CHEMISTRY
AND
LABORATORY MANUAL

MORGAN AND LYMAN

(Shrimp)
Clifton L. Thomley

CHEMISTRY

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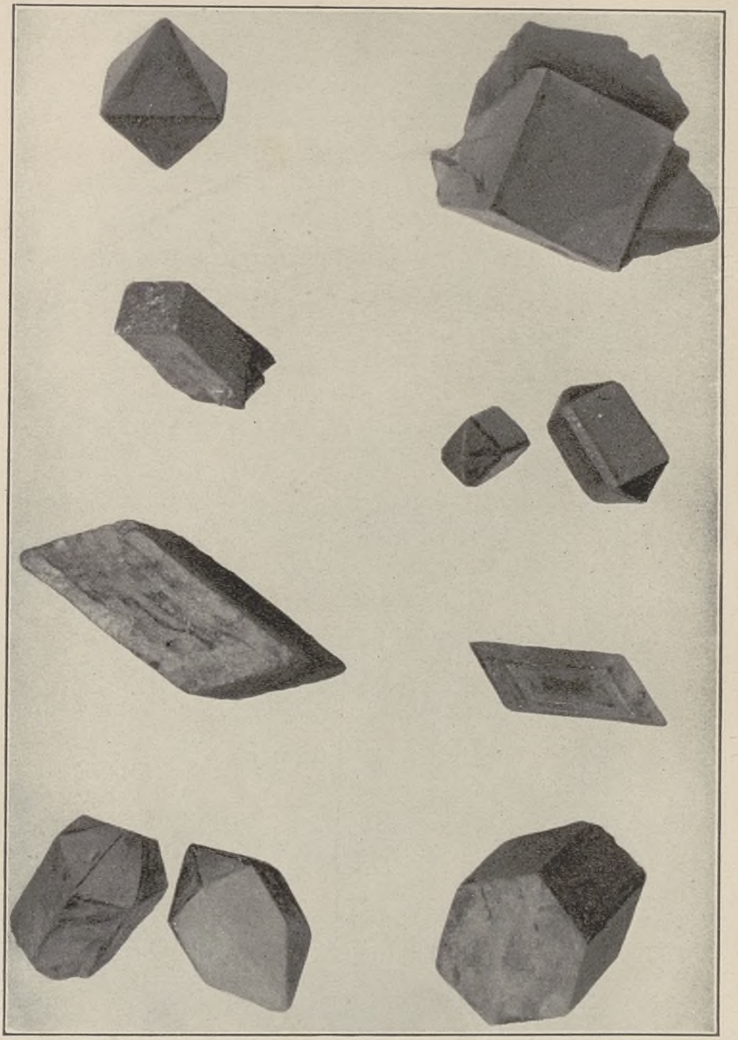

Natural Crystals

Chrome alum, $KCr(SO_4)_2 . 12\ H_2O$
Andalusite, $Al_2O_2SiO_2$
Blue vitriol, $CuSO_4 . 5\ H_2O$
Quartz, SiO_2

Fluor spar, CaF_2
Vesuvianite, $(CaMgAl)SiO_4$
Gypsum, $CaSO_4 . 2\ H_2O$
Beryl, $Be_3Al_2(SiO_2)_6$

CHEMISTRY

AN ELEMENTARY TEXT-BOOK

BY

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PREFACE

In the preparation of this text the authors have been actuated by the feeling that the student should never be allowed to get the idea that chemistry is a science that dwells inside laboratories and acts chiefly in beakers and test tubes. He should be conscious continually of its presence about him on every hand, in nature, in the home, and in the whirring world of industry. He should know that in the past chemistry has been one of the great forces which have determined the civilization and development of mankind, and should feel certain that in the future its importance will not be less. Consequently, the authors have tried to bring out the *humanistic* side of the science, to use as far as possible that material which is laden with intense human interest because of its significance to the race.

Many of the great triumphs of science have been achieved as the direct outcome of attempts to further the welfare of mankind rather than to advance the cause of pure science. Associate with the manufacture of nitrates from the atmosphere the thought of its significance in helping to solve the food problem of the race, and with the manufacture of soda the idea of the utilization of by-products and the great saving thereby accomplished, and a new element of attraction is added and a greater significance given to the subject. The average individual is and will continue to be more concerned with things which are of vital human interest than with the abstract ideas of science, however deep-seated its truths.

Yet to appreciate this side of chemistry an intelligent understanding of fundamental principles is necessary. The backbone of the science — so obvious in some of the manuals and texts — is still essential to any strong course, but can it not be clothed with flesh and blood and made a living thing by the inclusion of material snatched fresh from the world of common experience?

To put chemistry into the position that Spanish or German assumes to one who has taken up residence in Mexico or the Fatherland, *i.e.* to make it something of interest and use for every day, has been the purpose of the authors. To this end, much material of an informational character has been included; not with the idea that it is "all to be learned," but with the hope that it may prove interesting reading and give the proper atmosphere to the subject.

The authors have endeavored to produce a book which will not only furnish material, but also teach chemistry. That a student may understand, and not merely be able to state a principle, the text repeatedly points out the way in which reaction after reaction, as it appears during the development of the subject, illustrates some principle already discussed. No principle is stated which is not used afterwards.

Believing that those things are most important which are most far-reaching, the authors have made rather more of reversible reactions and equilibrium than other texts have done. Every chemist knows that this conception is of far greater significance to the science than most of the principles included in chemistry texts, and that reactions running in one direction are merely a commonly occurring special case of a more general principle. The idea that under proper conditions reactions are generally reversible but that special conditions often make reactions go in one way only, is in its simple form not difficult to present to students, and the authors have found them most intensely interested in this phase of the subject.

The book endeavors to encourage the student to think inductively. His attention is first directed to certain experimental facts; the general experience of the race along similar lines is then called to mind and the formulation of the law is the last point in the development. To use the deductive method in the presentation of scientific truths which have been derived inductively, is to fail to present the correct idea of the scientific method, a proper appreciation of which will be of as great value as anything that may be derived from the study of science.

The authors feel that when chemistry is presented as a descriptive subject mainly, it cannot be freed from the criticism of "too much memory work in education." Consequently much material found in the older style of chemistry texts — "occurrence, preparation, properties, and tests," for each element or compound — has been omitted, abbreviated, or given in tables in the Appendix.

Since the order — physics followed by chemistry — is reversed in many schools, special care has been taken in the earlier chapters to present the subject so fully that it shall be clear to the student who has had no previous instruction in science.

The text has been prepared primarily for high schools, but it may be used to advantage by freshman classes in many of our colleges.

In the preparation of this text, the authors have drawn freely from other books. Acknowledgment of this fact has not been made throughout the text for the reason that much of the material has now become common property, just as the original authors, now often unknown, would have wished.

To the friends, too numerous to be mentioned specifically, who have helped in the preparation of this book the authors wish to speak this word of acknowledgment and appreciation; also to the *Scientific American*, the Thermit Company, Charles Scribner's Sons, Allyn and Bacon, D. Appleton and Company, and Seeley and Company for permission to use some of the illustrations; and to Professor J. N. Le Conte, Mr. H. M. Tenney, and Mr. C. R. Keyes for the use of photographs.

THE AUTHORS.

BERKELEY, June, 1911.

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AN ELEMENTARY TEXT-BOOK

CHAPTER I

MATTER AND ENERGY

In everyday life each one of us is constantly coming in contact with numbers of different things which leave impressions on us. These impressions we gain by means of our senses. We touch a stone and experience a sensation of hardness, and of inertia or difficulty in moving it. We gain also an idea of its temperature, whether it is warmer or cooler than our own bodies. We see its form, size, color, and general character; we may note its odor or taste, and, in endeavoring to find an answer to many a question as to "how," "what," and "why," we gain our first-hand knowledge of things. The knowledge which we learn from others was, in the beginning, gained by means of the senses, also.

By means of our senses, then, we receive impressions of the world about us. These impressions may readily be divided into two kinds: those which come to us from something which occupies space and is definitely located in space, and those which are not so definitely fixed in position. A stone or a tree has a definite form and position relative to other things near it. Light and heat, however, have no form or position and do not occupy space. Although the cause may be definitely located, the light and heat produced are everywhere about the source from which they come. All things from which we get impressions of the first kind have weight. That light, electricity, heat, etc., have no weight is proved by the fact that a hot, electrically charged body emitting light, such as an incandescent bulb, weighs no more than when the current is turned off and the light and heat cease. Anything which gives us an impression of the first kind we call *matter;* of the second kind, *energy*.

Matter is anything which has weight or occupies space. It is the material out of which all things are made. There are many different forms of matter, such as iron, water, salt, gold, etc. These different kinds of matter are called *substances*. The world which we know is made out of many different substances, and investigation shows that the sun, stars, and other heavenly bodies consist of kinds of matter similar to those found on the earth.

Energy is not definitely bounded in space, and it has no weight. It is of an entirely different nature from matter, and may be most satisfactorily defined as the *power to do work*, for in all its forms it possesses this ability. Several different forms of energy are recognized : heat, light, electricity, magnetism, energy of motion, and energy of position. The swiftly moving cannon ball possesses energy which it loses when it comes to rest. Water on the mountain side, because of its position, possesses the power to do work as it runs to the sea, just as a coiled watch spring possesses energy which it does not have when unwound. Other forms of energy, also, are recognized.

Matter and energy are always associated. In nature, bodies always possess more or less heat or other form of energy, so that we know nothing of energy except as it plays upon matter, or of matter except as it is acted upon by energy.

States of matter. It is commonly said that matter exists in three different states, *solid*, *liquid*, and *gas*. Water is one of the few substances that exist in all three states under the conditions normally present on earth. If heat, which is one form of energy, be added to ice, its temperature rises to zero without any change of state. When this temperature is reached, however, ice melts and passes into the liquid condition, and as the heat energy is absorbed, no rise of temperature is noted until all of the solid has disappeared. Obviously, therefore, water equals ice plus energy, or, there is more energy in water than in the same weight of ice.

