic weights of the three elements we have for H, $2 \div 1 = 2$ atoms, for S, $32 \div 32 = 1$ atom, for O, $64 \div 16 = 4$ atoms. Hence the formula is H_2SO_4.

We have then this general procedure: Find the percentage composition of the substance and also its molecular weight. Multiply the molecular weight in succession by the percentage of each element present to find the amount of the element in the molecular weight of the compound. The figures so obtained will be the respective parts of the molecular weight due to the several atoms. Divide by the atomic weight of the elements, and the quotient will be the number of atoms present.

CHAPTER XVIII.

THE NITROGEN FAMILY.

The members of the Nitrogen Family given in the order of their atomic weights are nitrogen, phosphorus, arsenic, antimony and bismuth. Nitrogen has been studied in a former chapter. The remaining members of the family will now be discussed.

PHOSPHORUS.

History. The element phosphorus was discovered by the Alchemist Brandt of Hamburg in 1669, while searching for the philosopher's stone. Owing to its peculiar properties, and the secrecy which was maintained about its preparation, it remained a very rare and costly substance, until the demand for it in the manufacture of matches brought about its production on a large scale.

Occurrence. Owing to its great chemical activity, phosphorus never occurs free in nature. In the form of phosphates it is very abundant and widely distributed. *Phosphorite* and *sombrerite* are mineral forms of calcium phosphate, while *apatite* consists of calcium phosphate together with calcium chloride or fluoride. These minerals form very large deposits, and are extensively mined for use as fertilizers. Calcium phosphate is a constituent of all fertile soil, having been supplied to the soil by the disintegration of rocks containing it. It is the chief mineral constituent of bones of animals, and bone ash is therefore nearly pure calcium phosphate.

Preparation. Phosphorus is now manufactured from bone ash or a pure mineral phosphate, by heating the phosphate with sand and carbon in an electric furnace.

To understand the reaction which occurs, it must be remembered that a volatile acid anhydride is expelled from its salts when heated with an anhydride which is not volatile. Thus when sodium carbonate and silicon dioxide are heated together, the following reaction takes place:

$$Na_2CO_3+SiO_2=Na_2SiO_3+CO_2.$$

Silicon dioxide is a less volatile anhydride than phosphoric anhydride, P_2O_5, and when strongly heated with a phosphate, the phosphoric anhydride is driven out, thus:

$$Ca_3(PO_4)_2+3SiO_2=3CaSiO_3+P_2O_5.$$

If carbon is added before the heat is applied, the P_2O_5 is reduced to phosphorus at the same time, according to the equation

$$P_2O_5+5C=2P+5CO.$$

The phosphorus vapor, as it escapes from the furnace, is conducted under water, where it is condensed into solid form.

In the older process, which is still in use, bone ash is treated with sulphuric acid, forming calcium sulphate and phosphoric acid. The phosphoric acid is evaporated to a syrup and mixed with sawdust or carbon. The mixture is then dried, and finally heated intensely in an earthen retort, when phosphorus is set free according to the equation:

$$2\ H_3PO_4+5\ C=3\ H_2O+2\ P+5\ CO.$$

The phosphorus so prepared contains many impurities. These are removed in various ways, usually by melting the crude phosphorus in warm water, and pressing it through filters of bone black or chamois skin. The product is finally distilled.

Physical Properties. The purified phosphorus is a pale, yellowish, translucent, waxy solid which melts at 45°, and boils at 290°. It melts therefore in warm water, and can be cast into any convenient form under water. It is usually sold in the market in the form of sticks. It is quite soft, and can be easily cut with a knife. This must always be done while the phosphorus is covered with water, since the element is extremely inflammable, and the friction of the knife blade is almost sure to set it on fire if cut in the air. It is not soluble in water, but is freely soluble in some other liquids, notably in carbon disulphide. Its density is 1.8.

Chemical Properties. Exposed to the air, phosphorus slowly combines with oxygen, and in doing so, emits a pale light or phosphorescence, which can be seen only in a dark place. The heat of the room may easily raise the temperature to the kindling point, when phosphorus burns with a sputtering flame, giving off dense fumes of oxide of phosphorus.

The heat of the body is sufficient to raise phosphorus above its kindling temperature, and for this reason phosphorus should always be handled with forceps and never with the bare fingers. Burns occasioned by it are very painful and slow in healing. Phosphorus burns brilliantly in oxygen, and combines directly with many other elements, especially with sulphur and the halogens.

$$P + 3\ Cl = PCl_3.$$

Phosphorus is very poisonous, 0.2—0.3 gram being a fatal dose. Ground up with flour and water or similar substances, it is often used as a poison for rats and other vermin.

Red Phosphorus. When phosphorus is heated for some time at a temperature of about 250°—300°, it undergoes a remarkable change. It loses its transparency and is converted into a dark, chocolate colored, opaque powder having a density of about 2.1. It no longer takes fire easily, and can be handled in dry form like any other substance. It is not poisonous, and in fact seems to be an entirely different substance. When distilled, and quickly condensed, it changes back again into ordinary yellow phosphorus. Still another, or black modification of phosphorus is known, which is somewhat metallic in appearance. These allotropic forms recall the similar modifications of sulphur and carbon.