If the addition of heat be continued, the temperature of the water rises to 100°, after which a further addition of heat changes it into steam, *i.e.* into the gaseous condition. Therefore a gas equals a liquid plus energy. Since these relations hold for all substances, it follows that one essential difference between these three states of matter is that *weight for weight a liquid contains a greater amount of energy than a solid and a gas still greater than a liquid.*

Further proof of this statement is obtained from the fact that when steam condenses or water freezes, heat energy is liberated. *If we wish to change a solid into a liquid or a liquid into a gas, we must add energy to it; but if we wish to cause a gas to liquefy or a liquid to solidify, we must take energy from it.*

Properties. The impressions which matter makes upon us through our senses are said to be the *properties* of matter. When, for instance, contact with "blue stone" or "blue vitriol" gives one the impression of heaviness, of definite crystalline shape, of blue color and sour and puckery taste, we say that it is relatively heavy, has a crystalline form, is blue and sour and puckery. These and other impressions which we get we say are the properties of the "blue stone."

Properties are the marks or signs by which we know substances. By its signs or properties we realize that we have seen this or that particular substance previously, or that it is entirely new to us. *When we perceive that two bodies possess identical properties, we realize that they are composed of the same substances.* On the other hand, when we recognize that two bodies under the same conditions possess different properties, we assert that they are made of different substances. Thus, on comparing a piece of gold with a fragment of iron, we maintain that they are different substances because the gold is yellow in color, soft, malleable, and ductile; *i.e.* it may be hammered out into thin sheets or drawn out into fine wire. It is not attracted by a magnet and does not change its appearance when exposed to moist air. If the specimens which we are contrasting are of the same size, the gold seems much heavier than the iron, which is gray in color, tougher, and less malleable than gold. Iron is magnetic and, when exposed to the atmosphere, rusts rapidly.

There are certain properties that belong only to particular substances. Ammonia has a well-known odor of its own, copper a color peculiar to itself, diamond a luster that cannot be equaled. Other properties, however, may be shared by several different substances. Thus there are many kinds of matter which are white, or yellow, or heavy, or hard. No two substances have ever been found which possess the same set of properties, however. The peculiar combination of properties by which a substance may be recognized, identified, and distinguished from all other substances is called the *characteristic properties* of that substance. A substance retains its characteristic properties as long as it remains the same substance. When it is changed to another substance, the new substance takes on a new set of characteristic properties.

Not all characteristic properties are of equal value as a means of identifying substances. While *color* is one of the most striking properties, it is often not sufficiently constant. Color depends on the size of the particle viewed, on the nature of the light falling on the object, on the temperature, as well as on other conditions. In general, the larger the particle viewed and the higher the temperature, the deeper is the color. Many highly colored substances appear nearly white when finely powdered; *e.g.* copper sulfate. Sea water is dark blue or green, yet the foam of the breaking wave is white. Mercuric oxid is black when hot, and red when cold, and many other substances change their color entirely with comparatively small changes in temperature. Green objects are green only in white or green light; in red light they are black. Blue substances appear black in yellow light, etc.

Taste and *odor* are sometimes characteristic. In the average person, however, the senses of taste and smell are very little educated and are likely to deceive.

Pure substances melt and boil at definite temperatures; *i.e.* a solid changes to a liquid or a liquid to a gas at a definite temperature characteristic for each substance. Hence the *melting point* and the *boiling point* are properties very frequently used in identifying substances.

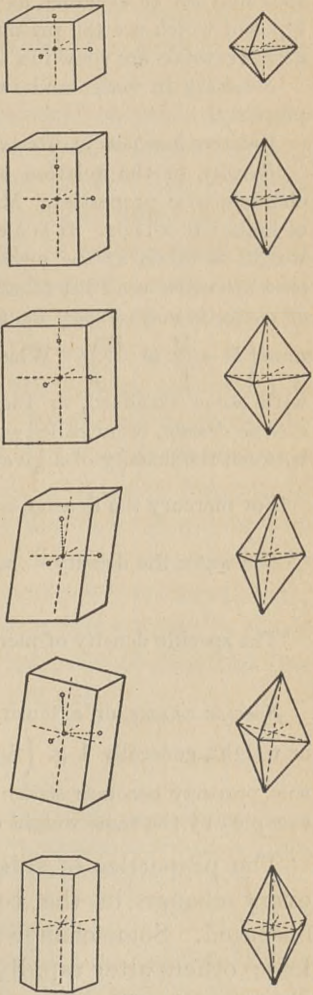


FIG. 1.

Some substances pass directly from the solid state into a gas without melting; they are said to *sublime*, and the process is known as *sublimation*.

On solidifying or separating from solution, most solids assume a definite *crystal form.* While crystals are of very many different shapes, they may all be regarded as modifications of six different forms, the types of which are the prisms and pyramids shown in Fig. 1. Some actual crystals are shown in the Frontispiece.

Solubility in water and in other solvents is a very characteristic property.

Relative *hardness* is often of service in determining minerals.

Density, or the relation of mass to volume, is one of the most characteristic properties. Mass is sometimes defined as the amount of matter in a body. It is a constant quantity. In any given locality, weight is taken as the measure of mass, and the terms *weight* and *mass* are often used interchangeably. *By density is meant the amount of matter in unit volume; i.e.* the mass (or weight) divided by the volume $\left(D = \frac{M}{V} \text{ or } \frac{W}{V}\right)$. When we compare all density determinations with some standard, as the density of water, we get relative or *specific density,* often called *specific gravity.* Specific density is a ratio between the density of a given substance and the density of water.

For mercury the density $= \frac{13.6 \text{ g.}}{1 \text{ ccm.}}$, for 1 ccm. weighs 13.6 g.

For water the density $= \frac{1 \text{ g.}}{1 \text{ ccm.}}$, for 1 ccm. weighs 1 g.

The specific density of mercury $= \dfrac{\frac{13.6 \text{ g.}}{1 \text{ ccm.}}}{\frac{1 \text{ g.}}{1 \text{ ccm.}}} = 13.6.$

Specific volume, or extensity, is the volume occupied by unit mass or weight, generally 1 g. $\left(\text{Sp. Vol.} = \frac{V}{M} \text{ or } \frac{V}{W}\right)$. The variation in this property becomes strikingly apparent in the different volumes occupied by the same weight of different substances.

The properties of substances change more or less with every change in the conditions under which they are observed. Some change so slightly that they seem changeless; others alter rapidly and to a marked degree. While changes in properties under the conditions ordinarily prevailing in any region are relatively small, it is well to remember that, to keep the properties of any substance constant, the conditions must be unchanging. We may make a general statement to the effect that *under given conditions the characteristic properties of a substance are unchanging and constant in all specimens.* This is known as the **law of properties.**

In science a **law** is simply a general statement of the way in which things act. It is based on observation and differs entirely in its nature from a civil law or legal statute. The latter is passed in order to make all people act in the way the law prescribes. A natural law states the way in which nature acts. In human society a law is first enacted, and then people do as the law states. In nature things act in certain definite ways; these actions are then noted and set down, and the general statement of the action is called a natural law. People do as civil laws compel, but nothing ever occurs because a natural law forces the event. Natural laws are of value in foretelling future happenings only because it has been found by experience that *nature always acts in the same way under the same conditions.* If we can duplicate previous conditions, we feel confident that the same thing will happen in all of the to-morrows of the future as happens to-day and has happened in all the yesterdays of the past.

SUMMARY

Matter and energy. Our knowledge of the world around us comes primarily from our senses. We get certain impressions from something definitely located in space and possessing weight. We call this *matter*, the material out of which all things are made. The different kinds of matter we call *substances.*

Other impressions come from something not definitely located in space and not possessing weight. This we call *energy.* The different kinds of energy are motion, heat, light, electricity, etc. Energy is the ability to do work. In nature matter and energy are inseparable.

Matter passes from the solid to the liquid state by absorbing energy, and from the liquid to the gas by taking on still more energy. Hence, a gas contains more energy than a liquid, and a liquid more energy than a solid. To change a solid to a liquid or a gas, we add energy. To convert a gas into a liquid or a solid, we abstract energy.

Properties. The impressions which matter makes on us through our senses are its *properties.* Substances are identical when they possess identical properties. Those properties by means of which we recognize, identify, and distinguish a substance are its *characteristic properties.* In general, each substance possesses a group of characteristic properties. Color is not always reliable. Among the properties usually reckoned as characteristic are melting point, boiling point, crystal form, solubility, hardness, density, and specific volume. These may change with changing conditions, but the *law of properties* states that under given conditions the characteristic properties of a substance are unchanging and constant in all specimens.

Natural laws. A natural law is a statement of the way things act. Nothing ever comes to pass because a natural law compels it. Natural laws are of value to us in enabling us to foretell future events by what has happened in the past, for experience teaches that nature always acts in the same way under the same conditions.

QUESTIONS

1. If we had no senses, what would we know of the properties of substances?

2. If a certain object is inaccessible to the human senses, what can we know of its properties?

3. What forms of energy are possessed by a watch; by a moving cannon ball; by an incandescent light bulb; by dynamite (see p. 16)?

4. When water vapor condenses and falls to the ground as rain, what becomes of the heat?

5. What are some characteristic properties that differentiate sugar from salt; copper from gold; water from alcohol; air from illuminating gas?

6. Of the above differences, which could not be recognized by a man lacking the sense of sight; of hearing; of feeling; of smelling; of tasting?

7. What properties are possessed by water at room temperature, about 20°? How are these changed at $-20°$; at 200°?

8. Is it correct to say that a stone falls to the ground because the law of gravitation compels it? Is it correct to say that a person pays taxes because the state law compels him? If either statement is incorrect, how would you change it?

CHAPTER II

CHANGES

It is not possible to isolate a body so that it shall never change in any respect, for conditions cannot be maintained absolutely constant. "In the world about us changes are constantly taking place. It storms or is fair. Day and night and the seasons succeed one another. As the cold of winter gives way to the warmth of summer, ice melts and changes into the liquid state and is finally dissipated as an invisible vapor. Only a return to the former condition is necessary to bring back water to its former state with all of its properties unchanged. On the other hand, when fire sweeps a mountain side, a return of summer does not bring back the mighty pines and firs that fell before it. When ores are smelted, and the metal obtained, a falling temperature is not followed by a reversal to the former state."

A piece of iron brought near a magnet becomes a magnet also, but when the first magnet is removed, the iron is perceived to be unchanged in every way. The same piece of iron exposed to moist air rusts rapidly. Removed from contact with moisture and air, however, it does not regain its original properties, but is seen to possess an entirely new set of characteristic properties that are permanent. We thus see that some changes are more deep-seated than others. Changes of the less permanent kind are said to be changes in the *condition* of a substance merely, while the more permanent kind are said to be due to changes in its *composition.* This distinction serves as a dividing line between physical and chemical changes.