Uses of Phosphorus. The chief use of phosphorus is in the manufacture of matches. Common matches are made by first dipping the match sticks into some inflammable substance such as melted paraffine, and afterward into a paste consisting of (1) phosphorus, (2) some oxidizing substance such as manganese dioxide, or potassium chlorate, and (3) a binding material, usually some kind of glue. On friction the phosphorus is ignited, the combustion being sustained by the oxidizing agent, and communicated to the wood by the burning paraffine.

In sulphur matches the paraffine is replaced by sulphur. In safety matches, *red* phosphorus, an oxidizing agent, and some gritty material such as emery is placed on a strip on the side of the box, while the match tip is provided as before with an oxidizing agent and an easily oxidized substance, usually antimony sulphide. The match cannot be easily ignited by friction, save on the prepared surface.

Compounds of Phosphorus with Hydrogen. Phosphorus forms several compounds with hydrogen, the best known of which is phosphine, PH_3, analgous to ammonia, NH_3.

Preparation of Phosphine. Phosphine is usually made by heating phosphorus with a strong solution of potassium hydroxide, the reaction being a complicated one. The experiment can be conveniently made in the apparatus shown in Fig. 56. A strong solution of potassium hydroxide together with several small bits of phosphorus are placed in the flask A, and a current of coal gas is passed into the flask through the tube B, until all the air has been displaced. The gas is then turned off, and the flask is heated. Phosphine is formed in small quantities, and escapes through the delivery tube, the exit of which

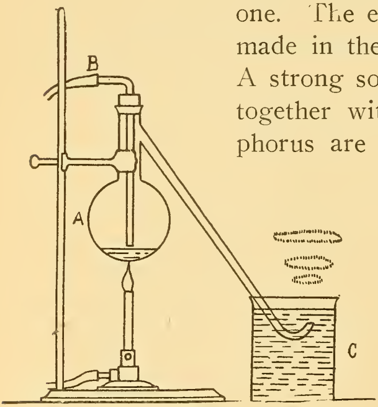


Fig. 56.

is just covered by the water in the vessel C. Each bubble of the gas, as it escapes into the air, takes fire, and the product of combustion forms beautiful small rings, which float unbroken for a considerable time in quiet air.

Properties. Phosphine is a gas of unpleasant odor, and is exceedingly poisonous. Prepared in the way just described, it is spontaneously inflammable, but this is due to impurities. It has much more feeble basic properties than has ammonia, forming unstable salts with the halogens acids, but with no others.

$$PH_3 + HCl = PH_4Cl$$

The product of this reaction is called phosphonium chloride, and is analogous to ammonium chloride.

Oxides of Phosphorus. Phosphorus forms two well known oxides: the trioxide, P_2O_3, and the pentoxide, P_2O_5, sometimes called phosphoric anhydride. When phosphorus burns in an insufficient supply of air the product is partially the trioxide; in oxygen or free access of air the pentoxide is formed. The pentoxide is much the better known of the two. It is a snow white, voluminous powder, whose most marked property is its great attraction for water. It has no chemical action upon most gases, so that they can be very thoroughly dried by allowing them to pass through properly arranged vessels containing phosphorus pentoxide.

Acids of Phosphorus. Both of the oxides of phosphorus are acid anhydrides: that is they combine with water to form acids. Unlike the corresponding nitrogen anhydrides, they show a marked tendency to form acids containing three hydrogen atoms, so that the relation between acid and anhydride is not so simple as with the nitrogen acids. Thus the trioxide combines with water to form the tribasic phosphorous acid:

$$P_2O_3 + 3\ H_2O = 2\ H_3PO_3.$$

This acid, as well as its salts, is not very often met with. Its most interesting property is its tendency to take up oxygen and pass over to phosphoric acid:

$$H_3PO_3 + O = H_3PO_4.$$

It is therefore a good reducing agent.

Phosphoric Acids. Phosphorus pentoxide is able to combine with water in three proportions to form three acids, the names and formulas of which are:

HPO_3 . . . . metaphosphoric acid
H_3PO_4 . . . . orthophosphoric acid
$H_4P_2O_7$ . . . . pyrophosphoric acid.

(1) *Metaphosphoric Acid.* This acid is formed when phosphorus pentoxide dissolves in water

$$P_2O_5 + H_2O = 2\ HPO_3$$

It is a crystalline solid, and is very stable towards heat, so that it can be fused and even volatilized without decomposition. On cooling from the fused state it forms a glassy solid, and the acid is on this account often called glacial phosphoric acid. It possesses the property of dissolving small quantities of metallic oxides, and acquiring characteristic colors from them. On this account it is often used to detect the presence of such metals in a compound as give these colors with metaphosphoric acid.

(2) *Orthophosphoric Acid.* When a solution of metaphosphoric acid is boiled, the acid combines with an additional amount of water, forming phosphoric acid, having the formula H_3PO_4.

$$HPO_3 + H_2O = H_3PO_4.$$

Phosphoric acid, sometimes called orthophosphoric acid, can be obtained in the form of large colorless crystals, by evaporating its solutions. When strongly heated, it loses water and metaphosphoric acid is formed again. It is not volatile, and will therefore drive most of the common acids from their salts when the salt and phosphoric acid are heated together.

Phosphoric acid is a tribasic acid; that is all three of its hydrogen atoms have acid properties. It can therefore form two acid salts and a normal salt, when acted upon by bases.

$NaOH + H_3PO_4 = NaH_2PO_4 + H_2O$. (primary acid phosphate.)
$2\ NaOH + H_3PO_4 = NaH_2PO_4 + 2\ H_2O$. (secondary acid phosphate.)
$3\ NaOH + H_3PO_4 = Na_3PO_4 + 3\ H_2O$. (tertiary acid phosphate.)

It can easily form mixed salts, that is salts containing two different metals. Microcosmic salt is such a mixed salt of sodium and ammonium: it has the formula, $Na(NH_4)HPO_4, H_2O$.

Orthophosphates. The orthophosphates form an important class of salts. The normal, or tertiary, phosphates are nearly all insoluble, and as we have seen, occur in large quantities in nature. The primary phosphates are for the most part soluble in water.

(3) *Pyrophosphoric Acid.* On heating a primary phosphate, it loses oxygen and hydrogen in the form of water, and a metaphosphate is formed.

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

On heating a secondary phosphate, water is eliminated form two molecules of the salt.

$$2\ Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

The product of this reaction is the sodium salt of the acid $H_4P_2O_7$, called, from its method of preparation, pyrophosphoric acid.

The relation of these four acids to the two anhydrides can be readily seen from the following equations:

$P_2O_3 + 3\ H_2O = 2\ H_3PO_3$. phosphorous acid.
$P_2O_5 + 1\ H_2O = 2\ HPO_3$. metaphosphoric acid.
$P_2O_5 + 2\ H_2O = H_4P_2O_7$. pyrophosphoric acid.
$P_2O_5 + 3\ H_2O = 2\ H_3PO_4$. orthophosphoric acid.

Fertilizers. When crops are produced year after year on the same field certain constituents of the soil essential to plant growth are removed, and the soil becomes impoverished and unproductive. To make the land once more fertile, these constituents must be replaced. The calcium phosphate of the mineral deposits or of bone ash serves well as a material for restoring phosphorus to soils exhausted of that essential element; but a more soluble substance, which the plants can more readily assimilate, is desirable. It is better therefore to convert the insoluble calcium phosphate into the soluble primary phosphate, before it is applied as fertilizer. This is commonly done by treatment of the normal calcium phosphate with the amount of sulphuric acid required to convert it into the primary phosphate, in accordance with the equation

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 = Ca(H_2PO_4)_2 + 2\ CaSO_4.$$

The resulting mixture is a powder, which is sold as "superphosphate of lime."

ARSENIC.

Occurrence. Arsenic occurs in considerable quantities in nature as the native element, as the suphides realgar, As_2S_2 and orpiment, As_2S_3, as oxide, As_2O_3, and as a constituent of many metallic sulphides such as arsenopyrite, $FeAsS$.

Preparation. The element is prepared by purifying the native arsenic, or by heating the arsenopyrite in iron tubes, when the following reaction occurs:

$$FeAsS = FeS + As.$$

The arsenic being volatile, condenses in chambers connected with the heated tubes. It is also made from the oxide by reduction with carbon:

$$2\ As_2O_3 + 3\ C = 4\ As + 3\ CO_2.$$

Properties. Arsenic is a steel gray, metallic looking substance, of density 5.73. Though resembling metals in appearance, it is quite brittle, being easily powdered in a mortar. When strongly heated it sublimes, that is it passes into a vapor without melting, and condenses again to a crystalline solid when the vapor is cooled. Like phosphorus it can be obtained in several allotropic forms. It alloys readily with some of the metals, and finds its chief use as an alloy with lead which is used for making shot, the alloy being harder than pure lead. Unlike most of its compounds it is not poisonous.

Arsine. When any compound containing arsenic is brought into the presence of nascent hydrogen, arsine, AsH_3, corresponding to phosphine and ammonia, is formed. The reaction when oxide of arsenic is so treated is

$$As_2O_3 + 12\ H = 2\ AsH_3 + 3\ H_2O.$$

Arsine is a gas with a peculiar garlic-like odor, and is intensely poisonous. A single bubble of the pure gas has been known to prove fatal. It is an unstable compound, decomposing into its elements when heated to a moderate temperature. It is combustible, burning with a pale bluish-white flame to form arsenic trioxide and water when air is in excess:

$$2\ AsH_3 + 6\ O = As_2O_3 + 3\ H_2O.$$

When the supply of air is deficient, water and metallic arsenic are formed:

$$2\ AsH_3 + 3\ O = 3\ H_2O + 2\ As.$$

These reactions make the detection of even minute quantities of arsenic a very easy problem.

Marsh's Test for Arsenic. The method devised by Marsh is the one most frequently employed. The form of apparatus used is shown in Fig. 57. Hydrogen is prepared in the generator A by the action of dilute sulphuric acid on zinc and is dried by passing through the tube B filled with calcium chloride. It is then conducted through the hard glass tube C and after all the air is expelled from the apparatus, is ignited at the jet D. The substance suspected to contain the arsenic is dissolved in dilute sulphuric acid and slowly added to the hydrogen generator through the funnel tube. Any arsenic present combines with the hydrogen to form arsine, which being a gas, escapes from the generator with the hydrogen. If the tube C is kept quite hot at some point near the middle, the arsine is decomposed at this point, the arsenic being deposited in the cooler portions of the tube just beyond the flame, in the form of a shining black mirror. If the tube is not heated the arsine passes along with the hydrogen and burns at the jet. If a small porcelain evaporating dish be crowded down into the flame, the temperature of the flame is reduced below the kindling temperature of arsenic, which is deposited on the white porcelain as a black spot. After the dish becomes heated the arsenic is no longer deposited: hence it is well to have the dish filled with cold water.