In a **physical change** *the substance concerned is still composed of the same material, and no new substances are formed.*	*In a* **chemical change** *the substance concerned disappears, and new substances with new properties appear.*
Physical changes are changes in the condition only of a substance, for a return of the original conditions usually brings back all the original properties.	*Chemical changes are changes in the composition of a substance. A return of the original conditions does not ordinarily bring back the original properties.*
Such changes are treated mainly in the study of *Physics.*	Such changes are considered in the study of *Chemistry.*

Any form of change either physical or chemical is spoken of as a *reaction*, and any substance that changes as a *reagent.*

Chemical changes. The most characteristic thing about any chemical reaction is that it is abrupt and instantaneous. The properties of the first substance do not change gradually into those of the second substance, nor are they replaced one by one. When iron rusts, as the reaction proceeds,— slowly, it may be, from particle to particle,— the properties of the former substance change suddenly into those of the latter. No particle of iron loses its magnetic character or its toughness before all of the other properties are changed. The dark metallic appearance of the iron does not fade gradually into the red color of the rust, nor does the density of the metal gradually decrease until that of rust is reached. As the change takes place in any particle, the transformation of that particle is at once complete; and because it possesses a complete set of new properties, we recognize the reaction product as distinct and different from the original substance.

While we can recognize a pretty clear distinction between physical reactions as one kind of change and chemical reactions as another, it must not be supposed that all changes may be classified in one way or the other without difficulty. When salt dissolves in water, we have evidence that a chemical reaction takes place, yet on most points solution shows itself rather as a physical than as a chemical change. Many other instances of the same character might be mentioned.

It must be remembered that any classification is made simply for convenience in handling large numbers of facts and is never intended to make facts conform to the classification. The classification of our knowledge of the world into different sciences, such as geology, botany, chemistry, physics, physiology, anatomy, etc., is purely artificial. In nature we find no such divisions. A single horse cropping the grass in a meadow presents problems in all these subjects.

Mixtures and compounds. If sugar is heated, it may be decomposed entirely into charcoal and water. It might seem that sugar is composed of nothing else than charcoal and water. Yet when charcoal and water are stirred together, the result is not sugar, but only a mixture of charcoal and water. From these facts it appears that substances may be put together in at least two different ways. The substance formed in one case is known as a *mixture*, in the other as a *chemical compound*.

The difference may be further illustrated by bringing together iron and sulfur, both finely powdered. When they have been intimately mixed, the resulting substance does not look like either of the ingredients, yet under the microscope small particles of yellow sulfur may be seen lying side by side with the dark iron. A magnet will attract and remove the iron, leaving the sulfur. If the mixture is treated with carbon disulfid, the sulfur dissolves and the iron is left behind. On evaporating the solvent, the sulfur may be recovered. All of these results indicate clearly that both sulfur and iron are present in the mixture with their properties entirely unchanged.

On the other hand, if the preceding mixture is heated, a glow passes through the mass and a chemical reaction takes place, resulting in the formation of a chemical compound. To make this compound, both sulfur and iron have been used. From the powdered mass, however, it is impossible to separate iron by the use of a magnet or to dissolve out sulfur with carbon disulfid. Before either can be obtained, a chemical reaction must take place in which the compound is decomposed. The properties of a chemical compound are entirely different from those of the substances out of which it is made, and different from a mixture of the substances. The complete disappearance of one or more substances and the sudden appearance of others when chemical reactions take place is one of the most striking things in nature.

Mixtures. *In making a mixture, no chemical reaction takes place between the ingredients. Each substance retains its own properties unchanged. The properties of the mixture are usually intermediate between the properties of the pure substances contained in it. The ingredients may usually be separated by physical means without resorting to chemical reactions.*

Compounds. *In making a compound, a chemical reaction takes place between the components. The properties of the substances used disappear. The properties of the compound are different from the properties of the substances used in making it. A chemical compound cannot be separated into its components by physical means, but a chemical reaction is necessary to recover any of them.*

Chemical affinity is the name given to the attraction between substances because of which they unite chemically.

We know but little about it, however. When the resulting compound is stable, we say that the chemical affinity between its components is strong. When the compound is unstable and decomposes readily, we say that it is weak. Increase in temperature tends to lessen the stability of all compounds. In some of the very hot stars substances seem to be decomposed largely into their simple elements.

How chemical changes are brought about. When substances are brought in contact, chemical action sometimes begins of its own accord and continues without any aid from the outside. Instances of this are the rusting of iron, the decay of wood, and the "setting" of cement, mortar, and plaster of Paris. In most such cases, at least one of the reacting substances is either a liquid or a gas, and, in general, it may be said that *gases and liquids react more readily than solids do.* When dealing with solid substances, especially, the assistance of some outside agency is usually required before chemical action can be started. As examples of this, the following instances may be mentioned:

1. *Energy applied mechanically* will sometimes start a chemical reaction, as when a gun cap or nitroglycerine is exploded by friction, pressure, or a blow.

2. *Light* sometimes produces chemical action, as in photography and in many of the processes accompanying the life and growth of plants.

3. *Electricity* is used to bring about chemical change in electroplating with metals, in the extraction of metals from their ores, and in many other processes.

4. *Solution in water* causes many reactions to be completed almost instantaneously which do not take place appreciably when the reagents are dry and in the solid state. Baking powder effervesces when brought in contact with water, but does not when dry.

5. *Heat* is an agency very frequently employed to aid chemical action. Instances of its use are the combustion of wood and coal, the cooking of meats and vegetables, and the production of iron, copper, and other metals from their ores at high temperatures. None of these processes will take place appreciably at ordinary temperatures.

We frequently speak of the speed of a chemical reaction, meaning by this term exactly what is meant by the speed of a train or a race horse; *i.e.* how much can it do in a given time, as a mile a minute. In a similar way we speak of the speed with which work is being done, as two cords a day or one thousand gallons a minute.

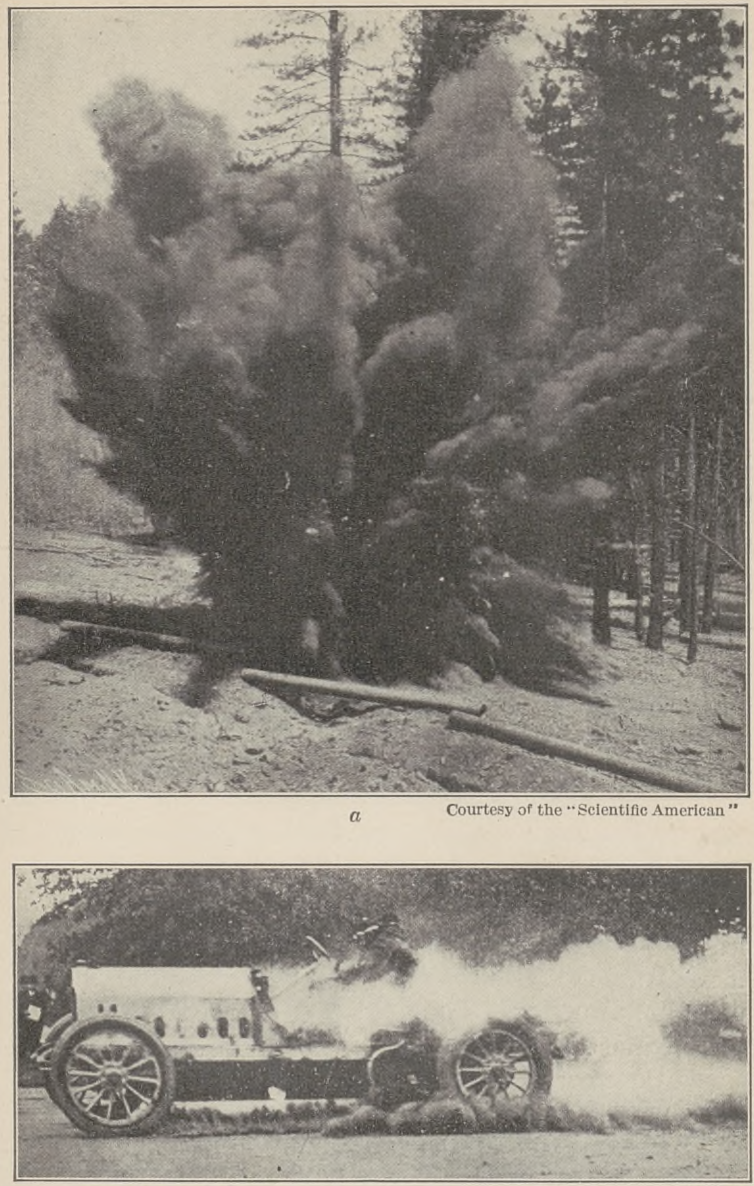
By **speed of reaction** is meant the amount of one substance transformed into another in a given time. The higher the temperature, the shorter is the time a reaction takes. In general, for every increase in temperature of 10° the reaction speed is doubled. By raising the temperature 100° we may increase the speed of a reaction more than a thousand fold, so that a reaction that might not take place appreciably in years at ordinary temperatures might be completed in a few minutes at 1000°. For these reasons chemists believe that any reaction that takes place at high temperatures takes place also at ordinary temperatures, but often so slowly as to be entirely inappreciable. Of the various methods of increasing the speed of a reaction, increase in temperature is very frequently used.

The fact that chemical reactions can be made to take place more rapidly under one condition than under another is of the greatest significance to the industrial world. Since "time is money," if one manufacturer is able to make a product in half the time that it takes in another factory, part of the cost of production has been saved.

Reactions spontaneous or forced. Many chemical reactions that require aid in starting, continue spontaneously as long as material is present to react. Others cease as soon as the external assistance is withdrawn. Instances of the first kind are the combustion of wood and coal, the cooking of food, the explosion of nitroglycerine, and many other reactions with which we shall become familiar later. Of the second kind are many of the reactions in which heat and light are used. The printing of a picture stops when the light is removed, and in electroplating the deposition of metal ceases when the current is shut off. Experience shows that *reactions which continue spontaneously when once started liberate some form of energy as the reaction proceeds*, usually heat, often light or electricity, sometimes mechanical motion. Such reactions are called *exothermic*, a term derived from Greek words signifying that energy is liberated. *Endothermic* reactions absorb energy as they proceed; hence they cease as soon as the source of energy is removed.