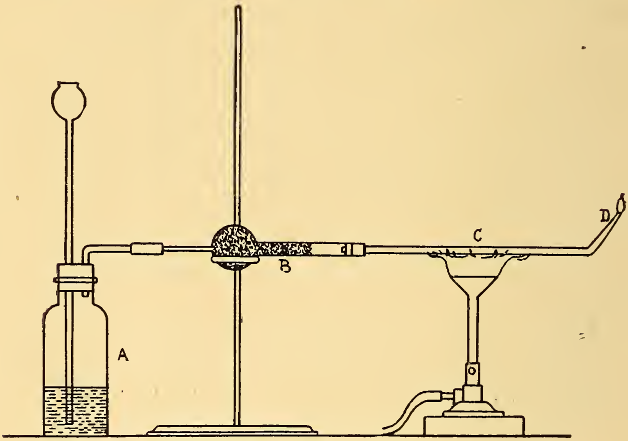


Fig. 57.

Oxides of Arsenic. Arsenic forms two oxides, As_2O_3 and As_2O_5, corresponding to those of phosphorus. Of these arsenious oxide, As_2O_3, is much better known, and is the substance usually called white arsenic or merely arsenic. It is found as a mineral, but is usually obtained as a by-product in burning pyrite in the sulphuric acid industry. The pyrite has a small amount of arsenopyrite in it, and when this is burned, arsenic trioxide is formed together with sulphur dioxide:

$$2\ FeAsS + 10\ O = Fe_2O_3 + As_2O_3 + 2\ SO_2.$$

The arsenious oxide is condensed in appropriate chambers. It is a rather heavy substance, obtained either as a crystalline powder, or as large, vitreous lumps, recalling lumps of porcelain in appearance. It is very poisonous, 0.2—0.3 gram being a fatal dose. It is used largely as a poison, since it is nearly tasteless, and does not act very rapidly. This slow action is due to the fact that arsenic is not very soluble, and is very slowly absorbed by the system. It is also used as a chemical reagent in glass making and in the dye industry.

Acids of Arsenic. Like the corresponding oxides of phosphorus, the oxides of arsenic are acid anhydrides. In solution they combine with bases to form salts, corresponding to the salts of the acids of phosphorus. Thus we have salts of the following acids

H_3AsO_3	arsenious acid.
$HAsO_3$	metarsenic acid.
H_3AsO_4	orthoarsenic acid.
$H_4As_2O_7$	pyroarsenic acid.

Several other acids of arsenic are also known. Not all of these can be obtained as free acids, since they tend to lose water and form the oxides. Thus instead of obtaining the acid H_3AsO_3 the oxide As_2O_3 is obtained.

$$2\ H_3AsO_3 = As_2O_3 + 3\ H_2O.$$

Salts of all the acids are known, however, and some of them have commercial value. Most of them are insoluble, and some of the copper salts which are green, are used as pigments. Paris green, which has a complicated formula, is a well known insecticide.

The most efficient antidote for arsenic poisoning is ferric hydroxide. This converts the soluble arsenious oxide into iron arsenite, which being insoluble, is not poisonous.

$$As_2O_3 + 2\ Fe(OH)_3 = 2\ FeAsO_3 + 3\ H_2O.$$

Magnesium hydroxide is administered at the same time to neutralize the acid naturally present in the stomach.

Sulphides of Arsenic. When hydrogen sulphide is passed into an acidified solution containing an arsenic compound, the arsenic is precipitated as a bright yellow sulphide. Thus,

$$2\ H_3AsO_3 + 3\ H_2S = As_2S_3 + 3\ H_2O.$$
$$2\ H_3AsO_4 + 5\ H_2S = As_2S_5 + 5\ H_2O.$$

In this respect, arsenic resembles the metallic elements, many of which produce sulphides under similar conditions. The sulphides of arsenic, both those produced artificially, and those found in nature, are used as yellow pigments.

ANTIMONY.

Occurrence. It occurs in nature chiefly as the sulphide, Sb_2S_3, called stibnite, though it is also found as oxide, and as a constituent of many complex minerals. It is a rather widely distributed and abundant element.

Preparation. Antimony is prepared from the sulphide in a very simple manner. The sulphide is melted with scrap iron in a furnace, the iron combining with the sulphur to form a slag or liquid layer of melted iron sulphide, while the heavier antimony settles to the bottom, and is drawn off from time to time. The reaction involved is represented by the equation:

$$Sb_2S_3 + 3\ Fe = 2\ Sb + 3\ FeS.$$

Physical Properties. Antimony is a bluish white, metallic-looking substance whose density is 6.7. It is highly crystalline, hard and very brittle. It has a rather low melting point (432°) and expands very noticeably on solidifying.

Alloys. Some metals when melted together thoroughly intermix, and on cooling form a homogeneous, metallic appearing substance called an alloy. Not all metals will mix in this way, and in some cases, definite chemical compounds are formed and separate out as the mixture solidifies, thus destroying the uniform quality of the alloy. In general the melting point of the alloy is below the average of the melting points of its constituents, and it is sometimes lower than any one of them.

Antimony alloys with many of the metals, and its chief commercial use is for such purposes. It imparts to its alloys high density, rather low melting point and the property of expanding on solidification. Such an alloy is especially useful in type founding, where fine lines are to be reproduced on a cast. Type metal consists of antimony, lead and tin. Babbitt metal, used for journal bearings in machinery, contains the same metals in a different proportion together with a small amount of copper.

Chemical Properties. In chemical properties, antimony resembles arsenic in many particulars. It forms the oxides, Sb_2O_3 and Sb_2O_5 and in addition Sb_2O_4. It combines with the halogens elements with great energy, burning brilliantly in chlorine to form antimony chloride, $SbCl_3$. Heated on charcoal with the blowpipe, it is oxidized and forms a coating of antimony oxide on the charcoal which has a characteristic bluish-white color.

Stibine. The gas stibine, SbH_3, is formed under conditions which are closely parallel to those which produce arsine, and it greatly resembles the latter compound, though still less stable than it. The mirror of antimony, produced as in the Marsh test for arsenic closely resembles the arsenic mirror, but it is more sooty in appearance, and the two can be distinguished with great precision by chemical tests.

Acids of Antimony. The oxides, Sb_2O_3, and Sb_2O_5 are weak acid anhydrides and are capable of forming two series of acids corresponding in formula to the acids of phosphorus and arsenic. They are much weaker however, and are of small practical importance.

Sulphides of Antimony. Antimony resembles arsenic in that hydrogen sulphide precipitates it as a sulphide when conducted into an acidified solution containing an antimony compound:

$$2\ SbCl_3 + 3\ H_2S = Sb_2S_3 + 6\ HCl.$$

$$2\ SbCl_5 + 5\ H_2S = Sb_2S_5 + 10\ HCl.$$

The two sulphides of antimony are called the trisulphide and the pentasulphide. They are orange colored substances when prepared in this way though the mineral stibnite is black.

Metallic Properties of Antimony. The physical properties of the elements are those of a metal, and the fact that its sulphide is precipitated by hydrogen sulphide shows that it acts like a metal in a chemical way. Many other reactions show that antimony is a metal rather than an acid forming element. The compound $Sb(OH)_3$, while able to act as a weak acid, is also able to form salts with strong acids. When treated with strong hydrochloric acid, antimony chloride is formed:

$$Sb(OH)_3 + 3\ HCl = SbCl_3 + 3\ H_2O.$$

A number of elements act in this same way, their hydroxides acting under some conditions as weak acids, and under others as weak bases.

Hydrolysis of Antimony Chloride. When antimony chloride is treated with water it is decomposed into antimony hydroxide and hydrochloric acid:

$$SbCl_3+3H_2O=Sb(OH)_3+3HCl.$$

This reaction is a reversible one, and the relative amounts of acid and water present determine in which direction and to what extent the reaction will go. When excess of water is present, it goes as represented in the equation; if excess of hydrochloric acid is added to antimony hydroxide, it goes in the reverse way. Sometimes the decomposition is not complete, and a basic salt is formed, thus:

$$SbCl_3+2H_2O=Sb(OH)_2Cl+2HCl.$$

The decomposition of a salt by water in either of these ways is called hydrolysis.

BISMUTH.

Occurrence. Bismuth is usually found in the uncombined form in nature, and less frequently as oxide and sulphide. Most of the bismuth of commerce comes from Saxony, and from Mexico and Colorado, but it is not an abundant element, and is rather costly.

Preparation. It is prepared by merely heating the ore containing the native bismuth and allowing the melted metal to run out into suitable vessels.

Physical Properties. Bismuth is a heavy, crystalline, brittle metal nearly the color of silver, but with a slightly rosy tint which distinguishes it from other metals. It melts at a low temperature (270°), and has a density of 9.8. It is not acted upon by the air at ordinary temperatures.

Chemical Properties. Heated strongly in the air it burns to form the oxide Bi_2O_3, and before the blowpipe on charcoal bismuth gives a coating of oxide of a yellowish-brown color which is easily distinguished from the one formed by other metals. It combines very readily with the halogens elements, powdered bismuth burning readily in chlorine. It is not very easily acted on by hydrochloric acid, but nitric and sulphuric acids act upon it in the same way that they do upon copper.

Uses. Bismuth finds its chief use as a constituent of alloys, particularly in those of low melting point. Some of these melt in hot water, as Wood's metal, consisting of bismuth, lead, tin and cadmium.

Compounds of Bismuth. Unlike the other elements of this group, bismuth has almost no acid properties. Its chief oxide, Bi_2O_3, is basic in its properties. It dissolves in strong acids and forms salts of bismuth:

$$Bi_2O_3 + 6\ HCl = 2\ BiCl_3 + 3\ H_2O.$$
$$Bi_2O_3 + 6\ HNO_3 = 2\ Bi(NO)_3 + 3\ H_2O.$$

When the salts of bismuth are treated with water they are partially decomposed, giving basic salts. Thus:

$$BiCl_3 + 2\ H_2O = Bi(OH)_2Cl + 2\ HCl.$$
$$Bi(NO_3)_3 + 2\ H_2O = Bi(OH)_2NO_3 + 2\ HNO_3.$$

When these basic salts are treated with *excess* of acid, the normal salt is once more formed.

$$Bi(OH)_2NO_3 + 2\ HNO_3 = Bi(NO_3)_3 + 2\ H_2O.$$

In this respect the salts of bismuth are similar to antimony chloride. In the presence of water they undergo hydrolysis, forming basic salts. In very dilute solution they may be completely hydrolyzed into hydroxide and free acid.

$$BiCl_3 + H_2O = Bi(OH)_2 + 3\ HCl.$$

The basic nitrate and carbonate of bismuth are used in medicine.