Chemical energy. When heat, light, electricity, etc., are liberated in a chemical reaction, the reagents are said to possess *chemical energy*. This chemical energy is set free by the reaction and converted into that form of energy which is given off during the reaction. Some illustrations of chemical energy are shown in Fig. 2.

Decomposition and combination. In many chemical reactions one substance decomposes into two or more substances, no one of which weighs as much as the original substance. *Analysis* is the name given to reactions of this kind, a term derived from Greek words signifying "a taking apart." *Synthesis* is the name given to reactions in which two or more substances unite to form a new substance, the weight of which equals the sum of the weights of the reagents. The term *synthesis* signifies "a putting together."



a Courtesy of the "Scientific American"

b Courtesy of the "Scientific American"

FIG. 2. — CHEMICAL ENERGY

The explosion of the dynamite (*a*) is a chemical reaction not unlike the explosion of the gasoline vapor in the cylinders of the automobile (*b*) which furnishes the energy necessary for "80 miles an hour."

Compound building. To illustrate the way in which substances combine chemically, it may be stated that oxygen unites with sulfur to form an oxid of sulfur, and this with water to form sulfuric acid. The latter reacts with aluminum to give aluminum sulfate and with potassium to form potassium sulfate. These unite to produce alum, and then take up twenty-four parts of water to produce a crystal of alum. This is a fairly complex inorganic or mineral compound, but it is relatively simple compared with the products formed in the laboratories of the leaf cells, and much less complex than those of the animal world. More than seven hundred parts of carbon and over a thousand parts of hydrogen, about two hundred and fifty parts of oxygen and nearly the same amount of nitrogen, together with a little sulfur, seem to be needed to make up egg albumen.* There seems to be no limit to the process of synthesis.

Limit of analysis. As a result of analysis, however, we soon come to a point beyond which we cannot cause any further decomposition. *Substances which have not been decomposed into anything simpler are called elements.*†

Elements. Some substances, once considered elementary, have been decomposed later, as when Davy electrolyzed fused "potash and soda lyes" and obtained the then new elements, potassium and sodium. In a similar way he obtained calcium from quicklime. Other elements, such as chlorin, long thought to be compounds, have never yet been simplified.

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* The chemical formula (see p. 70) which indicates the composition of egg albumen is $C_{720}H_{1134}O_{248}N_{218}S_5$.

† In recent years evidence has accumulated indicating that in the X-ray tube, and under some other conditions, several (possibly all) of the elements undergo some sort of a decomposition. Consideration of this fact will be taken up later (p. 403), and it need not affect the present conception of chemical elements.

The substances now recognized as elements number something less than one hundred. Those which are found most frequently are estimated to occur in the earth's crust in about the proportions given in the following table. Only nine elements are present in proportions as great as one per cent.

Oxygen	50 %	Calcium	3.2 %	Hydrogen	1.0 %
Silicon	26 %	Magnesium	2.2 %	Titanium	0.4 %
Aluminum	7.3 %	Sodium	2.3 %	Carbon	0.2 %
Iron	4.1 %	Potassium	2.3 %	Chlorin	0.2 %

All the silver, gold, copper, lead, tin, zinc, nickel, etc., known in the world, together with all the remaining elements, make up less than one per cent of the earth's crust.

Names of the elements. An element may be named because of some characteristic property, from the country in which it was first found, or for any other reason that appealed to the man who first discovered it. The ending *-ium* or *-um* signifies the possession of metallic properties. Gold, silver, copper, lead, mercury, tin, iron, and certain other metals have been long known, and although the names of these elements do not end in *-ium*, chemists retain the old and commonly used forms. A list of the elements generally accepted by chemists is found in the Appendix. Several other substances seem to be of the same character as the elements listed. They are so rare, and so little is positively known in regard to them, that they have not been included in the list.

Symbols. In expressing the results of chemical action, instead of writing the full names of the elements concerned, it is more convenient for some purposes to represent them by abbreviations known as *symbols*. The first letter of the name of an element is usually adopted as its symbol. Thus, O stands for oxygen, C for carbon, N for nitrogen.

FIG. 3. — JOHANN JACOB BERZELIUS (1779–1848)

A Swede, one of the greatest of the earlier chemists. He made the first atomic weight determinations and introduced the present system of chemical symbols and formulas.

But in most cases there are two or more elements whose names begin with the same letter, and it is then necessary to add to the initial some other letter of the name, usually the second. Thus, C stands for carbon, Ca for calcium, Cl for chlorin, Co for cobalt, Cr for chromium, Cs for cæsium. In several instances symbols are obtained from the Latin names of the elements, as Fe for iron, from "ferrum," to avoid confusion, since I and Ir stand for iodin and iridium. Similarly, silver has for its symbol Ag, from "argentum," instead of S or Si, which stand for sulfur and silicon.

Symbols are a sort of chemical shorthand. The present system was suggested by the great Swedish chemist, Berzelius, about 1811, and since that time it has come into use in all countries, so that chemical symbols are a kind of universal language. A portrait of Berzelius is shown in Fig. 3.

SUMMARY

Changes. Every portion of matter is in a continual state of change, but some changes are more permanent and deep-seated than others. Changes that do not result in the formation of a new substance are *physical*, and are treated mainly in Physics. Changes that result in the formation of new substances are *chemical*, and are considered in Chemistry.

Mixtures and compounds. In a *mixture* the ingredients that were used are still in existence, and no new substance is formed. In a *compound* the ingredients have lost their identity and have united to form a totally new substance. *Chemical affinity* is the name given to the attraction that causes substances to unite chemically and form compounds.

Chemical action in some cases begins of its own accord when substances are brought in contact, especially if they are liquids or gases. In other cases, especially with solids, some external agency is necessary to start chemical action, such as energy mechanically applied, light, electricity, heat, and solution in water. Heat causes an increase in the speed of chemical reactions. In general the speed is about doubled by an increase in temperature of 10°.

Chemical action and energy. *Exothermic reactions* liberate energy. They continue as long as material is present to react. *Endothermic reactions* absorb energy, and cease as soon as the external assistance is withdrawn.

Analysis and synthesis. Analysis is the breaking up of a substance into its constituents. Synthesis is the compounding of ingredients so as to form another substance.

Elements are substances that we do not know how to analyze into simpler substances. Somewhat less than 100 are known, only nine of which exist in amounts greater than one per cent. Names of metallic elements generally end in *-ium*. For some purposes it is convenient to represent the elements by abbreviations known as *symbols*. The symbols are the initial letters of the names, followed when necessary by another letter.

QUESTIONS

1. Are the following changes chemical or physical reactions?

Rusting of iron
Sawing wood
Ringing of a bell
Stretching of rubber
Burning of wood
Explosion of gunpowder
Magnetizing a knife blade
Freezing of water
Washing clothes
Making butter
Developing a photographic plate
Boiling of water
Lighting a match
Decay of meat
Souring of milk
Fading of a color
Withering of leaves
Boiling an egg
Dissolving sugar in water
Wilting of flowers
Bleaching clothes
"Clearing up" of fog

2. Are the following mixtures or compounds?

flour
salt
bread
water
milk
granite
sugar
quartz
candy
earth
bone
lemonade

3. Select 10 familiar chemical changes, and state what agency, if any, is needed to start or to maintain these chemical reactions.

4. So far as you can tell, are the chemical changes mentioned in answer to question 3 endothermic or exothermic?

5. Mention several chemical reactions which liberate energy as they proceed.

6. If a piece of meat is cooked by boiling in 2 hours, how long should it take in a "hay box," or fireless cooker, at an average temperature of perhaps 80°?

7. Would you make use of analysis or synthesis in preparing (*a*) an element from its compounds; (*b*) a compound from its elements?

8. Large quantities of food are frequently cooked by heating with steam under pressure because this process saves time. Explain why. On a high mountain beans and potatoes require 10–15 hours boiling to cook them. Explain why.

CHAPTER III

FIRE AND OXYGEN

THROUGHOUT all time no chemical reaction has attracted more attention than fire. The bright flame, the genial warmth, and the disappearance of the burning substance, alike interest young and old, the civilized and the savage man. In his own experience every one has noted two types of combustion or burning: one with flame, as when wood, oil, and gas burn; and the other without flame, such as charcoal and hard coal exhibit.

Flame. Investigation shows that flame is nothing more or less than burning gas. Iluminating gas is volatile at ordinary temperatures, oil is readily vaporized when heated, and when wood or a candle or other similar substance is heated to the temperature of a flame, it is decomposed and various substances are formed that pass off as gases. The burning of these gases produces the flame observed when wood burns. The charcoal which is left does not vaporize until temperatures much higher than an ordinary flame are reached. Hence its combustion shows only glowing coals, the embers which are left after the flame disappears from burning wood.

The tongues of flame that so obviously leave a burning substance, together with the disappearance of the latter, wholly or in part, gave rise to the belief about three hundred years ago that combustion consisted in the liberation of a volatile substance called *phlogiston.* This idea seemed to explain satisfactorily enough the combustion of such substances as disappear completely or leave an ash that weighs less than the original substance.

The ash. Investigators realized, however, that certain other substances burn, each of which leaves behind an ash that weighs more than the original substance. Metals generally belong to this class. They do not burn readily, but when heated continuously a metal changes into ash just as coal and wood do. The plumber must be careful not to burn his copper "soldering iron" or the lead in his pot by excessive heating, for the copper will change into a black scale and the lead into a yellow powder. Combustion of this kind cannot be caused by the disappearance of any substance, for the ash weighs more than the original substance.

But whether the ash weighs more or less than the original substance, in either case the combustion seems to be essentially the same. The question arises, therefore: In those cases where the ash is lighter than the original substance, is the solid ash the only product formed? When oil or a candle burns up completely, may it not be that the ash or product of combustion is gaseous and so escapes notice? A simple experiment gives us an answer.

A candle balanced on a balance loses weight as it burns, and the matter of which it was composed seems to disappear completely. Let us place another candle on a balance in such a position that it may burn under a chimney loosely filled with pieces of "lye" (Fig. 4). As it burns,

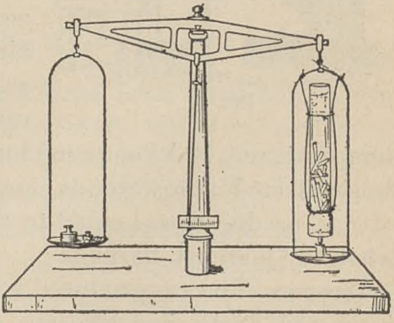

FIG. 4.

the side of the balance holding the candle will sink, thus showing a gain in weight. The candle, as it burns, produces an ash that is a gas. This gas is absorbed by the "lye," however, and so can be weighed.