CHAPTER XIX.

SILICON — BORON.

Next to oxygen, silicon is the most abundant element. It does not occur free in nature, however, but its compounds are very abundant and of the greatest importance. It occurs almost entirely in combination with oxygen as silicon dioxide, SiO_2, often called silica; or with oxygen and various metals in the form of salts of silicic acids, or silicates. These compounds form a large fraction of the earth's solid crust. Most plants absorb small amounts of silica from the soil. It is also found in minute quantities in animal organisms.

Preparation. The element is prepared by reducing pure powdered quartz with magnesium powder:

$$SiO_2 + 2\ Mg = 2\ MgO + Si$$

or by a more complicated reaction in which sodium fluosilicate Na_2SiF_6, is heated with sodium:

$$Na_2SiF_6 + 4\ Na = 6\ NaF + Si.$$

Properties. As an element it resembles carbon in many respects. It can be obtained in several allotropic forms, corresponding to those of carbon. The crystallized form is very hard, and inactive toward reagents. The amorphous variety has in general properties more similar to charcoal.

Compounds of Silicon with Hydrogen and the Halogens. Silicon hydride SiH_4, corresponds in formula to methane, CH_4, but its properties are more like those of phosphine, PH_3. It is a very inflammable gas of disagreeable odor, and as ordinarily prepared, takes fire spontaneously, from the presence of impurities.

Silicon combines with the elements of the chlorine family to form such compounds as $SiCl_4$, SiF_4. Of these, silicon fluoride is the most familiar and interesting. As stated in the discussion of fluorine it is formed when hydrofluoric acid acts upon any compound of silicon. With silica the reaction is thus expressed:

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

It is a very volatile, invisible, poisonous gas. In contact with water it is partially decomposed as shown in the equation:

$$SiF_4 + 4\ H_2O = 4\ HF + Si(OH)_4.$$

The hydrofluoric acid so formed combines with an additional amount of silicon fluoride forming the complex fluosilicic acid, H_2SiF_6,

$$4\ HF + 2\ SiF_4 = 2\ H_2SiF_6.$$

Silicides. As the name indicates, silicides are binary compounds, consisting of silicon and some other element. They are very stable at high temperatures, and are usually made by heating the appropriate substances in the electric furnace. The most important one is *carborundum* which is a silicide of carbon of the formula CSi. It is made by heating coke and sand which is a form of SiO_2 in an electric furnace, the process being extensively carried on at Niagara Falls.

$$SiO_2 + 3\ C = CSi + 2\ CO.$$

The substance so prepared, consists of beautiful purplish black crystals, which are very hard. Carborundum is used as an abrasive, that is to polish and grind very hard substances. Ferro-silicon is a silicide of iron, alloyed with an excess of iron, which finds extensive use in the manufacture of certain kinds of steel.

Oxide of Silicon. Silicon forms but one oxide, SiO_2, called the dioxide or silica. This substance is found in a great variety of forms in nature, both in the amorphous, and in the crystalline condition. In the form of quartz it is found in beautifully formed prismatic crystals, sometimes of great size, and when pure, it is perfectly transparent and colorless. Some colored varieties are given special names, as amethyst (violet), rose quartz (pale pink), smoky and milky quartz (colored and opaque). Other varieties of silicon dioxide some of which also contain water are chalcedony, onyx, jasper, opal, agate and flint. Sand and sandstone are largely silicon dioxide.

Properties. As obtained by chemical processes, silicon dioxide is an amorphous, white powder. In the crystallized state, it is very hard, and has a density of 2.6. It is insoluble in water, and in most chemical reagents, and requires the hottest oxyhydrogen flame for fusion. Acids, excepting hydrofluoric acid, have little action on it, and it requires the most energetic reducing agents to deprive it of oxygen. It is the anhydride of an acid, and consequently it dissolves in fused alkalis to form silicates. Being nonvolatile, it will drive out most other anhydrides when heated to a high temperature with their salts, especially when the silicates so formed are fusible. The following reactions illustrate this property:

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$
$$Na_2SO_4 + SiO_2 = Na_2SiO_3 + SO_3.$$

These reactions illustrate the law of mass action very well. The anhydrides CO_2 and SO_3 being gases at the temperature of the reaction, escape as fast as they are formed. Their active mass is therefore kept very small, and the reaction proceeds to the end instead of reaching an equilibrium.

Silicic Acids. Silicon forms two simple acids: orthosilicic acid, H_4SiO_4, and metasilicic acid H_2SiO_3. Orthosilicic acid is formed as a jelly-like mass when orthosilicates are digested with strong acids such as HCl. On attempting to dry this acid, it loses water, passing into metasilicic, or common silicic acid.

$$H_4SiO_4 = H_2SiO_3 + H_2O.$$

Metasilicic acid when heated, breaks up into silica and water thus:

$$H_2SiO_3 = H_2O + SiO_2.$$

This reaction recalls the corresponding decomposition of carbonic acid into carbon dioxide and water.

$$H_2CO_3 = H_2O + CO_2.$$

Kaolin, $Al_4(SiO_4)_3$, is the aluminium salt of orthosilicic acid, and clay is simply kaolin mixed with other mineral substances.