In ordinary combustion most of the ash produced is gaseous. If experiments are properly arranged to absorb all gases, increase in weight is always found.

Combustion does not consist in the giving off of any kind of matter by the burning substance, but instead it is the addition of some substance which must come from the atmosphere. A simple experiment performed by the great French chemist, Lavoisier, in 1775, shows us what this substance is.

In the apparatus shown in Fig. 5, a weighed amount of mercury was heated in a measured volume of air at a temperature just below its boiling point. As the mercury burned and changed slowly into a red ash, the volume of air grew less. After several days' heating, the reaction ceased when one fifth of the air had been absorbed. The red ash was then placed in a retort and heated to a higher temperature. It decomposed into mercury and a gas which was collected over water as shown in Fig. 6. The volume of gas produced was equal to the volume of air absorbed when the mercury burned.

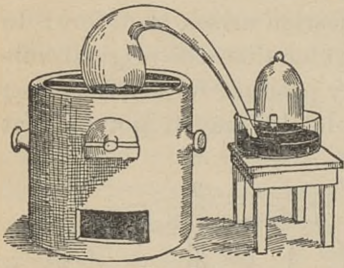

FIG. 5.

Oxygen. The gas produced when the red ash of mercury is heated, looks just like air, but substances burn in it more vigorously than in air. A glowing splinter of wood thrust into it bursts into flame and burns much more rapidly than it does in air. To this gas Lavoisier gave the name *oxygen*. Compounds formed by it are called *oxids*. The experiment showed that about one fifth of the air is oxygen. Because of the presence of oxygen, air supports combustion. When the oxygen is removed from air, substances no longer burn in the remaining gas.

Combustion is the union of oxygen with the burning substance. If a combustible substance, such as a piece of phosphorus, be inclosed in a large flask filled with air or oxygen, the whole may be carefully counterpoised on a balance. Combustion may then be started by concentrating the rays of the sun on the phosphorus with a "burning glass" or lens. The substance burns exactly as in the air, but at the end of the experiment the flask will weigh identically what it did before the reaction took place. During the combustion there has been neither a loss nor a gain in weight. The amount of matter is the same after as before the experiment, although it has changed its form.

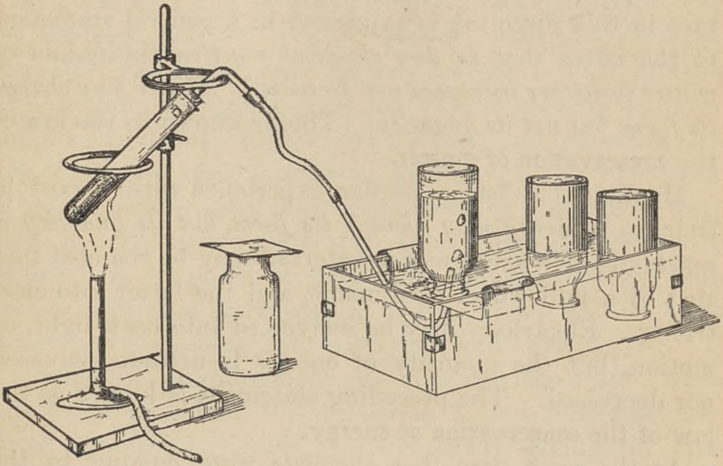

Fig. 6.

These results show how far from correct our first observations and inferences may be. They should lead us to be cautious in our judgments and certain that no facts have been overlooked.

Conservation of matter. In every chemical reaction that has been investigated, similar results have been obtained. We have never noticed a change of weight in any reaction, and we have no reason for believing that matter is ever created or destroyed. The long experience of the human race in this direction is expressed in a general statement to the effect that *in any chemical reaction the amount of matter is neither increased nor decreased. Matter may change its form, but not its quantity.* This is known as the law of the **conservation of matter.**

Mankind has had a similar experience with regard to energy. *Energy may change its form, but its quantity is constant.* The energy of a waterfall may be changed into that of a mill wheel or dynamo, and the latter into electricity. Electricity may be converted into heat, light, or motion, but the quantity of energy is neither increased nor decreased. The preceding statement is known as the law of the **conservation of energy.**

At the same time that chemists were coming to the realization of the conservation of matter because of their experiments with it, they came to perceive another important law also; for whenever they investigated the red oxid of mercury, they found that it always consisted of the same elements combined in the same invariable proportions. It makes no difference from what part of the world it comes or by which of several different processes it is prepared; when pure, it always has a perfectly definite composition. And the same fact is noted in the examination of every other pure substance. The law of **constant composition and definite proportions** states that, "*Every pure substance is always composed of the same* *elements in the same definite proportions.*" The law merely summarizes all past experience of the scientific world. An analysis of a substance, once correctly made, holds true for any part of the world, and for all time, so far as we know. We thus see the great value to future generations of the work carefully and accurately done to-day.

Oxygen is the most abundant element. Of its extraction from the air by means of mercury and its preparation by heating mercury ash, or mercury oxid, as we shall hereafter call it, we have already learned. This process of obtaining oxygen is slow and expensive, and we naturally seek a more satisfactory method of preparing it. Of course we cannot hope to get oxygen except from some substance which has been shown by analysis to contain it. Potassium chlorate, often called "chlorate of potash," is composed of potassium, chlorin, and oxygen. When heated, it liberates all of its oxygen and leaves a substance containing only potassium and chlorin.

Potassium chlorate does not liberate its oxygen with any great readiness, for it may be heated somewhat beyond its melting point, 350°, without giving off any appreciable amount of gas. On further heating, oxygen is liberated abundantly, the speed of the reaction being increased by increasing the temperature. If to a second portion of the potassium chlorate fused as before a little sand or finely powdered manganese dioxid is added, an abundant evolution of oxygen takes place immediately, without further heating. At the end of the reaction the sand or manganese dioxid is found in its original quantity and condition. Apparently it has not changed, yet it assists the decomposition of the potassium chlorate. Other substances, such as the oxids of iron and copper and finely divided platinum, act similarly. *Whenever the addition of a substance causes a chemical reaction to take* *place more rapidly, yet the substance is found at the end of the reaction apparently unchanged, the substance is called a* **catalytic agent,** *and the process is called* **catalysis.** Catalysis is a second method of increasing the speed of a chemical reaction.

Physical properties. Under ordinary conditions oxygen is a colorless, odorless, tasteless gas, but at 183° below zero it condenses to a blue liquid just as steam condenses to water at 100° above zero. The ordinary temperature (approximately 17°) is about 200° above the boiling point of oxygen (–183°), so that at ordinary temperatures oxygen is in much the same condition that water would be in at 300°. The boiling point of oxygen is relatively low. At still lower temperatures (–227°) it changes to an icelike solid, just as water freezes at zero.

The preceding paragraph states some of the physical properties of oxygen. By *physical properties* are meant those properties which may be ascertained without causing any chemical change in the substance under consideration. By *chemical properties* are meant those properties which are shown when the substance undergoes a chemical change.

Chemical properties. As has been stated previously, a glowing splinter of wood, thrust into a jar of oxygen, bursts into flame. Sulfur, phosphorus, a candle, all substances which burn in air, burn more rapidly in oxygen. Moreover, some substances, such as iron, which do not ordinarily burn in air, burn without difficulty in oxygen. In every case the process consists in the addition of oxygen to the burning substance. Oxids are formed, and the process is known as *oxidation.* Combustible material consists largely of carbon which is converted into carbon dioxid. As every one knows, when this reaction takes place heat and light are given off, the chemical energy of the carbon and oxygen being converted into these other forms of energy. Combustion is rapid oxidation accompanied by the liberation of heat and light.

Non-combustible substances belong to one of two classes. Either they are already oxidized as far as they can be, or else the oxidization of these substances does not take place readily under the conditions ordinarily reached. To the first class belong earth, sand, brick, and stone; to the second, iron and steel. Hence these materials are used in fireproof buildings.

At high temperatures oxygen is a very active element, uniting with most substances very vigorously. Were the atmosphere composed of oxygen only, the kindling of a fire in a stove would result not alone in the combustion of the wood and coal. The stove would burn up also, together with the house and every combustible thing. A wave of fire would sweep over the earth, leaving in its wake nothing but ashes.

Slow oxidation. At ordinary temperatures, however, oxygen does not readily act on other substances, otherwise all things in contact with the air would immediately undergo chemical change. Still, many substances that are exposed to the air do become gradually altered, owing to the action of oxygen. The process goes on slowly, requiring days, months, or even years for its completion. This *slow oxidation*, as it is called, is not striking in its immediate effects, but its final results are important and far-reaching. The products formed are of the same nature as those produced by rapid oxidation. The heat liberated is the same in quantity, but the reaction takes place so slowly that the temperature may not became noticeably higher than surrounding objects. Familiar examples are the rusting of iron and the decay of animal and vegetable material. The contrast between rapid and slow oxidation is shown in Fig. 7.

Respiration is another instance of slow oxidation. Oxygen is absorbed by the blood and carried to all parts of the body, the waste material from which is slowly oxidized. The final product of this oxidation, carbon dioxid, may be detected in the air expelled from the lungs. The heat liberated in this reaction maintains the animal heat of the body. Besides furnishing material to take the place of that which has been worn out, the food which we eat is burned inside the body much as fuel is burned in a furnace.

When a small animal, such as a mouse, is placed in a jar of oxygen, it exhibits great activity and eats ravenously. It tires out quickly, however, and soon dies, apparently being completely used up in a short time.

Spontaneous combustion. If the heat liberated by slow oxidation is prevented from escaping, the temperature of the material may rise gradually. With increasing temperature, reactions take place more rapidly and heat is liberated more quickly, causing a further rise in temperature. This continues, until the substance begins to glow or bursts into flame, and *spontaneous combustion* is said to take place. In common language, the substance begins to burn.

That temperature at which burning begins spontaneously is called the **kindling temperature.** The kindling temperature varies greatly with different substances. Phosphorus takes fire readily, sulfur requires considerable heating, and iron will burn only at very high temperatures not ordinarily reached.