Polysilicic Acids. Silicon has the power to form a great many complex acids which bear somewhat the same relation to orthosilicic acid that pyrophosphoric acid bears to orthophosphoric acid. Several molecules of the ortho acid unite with the loss of water. Thus we have

$$3\ H_4SiO_4 = H_4Si_3O_8 + 4\ H_2O.$$

These acids cannot be prepared in pure state, but their salts form many of the crystalline rocks in nature. Feldspar for example, has the formula $KAlSi_3O_8$, and is a mixed salt of the acid $H_4Si_3O_8$, whose formation is represented in the equation above. Many other examples will be met in the study of metals.

Glass. When sodium and calcium silicates, together with silicon dioxide, are heated to a very high temperature, the mixture fuses to a transparent liquid which on slowly cooling, passes into the solid called glass. Instead of starting with sodium and calcium silicates, it is more convenient and economical to heat sodium carbonate (or sulphate), and lime with an excess of clean sand, the silicates being formed during the heating.

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$
$$CaO + SiO_2 = CaSiO_3 + CO_2.$$

The mixture is heated below the fusing point for some time so that the escaping carbon dioxide may not spatter the hot liquid; the heat is then increased and the mixture kept in a state of fusion until all gases formed in the reaction have escaped.

The way in which the melted mixture is handled in the glass factory depends upon the character of the article to be made. Many articles such as bottles are made by blowing the plastic glass into hollow moulds of the desired shape. Other objects, such as lamp chimneys, are made by getting a lump of plastic glass on the end of a hollow iron rod, and blowing it into the desired shape without the help of a mould, great skill being required in the manipulation of the glass. Window glass is made by blowing large hollow cylinders of glass, about 8 ft. long by 2 ft. in diameter, cutting them open longitudinally, softening them in an oven, and rolling them into flat plates. Plate glass is cast into flat slabs which are then ground and polished to perfectly plane surfaces.

The ingredients mentioned above make a soft, easily fusible glass. If potassium carbonate is substituted for the sodium carbonate the glass is much harder and less easily fused; increasing the amount of sand has somewhat the same effect. Potassium glass is much used in making chemical glassware, since it resists the action of reagents better than the softer sodium glass. If lead oxide is substituted for the whole or a part of the lime, the glass is very soft, but has a high index of refraction and is valuable for making optical instruments and artificial jewels.

Various substances fused along with the glass mixture give the glass characteristic colors. The amber color of common bottles is due to iron compounds in the glass; in other cases iron colors the glass green. Cobalt compounds color it deep blue, while manganese gives it an amethyst tint, and uranium compounds a peculiar yellowish green. Since iron is nearly always present in the ingredients, glass is usually slightly green. This color can be removed by adding the proper amount of manganese dioxide, for the amethyst color of manganese and the green of iron together produce white light.

Glass is not a definite chemical compound, and its composition varies between wide limits. It is really a solution of various silicates, such as those of calcium and lead, and of silicon dioxide in fused sodium or potassium silicate. This solution gradually turns into a solid on cooling without the dissolved substances separating from the solvent. The compounds which are used to color the glass are often converted into silicates which then dissolve in the glass, giving it a uniform color. In other cases, as in the milky glasses which resemble porcelain in appearance, the color or opaqueness is due to the finely divided color material evenly distributed throughout the glass, but not dissolved in it. Milky glass is made by melting tin oxide or some similar substance into the glass, while copper or gold in metallic form scattered through the glass, give it shades of red.

Carbon and Silicon are thus seen to be the central elements in the framework of nature, in the organic and inorganic worlds respectively. They resemble each other in the abundance and complexity of their compounds; but this complexity is due to entirely different causes. The variety and complexity of carbon compounds is due to the ability of the carbon atoms to unite with each other in chains or rings, while with silicon it is due to the formation of complex silicic acids.

BORON.

Boron is a somewhat rare element which the periodic law assigns to the aluminium family, but which can best be studied in connection with carbon and silicon.

Occurrence. Boron is never found free in nature. It occurs as boric acid, H_3BO_3, and in salts of polyboric acids, which usually have very complicated formulas.

Preparation and Properties. Boron can be prepared from its oxide by reduction with magnesium exactly as in the case of silicon. It resembles silicon very strikingly in properties, occurring in several allotropic forms, being very hard when crystallized, and being rather inactive toward reagents. It forms a hydride BH_3, and combines directly with the elements of the chlorine family. Boron fluoride, BF_3, is very similar to silicon fluoride in its mode of formation and chemical properties.

Oxides of Boron. Boron forms one well known oxide, B_2O_3, called boric anhydride. It is formed as a glassy mass by heating boric acid to a high temperature. It absorbs water very readily, uniting with it to form boric acid again:

$$B_2O_3 + 3\ H_2O = 2\ H_3BO_3.$$

In this respect it differs from silicon dioxide.

Acids of Boron. Boric acid, H_3BO_3, is found in nature in considerable quantities, and forms one of the chief sources of boron compounds. It is found dissolved in the water of hot springs in some localities, particularly in Italy. Being volatile with steam, the steam which escapes from these springs has some boric acid in it. It is easily obtained from these sources by condensation and evaporation, the necessary heat being supplied by other hot springs.

Boric acid crystallizes in pearly flakes, which are greasy to the touch. In the laboratory the acid is easily prepared by treating a strong, hot solution of borax with sulphuric acid. Boric acid being sparingly soluble in water, crystallizes out on cooling.

$$Na_2B_4O_7 + 5\ H_2O + H_2SO_4 = Na_2SO_4 + 4\ H_3BO_3.$$

The substance is a mild antiseptic and is often used on this account in medicine, and as a preservative for canned foods and in milk.