The relation between the kindling temperatures of various substances is illustrated in the use of a common match. When it is scratched, the heat generated by friction is sufficient to kindle the phosphorus compound, which is one of the ingredients of the head of the match. In burning this generates enough heat to raise the coating of sulfur or wax to its kindling temperature, and the latter in turn sets fire to the wooden splint.

a

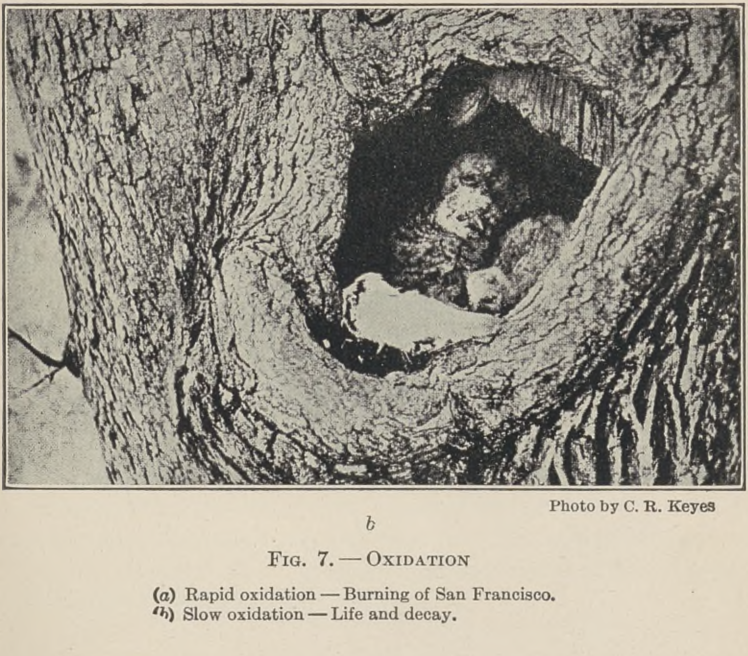

Photo by C. R. Keyes

b

FIG. 7. — OXIDATION

(*a*) Rapid oxidation — Burning of San Francisco.
(*b*) Slow oxidation — Life and decay.

Oxygen in nature. From what has been said about the union of oxygen with other substances, either by slow or rapid combustion, it will be seen that in time the amount of oxygen in the atmosphere must grow less, and unless some source of supply exists, sooner or later it would become so small that animal life could not exist. This source of supply is found in the plant world, which absorbs carbon dioxid from the atmosphere and decomposes it. The carbon goes to make up the tissues of the plant, while the oxygen is given off through the pores of the leaves. In this way the amount of oxygen in the atmosphere is maintained practically constant.

The results of analysis indicate that oxygen is more abundant in nature than any other element. The whole of the earth, so far as we know anything of its composition, consists almost entirely of compounds of oxygen. Clay, sand, feldspar, granite, limestone, and marble all contain about 50 per cent of oxygen. From most compounds of oxygen the element cannot be liberated readily, but from a few common substances it may be obtained without difficulty. By passing an electric current through water and various other substances, oxygen may be obtained.

History. Scheele, a Swedish apothecary, first prepared oxygen in 1773 by heating manganese dioxid, and also saltpeter, to very high temperatures. Priestley, an English clergyman, obtained oxygen by decomposing the red oxid of mercury early in 1774, and published his results before Scheele did his. Hence, Priestley is said to have "discovered oxygen." Lavoisier, whose portrait is shown in Fig. 8, was the first to explain the action of oxygen in supporting combustion, and it is often said that "modern chemistry began with Lavoisier." He gave oxygen its name because it is found in many acids; for oxygen means "acid former."

Metals and non-metals. Oxygen is a type of a class of elements known as non-metals, in contrast to those commonly known as metals. The latter possess metallic luster and the power of conducting heat and electricity. They are generally malleable and ductile and frequently have a high density. Many less familiar but equally important *metallic properties* will be noted as the study progresses. Contrasted with these, the non-metals do not have a luster nor conduct heat nor electricity. They differ from metals in many other ways, and are said to possess *non-metallic properties.* Any element whose properties are similar to those of oxygen is a non-metal.

SUMMARY

Combustion, or burning, is one of the most familiar of chemical reactions. It may take place with or without a flame. A flame is simply burning gas. When a solid burns without decomposing into a gas that will burn, no flame is present. The ash formed when a substance burns may be either a gas or a solid, but it always weighs more than the original substance. This suggests that something has been added to the combustible substance during the burning. This something is oxygen, which forms about one fifth of the air and is the most abundant of the elements.

Oxidation is the chemical union of oxygen with some other substance. A compound of oxygen and another substance is an *oxid.* Oxidation may be rapid or slow. When a given amount of any substance is oxidized, the same amount of heat is set free whether the oxidation be rapid or slow; but in slow oxidation the heat escapes about as fast as it is evolved, while in rapid oxidation the heat is produced so fast that the substance becomes incandescent and burns. *Burning* or *combustion* is oxidation accompanied by an evolution of heat and light. The temperature at which burning begins is the *kindling temperature.*

Oxygen may be prepared only from substances that contain it. Scheele, in 1773, and Priestley, in 1774, obtained it, and Lavoisier gave to it its name. It is usually prepared by heating potassium chlorate. The addition of a little manganese dioxid or sand to the potassium chlorate causes the oxygen to escape at a lower temperature, but the manganese dioxid or sand are apparently unchanged. A substance that hastens chemical action but is itself left apparently unchanged is a *catalytic agent*, and its action is *catalysis*.

Properties of oxygen. Oxygen is a colorless, odorless, tasteless gas. It is slightly soluble in water and condenses to a blue liquid at a low temperature. It is active, forming compounds with nearly all of the other elements, and its activity increases as the temperature is raised. Elements having properties more or less similar to those of oxygen are called *non-metals*.

Conservation of matter. In oxidation, and also in other cases of chemical action, no increase or decrease in the total quantity of matter concerned has ever been detected. A similar statement holds true of energy.

Definite proportions and constant composition. From the universal experience of chemists this law has been derived also. Every pure substance always consists of the same elements in the same invariable proportions.

QUESTIONS

1. When heated in air, a pound of tin gains in weight about four ounces. How much would it gain if heated in a vacuum?

2. What reasons can you give for supposing that air contains oxygen?

3. With what kind of a substance must the oxygen in the air be mixed?

4. In your experience, have you ever noticed whether rusting and decaying bodies are warmer than their surroundings?

5. Why should cloths used in cleaning lamps, or oily rags in general, not be kept in a closet?

6. Why does a lighted candle placed in a closed vessel soon go out?

7. When iron wire is burned in oxygen, why is it tipped with sulfur?

8. Explain the ordinary method of making a fire by the use of paper, kindling wood, and coal.

9. When a match is lighted, why does not its whole length catch fire at once?

10. Which is the more necessary to our well-being, slow oxidation or rapid oxidation?

11. What changes would there be on the earth if combustion were to become impossible? If slow oxidation were to cease?

12. What changes would result in us and in the world around us if the atmosphere should become richer in oxygen gas? What changes if it should become poorer?

13. Explain, in chemical language, the results of closing the air inlets at the base of a stove, and also the results of opening them wider.

14. Explain chemically the results of opening and of closing the damper in a stovepipe.

15. In what ways may a candle flame be extinguished? Explain the results in chemical language.

16. The following substances are liable to spontaneous combustion; that is, they sometimes take fire of their own accord: oily cotton waste around machine shops; coal and coal dust in the bunkers of ships; damp hay in mows; flour dust in mills. Explain this action.

17. Linseed oil, used in making paints, may be kept in a closed bottle or can without change. When opened, a "skin" forms on the surface of the can of paint exactly like the resinous substance which, on a painted surface, holds the pigment and protects the material beneath. Explain in chemical terms the "drying of paint."

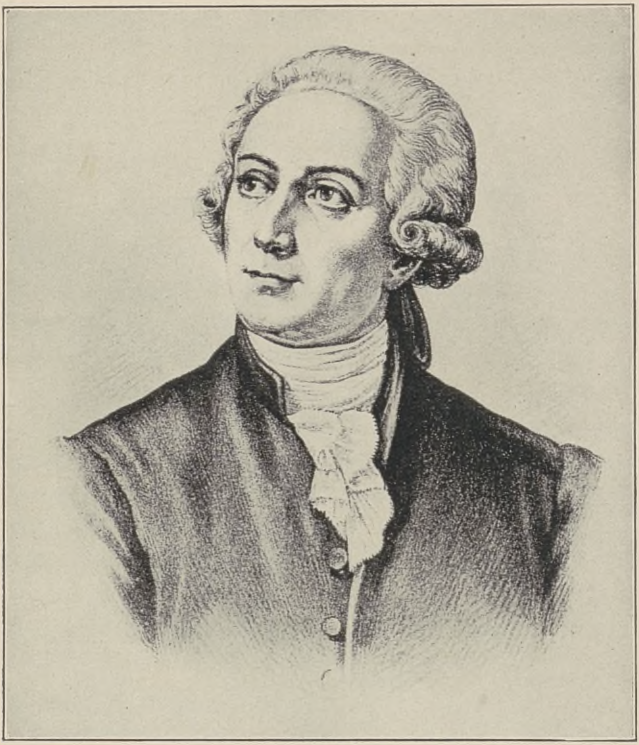

FIG. 8. — ANTOINE LAURENT LAVOISIER (1743–1794)

Overthrew the phlogiston idea of combustion and established modern chemistry on the basis of the oxidation theory of combustion. He first burned the diamond to carbon dioxid and proved it to be a form of carbon. A man of wealth and high official position under Louis XVI, he brought about many reforms in the financial policy of the monarchy and in the levying of taxes. He introduced the potato and the sugar beet into France and improved the methods of agriculture and the manufacture of gunpowder. Despite these services he became disliked during the French Revolution, was imprisoned and sentenced to death. It was asked that he be allowed six weeks of life in which to finish an investigation, but the request was denied with the remark, "The Republic has no need of savants." On the next day the guillotine put an end to the life of one of the greatest men of science the world has produced.