Metaboric and Polyboric Acids. When boric acid is gently heated, it is converted into metaboric acid, HBO_2.

$$H_3BO_3 = HBO_2 + H_2O.$$

On heating metaboric acid to a somewhat higher temperature, tetraboric acid, $H_2B_4O_7$ is formed.

$$4HBO_2 = H_2B_4O_7 + H_2O.$$

Many other complex acids of boron are known.

Borax. Borax is the sodium salt of tetraboric acid, having the formula $Na_2B_4O_7$, 10 H_2O. It is found in some arid countries, as southern California and Thibet, but is now made commercially by boiling colmanite (calcium polyborate) with sodium carbonate, calcium carbonate being precipitated, and borax crystallizing from the solution.

When heated, borax at first swells up greatly while the water of cystallization is being given off, and then melts to a clear glass. This glass has the property of easily dissolving many metallic oxides, and on this account borax is used as a flux in soldering to clean the metallic surfaces to be soldered from the film of oxide with which they are likely to be covered. These oxides often give a characteristic color to the clear borax glass, and borax beads are therefore often used in testing for the presence of metals instead of the metaphosphoric acid bead already described.

The reason that oxides dissolve in borax is that borax contains an excess of acid anhydride, as can be more easily seen if its formula is written 2 $NaBO_2 + B_2O_3$. The metallic oxide combines with this excess of acid anhydride forming a mixed salt of metaboric acid.

Borax is used a great deal in domestic ways as a mild alkali to replace lye and soap. It is strongly alkaline to indicators such as litmus, and its solutions have the properties of an alkali.

This may seem strange, especially when it is remembered that borax contains an excess of acid anhydride. The explanation is to be found in the fact that the acids of boron are very weak ones — that is they are very little dissociated into ions. In solution the salts of such weak acids are hydrolysed somewhat, that is, they fall apart into free acid and free base.

$$Na_2B_4O_7+2H_2O=2NaOH+H_2B_4O_7.$$

Since the acid is little dissociated, there are few hydrogen ions in the solution; the base, on the other hand, freely dissociates into its ions Na and OH. The hydroxyl ions therefore largely exceed the hydrogen ions in number, and the solution has a strong alkaline reaction.

Borax is also used in the making of enamels, and for the manufacture of soaps designed to be used with hard water.

An Introduction
TO
Inorganic Chemistry.

LIST OF THE ELEMENTS, THEIR SYMBOLS AND ATOMIC WEIGHTS.

		H=1	O=16
Aluminium	Al	26.9	27.1
Antimony	Sb	119.1	120
Argon	A	39.6	39.9
Arsenic	As	74.4	75
Barium	Ba	134.4	137.4
Bismuth	Bi	206.9	208.5
Boron	B	10.9	11
Bromine	Br	79.36	79.96
Cadmium	Cd	111.6	112.4
Cæsium	Cs	132	133
Calcium	Ca	39.7	40
Carbon	C	11.91	12
Cerium	Ce	139	140
Chlorine	Cl	35.18	35.45
Chromium	Cr	51.7	52.1
Cobalt	Co	58.56	59
Columbium	Cb	93.3	94
Copper	Cu	63.1	63.6
Erbium	E	164.8	166
Fluorine	F	18.9	19
Gadolinium	Gd	155	156
Gallium	Ga	69.5	70
Germanium	Ge	71.5	72
Glucinum	Gl	9.03	9.1
Gold	Au	195.7	197.2
Helium	He	4	4
Hydrogen	H	1	1.01
Indium	In	113.1	114
Iodine	I	125.9	126.85
Iridium	Ir	191.5	193
Iron	Fe	55.6	56
Krypton	Kr	81.2	81.8
Lanthanum	La	137	138
Lead	Pb	205.35	206.9
Lithium	Li	6.98	7.03
Magnesium	Mg	24.18	24.36
Manganese	Mn	54.6	55
Mercury	Hg	198.8	200.3
Molybdenum	Mo	95.3	96
Neodymium	Nd	142.5	143.6
Neon	Ne	19.9	20
Nickel	Ni	58.3	58.7
Nitrogen	N	13.93	14.04
Osmium	Os	189.6	191
Oxygen	O	15.88	16
Palladium	Pd	105.2	106
Phosphorus	P	30.77	31
Platinum	Pt	193.3	194.8
Potassium	K	38.86	39.15
Praseodymium	Pr	139.4	140.5
Rhodium	Rh	102.2	103
Rubidium	Rb	84.76	85.4
Ruthenium	Ru	100.9	101.7
Samarium	Sa	148.9	150
Scandium	Sc	43.8	44.1
Selenium	Se	78.5	79.1
Silicon	Si	28.2	28.4
Silver	Ag	107.12	107.93
Sodium	Na	22.88	23.05
Strontium	Sr	86.94	87.6
Sulphur	S	31.83	32.06
Tantalum	Ta	181.6	183
Tellurium	Te	126	127
Thallium	Tl	202.6	204.1
Thorium	Th	230.8	232.5
Thulium	Tu	170	171
Tin	Sn	117.6	118.5
Titanium	Ti	47.7	48.1
Tungsten	W	182.6	184
Uranium	U	237.7	239.5
Vanadium	V	50.8	51.2
Xenon	X	127	128
Ytterbium	Yt	172	173
Yttrium	Y	88.3	89
Zinc	Zn	64.9	65.4
Zirconium	Zr	90	90.7