CHAPTER IV

SOME PROPERTIES OF GASES

Effect of temperature. It is a well known-fact that all substances tend to expand when heated and to contract when cooled. Solids and liquids expand but little and show no uniform action. Each particular substance expands a small but definite fraction of its volume at 0° for each degree that its temperature is increased. Gases respond remarkably, however, to slight changes in temperature, and, what is most surprising, *all gases behave alike* whatsoever their nature may be. They all expand uniformly. For every increase in temperature of 1° they expand $\frac{1}{273}$ of their volume at 0°. The French physicist, Charles, first announced the law that goes under his name; viz. *all gases expand* $\frac{1}{273}$ *of their volume at* 0° *for each increase of* 1° *in temperature.*

Conversely, gases contract $\frac{1}{273}$ of their volume at 0° for each degree that their temperature falls. At $-10°$ they lose $\frac{10}{273}$ of their volume at 0°, at $-100°$ they lose $\frac{100}{273}$, and at $-273°$ they should lose $\frac{273}{273}$ of their volume. That is, if Charles's law should hold at these very low temperatures, a gas should have no volume at $-273°$. Before this temperature is reached, however, all gases have become liquids and solids.

Absolute temperature. The point $-273°$ is called *absolute zero*, for the absolute scale for measuring temperature starts from this point as zero. It uses the same degrees as the centigrade scale. Since the zero of the absolute scale is 273° lower than the zero on the centigrade scale, any particular temperature on the absolute scale is 273° higher than it is on the centigrade scale. Therefore, to convert centigrade temperature into absolute temperature, add 273 algebraically to the centigrade temperature.

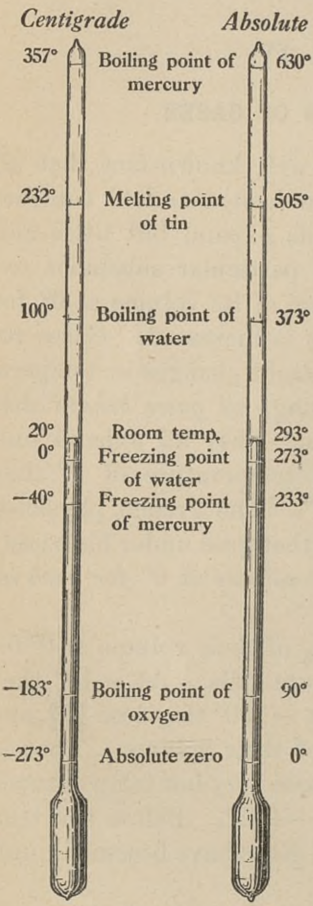

Fig. 9.

Absolute temperature is usually denoted by a capital T. The boiling point of water, 100° C., is 373° T. Analogously, − 100° C. is 173° T. A comparison of temperatures as measured on these two scales is shown in Fig. 9.

Considering the volume at 0° C., *i.e.* 273° T., as unity, the volume of a body of gas is directly proportional to the absolute temperature. At 273° T. the volume is $\frac{273}{273}$; at 373° T. the volume is $\frac{373}{273}$; at 173° T. the volume is $\frac{173}{273}$. We can readily calculate what the volume of a gas, measured at any temperature, will be at any other temperature by the proportion

$$x : v :: T_x : T_v$$

in which x equals the new volume, v the former volume, T_x the new temperature, and T_v the former temperature, both temperatures being measured on the absolute scale. This proportion may be expressed as an equation:

$$x = v\frac{T_x}{T_v}$$

No difficulty will be found in remembering this expression; for, if the temperature is increased, so will the volume be, and the former volume must be multiplied by a fraction greater than 1. If the new temperature is lower then the former temperature, the volume will be smaller and the fraction to be used as a multiplier will be less than 1. The following examples will make this principle clear:

1. What will be the volume at 0° C. of 215 ccm. of gas measured at 20° C.?

$$x = 215 \times \frac{273}{293}, \text{ whence } x = 200 \text{ ccm.}$$

2. One liter* of gas measured at 0° C. will occupy what volume at 100° C.? What volume at – 100° C.?

$$x = 1000 \times \frac{373}{273}, \text{ whence } x = 1366 \text{ ccm.}$$

$$x = 1000 \times \frac{173}{273}, \text{ whence } x = 634 \text{ ccm.}$$

Effect of pressure. Changes in pressure tend to affect the volumes of substances, increased pressure causing decrease in volume, and *vice versa.* Solids and liquids show but little change and no uniform behavior. Gases are very susceptible to slight changes in pressure, however, and they all expand or contract alike. Boyle, "the father of modern science," first perceived this uniform action and stated the law which bears his name. *The volume of a gas varies inversely as the pressure:* with half the pressure, twice the volume; with five times the pressure, one fifth the volume, etc. These relations may be expressed by the proportion:

$$x : v :: p_v : p_x$$

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*See Appendix, p. 408.

where x equals the new volume, v the former volume, p_v the former pressure, and p_x the new pressure. This proportion may be expressed by the equation:

$$x = v \times \frac{p_v}{p_x}$$

In remembering this fraction the same reasoning applies as in the previous case. If the pressure is greater than the former pressure, we know that the new volume must be less than the former volume; hence, multiply the former volume by a fraction smaller than 1. If the new pressure is less than the former pressure, the new volume will be greater than the former volume, and we must multiply the former volume by a fraction greater than 1. The following examples will make this principle clear:

1. What will be the volume under 750 mm. pressure of 500 ccm. of gas measured under 765 mm. pressure?

$$x = 500 \times \frac{765}{750}, \text{ whence } x = 510 \text{ ccm.}$$

2. A balloon holding 100 cubic meters of gas at 760 mm. pressure rises in the air until the pressure indicated by the barometer is only 100 mm. What volume will its gas occupy under these conditions?

$$x = 100 \times \frac{760}{100}, \text{ whence } x = 760 \text{ cubic meters.}$$

Changes in both temperature and pressure may occur at the same time, but each takes place independently of the other. We may make but one calculation to determine what the volume will be when both temperature and pressure have changed, but the correction for each change is made independently of the other. To illustrate by an example:

What will be the volume at 0° C. and 760 mm. pressure of 2 liters of gas measured at 20° C. under a pressure of 700 mm.?

The new temperature is less than the former temperature, hence the new volume will be less than the former volume; therefore multiply the former volume by the temperature fraction less than 1. The new volume caused by the change in temperature is given by the expression $2000 \times \frac{273}{293}$. Now suppose the change in pressure to act on this volume of gas. The new pressure is greater than the former pressure, hence the new volume will be less than the former volume; therefore multiply the volume by a pressure fraction less than 1. That is, multiply $\left(2000 \times \frac{273}{293}\right)$ by $\frac{700}{760}$. The whole expression then becomes

$$x = 2000 \times \frac{273}{293} \times \frac{700}{760}, \text{ whence } x = 1716 \text{ ccm.}$$

Solution of this problem in two steps will give the same result.

Use of gas laws. The effects of temperature and pressure on the volume of solids and liquids are of little concern to the chemist, for he is accustomed to measure his quantities by weight, and the expansion or contraction of a body does not alter its weight. With gases the situation is different. They are so light that relatively large volumes have very little weight. Since a gas differs from a solid and a liquid in that it has no definite volume, but will expand indefinitely and fill any space, it must be placed in a container, which usually weighs many times more than the gas does. Hence in any ordinary method of weighing, large errors are sure to be made. For this reason gases are usually measured by volume.

The volume of a given weight of gas varies greatly with temperature and pressure, however. In order to get results that may be of use to others, it is necessary for all scientists to measure gases at the same temperature and pressure. The temperature agreed upon is 0° C., and the accepted pressure is that equal to the weight of a column of mercury 760 mm. high, for this is the average height of the barometer at sea level. When at this temperature and pressure, a gas is said to be under *standard conditions.* A liter of gas measured under standard conditions is called a *standard liter.*

To actually measure all gases at 0° C. and 760 mm. pressure would be a task of unending inconvenience. It is a very simple matter, however, to calculate what will be the volume under standard conditions of any volume of gas measured at any temperature and pressure. Therefore gases are measured under ordinary conditions, the temperature being indicated by the thermometer and the pressure by the barometer at the time the volume is read. This volume is then reduced to standard conditions in the way already shown.

Measurement of gases. Gases are ordinarily collected over water or mercury. In order that a gas be under the pressure exerted by the atmosphere as indicated by the barometer, the level of the liquid must be the same inside the measuring tube as outside, as shown in Fig. 10, *a*. Along the dotted line the pressures are equal. Inside the tube the gas presses on the liquid; outside the tube the atmosphere presses on the liquid. The pressure must be the same inside the tube as outside, otherwise the liquid would flow in the direction of the greater pressure.

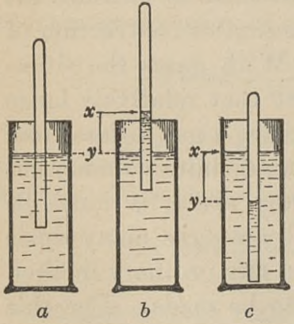

FIG. 10.

Under the conditions shown in *b* the gas is under reduced pressure. The pressures along the dotted line are equal. Outside the tube it is the atmosphere. Inside the tube it is the pressure of the gas plus the weight of the column of liquid above the line. The pressure on the gas equals the pressure of the atmosphere minus the column of liquid, *xy*.

In *c* the gas is under increased pressure, for the pressure along the line is everywhere the same. Inside the tube it is simply the gas pressure, while outside the tube it is the atmosphere plus the weight of a column of liquid above the line. The pressure on the gas equals the atmosphere plus the column of liquid, *xy*.

If the gas is collected over mercury, simply add to or subtract from the height of the barometer the height of the column of mercury, xy. If the liquid is water, divide the height of the column, xy, by 13.6; for mercury is 13.6 times as heavy as water. Then add this result to, or subtract it from, the height of the barometer, as before.

Every liquid gives off from its surface particles which form a gas or vapor above it. If this vapor is confined, it exerts a pressure on the liquid below it. Vapor pressure increases rapidly with the temperature, as is shown by the table in the Appendix, which gives the pressures due to water vapor at different temperatures. It makes no difference whether another gas is present or not. If oxygen is collected over water, water vapor is mixed with the oxygen. *In a mixture of gases each gas behaves entirely independently and exerts a pressure of its own.* Consequently, part of the pressure is due to oxygen and part to water vapor. In order to get the true pressure exerted by the oxygen, the pressure of the water vapor must be subtracted from the total pressure before the reduction is made to standard conditions. The pressure due to mercury vapor is so small that it need not be considered except in very exact investigations. An illustration showing all the corrections to be applied in order to reduce the results to standard conditions is given below.

One gram of potassium chlorate liberates, when heated, 305 ccm. of oxygen collected over water and measured at room temperature (20° C.) when the barometer stands at 750 mm. The potassium chlorate loses in weight during the heating 0.3915 gram. Calculate the weight of a liter of oxygen under standard conditions.

Barometer	750 mm.
Pressure water vapor at 20° C.	17.4 mm.
Actual pressure of oxygen	732.6 mm

$$x = 305 \times \frac{732.6}{760} \times \frac{273}{293}, \text{ whence } x = 274 \text{ ccm.}$$

274 ccm. of oxygen under standard conditions weigh 0.3915 gram.

Therefore $274 : 1000 :: 0.3915 : x$, whence $x = 1.429$.

The weight of a liter of oxygen under standard conditions is 1.429 grams.

Structure of matter. The preceding considerations have shown us that gases are exceedingly compressible. The degree to which compression may take place is almost unbelievable. By means of air pumps or other contrivances, a container may be exhausted until the gas remaining in it has a pressure of less than one millionth of an atmosphere. On the other hand, gas may be compressed until ten thousand atmospheres pressure is reached. In the second case the amount of matter in a given space is ten thousand million times greater than in the first case.

In the light of such facts as this, we may give an answer to the old question: "Is matter continuous or discontinuous?" That is, to the mind's eye does matter appear continuous like a bowl of jelly or composed of grains like a pile of sand or shot? If matter is continuous, it is inconceivable that matter can be as compressible as gases are. Matter must be discontinuous, and in the gaseous state must resemble a room full of motes of dust rather than a pile of shot; for in order to account for the degree of compressibility which is true for all gases, the distances between the particles must be very great compared to the size of the particles. These particles of which a gas is composed are called *molecules*, a word derived from a Latin noun meaning "a little mass."

The molecules of a gas are very small, for they cannot be seen with the most powerful microscopes. They are in motion, as is shown by the fact that a gas will expand indefinitely and fill any container however large. There is no tendency for a gas to settle as dust particles will, no matter how long the gas may stand in one position. Further evidence of the motion of gas particles is furnished by the fact that if two different gases are brought together and communication is opened between their containers, each gas soon passes out into the other, and the mixture becomes the same everywhere. Each is said to *diffuse* into the other. Since this process takes place more rapidly at high temperatures than at low temperatures, it is evident that the effect of heating a gas is to increase the speed of its molecules.

The same considerations apply to liquids and to solids, for they are compressible and diffuse one into another to a smaller degree, but in exactly the same way as gases do. Hence all matter is believed to consist of very small particles called molecules, which, even in the case of solids, are not in contact with one another, but are separated by spaces in which they move constantly. This idea is known as the *kinetic theory of matter.*

SUMMARY

Charles's law. Gases expand $\frac{1}{273}$ of their volume at 0° for each increase in temperature of 1°. They contract in the same ratio when the temperature falls. If the law should hold at – 273°, a body of gas would have lost all its volume and could not contract any more. Before this temperature is reached, all gases have been converted into liquids and solids, however. Minus 273° is taken as the zero point on the absolute scale of temperature. Another statement of Charles's law is: The volume of any gas is proportional to its temperature on the absolute scale. Hence the volume at any temperature may be found by the expression:

$$x = v\frac{T_x}{T_v}$$

Boyle's law. The volume of any gas varies inversely as the pressure. Hence, the volume at any pressure may be found by means of the expression:

$$x = v\frac{p_v}{p_x}$$

Both temperature and pressure may change at the same time, but neither affects the results produced by the other.

Standard conditions. As gases are very light, it is more convenient to measure them by volume than by weight. As volume alters with the temperature and pressure, it is convenient to have a standard temperature and pressure for universal use. Scientists have chosen 0° C. and 760 mm. as the standard conditions. By means of the two formulas just given, gas volumes may be reduced to standard conditions.

Moisture. If a gas is collected over water, it contains water vapor. This vapor exerts pressure, and if the volume of the dry gas under standard conditions is required, the pressure of this water vapor must be deducted from the total gas pressure, in order to obtain the pressure of the pure gas. The pressure of aqueous vapor varies with the temperature, as shown in the table in the Appendix.

Kinetic theory of matter. Gases are so compressible that we are forced to believe that they consist of very small particles, called *molecules*, separated from each other by spaces in which the molecules move constantly. Liquids and solids must be similar in structure to gases, for they show the same properties, though to a much smaller degree than gases do.

QUESTIONS

1. What will be the volume occupied by 100 ccm. of gas if its temperature is raised from 20° to 100°?

2. What will be its volume if its temperature is lowered to −10°?

3. What space will be occupied by 200 ccm. of gas measured at 750 mm., if the atmospheric pressure changes to 770 mm.?

4. What will be its volume if the atmospheric pressure changes to 740 mm.?

5. A body of gas that occupies 150 ccm. at 0° and 760 mm. will occupy what space at 20° and 750 mm.?

6. A body of moist gas at 20° and 765 mm. occupies a space of 100 ccm. What is its volume dry and under standard temperature and pressure?

7. A body of gas collected over mercury at 20° and 755 mm. has a volume of 105 ccm. What would be its volume if it had been collected over water under the same temperature and pressure?

8. To what temperature must 1 liter of gas measured at 0° C. be heated to double its volume, the pressure remaining constant? At what temperature would the liter of gas lose one third of its volume because of contraction?

CHAPTER V

HYDROGEN

WHEN an attempt is made to pass an electric current through pure water, but little action is noted. If a little sulphuric acid is added to the water, the current flows and gases are liberated at each electrode (Fig. 11). At one, which is called the *positive pole* or *anode*, oxygen collects. At the other, known as the *negative pole* or *cathode*, a second gas collects in twice as great a volume. We may assume that this gas is different from oxygen, for, since any oxygen is just like all other oxygen, we may expect all the oxygen to be liberated in one place.

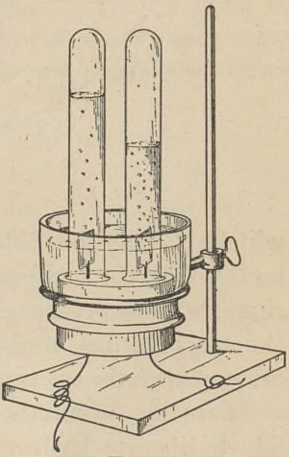

FIG. 11.

If the process is continued for a long time, it will be noted that part of the water has disappeared. It has been decomposed into the two gases just mentioned. By evaporating the remaining solution, the acid may be obtained in the same quantity and condition in which it was put into water. Apparently it has remained unchanged, and obviously this is another instance of the action of a catalytic agent. In experiments such as this many other substances have a catalytic action similar to that of acid.

Any substance which will conduct an electric current when in solution is called an **electrolyte.** *Decomposition caused by electricity is known as* **electrolysis.** The term is derived from Greek words meaning "to loosen by means of electricity."

In order to identify this second gas, let us test it with a burning splinter, somewhat as we tested oxygen. When plunged into this gas, the splinter is immediately extinguished, but the gas itself takes fire and burns (Fig. 12). Although colorless, tasteless, and odorless, this gas proves to be entirely different from oxygen. It is called *hydrogen.*

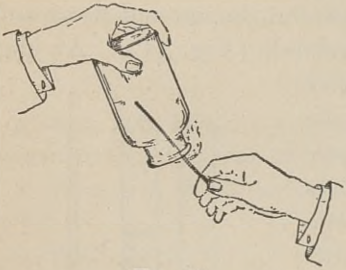

FIG. 12.

Preparation. When we seek for a better method of preparing hydrogen, many other compounds containing it are found, from some of which it may be obtained without difficulty. Several metals liberate hydrogen from water. Sodium and potassium do so at ordinary temperatures, magnesium requires the temperature of boiling water, while iron and some other materials act rapidly at a red heat.

There are a number of substances other than water which liberate hydrogen in abundance when brought in contact with these and other metals. Since all these substances are sour and acid to the taste, they are called *acids.* Sulfuric acid is a common substance that analysis shows to be composed of hydrogen, oxygen, and sulfur. Hydrochloric acid, often called muriatic acid, is composed of hydrogen and chlorin. Vinegar is scarcely more than acetic acid diluted with water. Acetic acid consists of hydrogen, oxygen, and carbon.

Whenever we find a number of different substances all of which possess certain properties and act alike in one or more ways, we have learned by experience that some common constituent is the cause of the common action. For we have found that a number of entirely different substances do not have the same properties and action. The only constituent present in all acids is hydrogen. We believe that acid properties are due to hydrogen, for no substance possesses acid properties that does not contain hydrogen.

But many substances, such as sugar, wood, petroleum, and the like contain hydrogen, but do not possess acid properties. The hydrogen in acids, therefore, must be in a different condition from the hydrogen in these other compounds. We shall learn later just what this difference is.

Either hydrochloric or sulfuric acid acts more readily on metals than acetic acid does, and is therefore preferable. Iron or zinc, two of the cheapest metals, readily liberate hydrogen from acids. It may be collected over water according to the method used for oxygen. Water is used to dilute the acids and moderate the action. Besides the hydrogen, in each case another product of the reaction remains dissolved in the water. Of these substances we shall learn more later.

An automatic generator for hydrogen and other gases which are similarly prepared is shown in Fig. 13. It is named after its inventor and called the Kipp generator. The metal is placed in *B* and the diluted acid in *A*, from which it runs into *C* and then rises into *B*, where it generates gas as long as the stopcock is open. When this is closed, the pressure of the gas generated forces the acid off the metal down into *C*, and finally up into *A*.

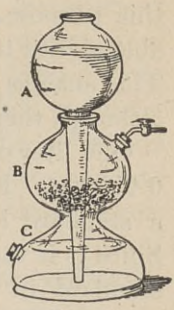

FIG. 13.

Physical properties. Hydrogen is a colorless, odorless, tasteless gas that burns, but will not support combustion. When pure it is not poisonous, though living things could not long survive in an atmosphere of it because of the lack of oxygen necessary for respiration. All living things would drown in it exactly as a human being drowns in water. Hydrogen made from ordinary chemicals has an odor due to impurities, and is likely to be injurious.

Hydrogen is the lightest substance known. When a jar of it is left uncovered with its mouth downward, the gas does not flow out as water would. On the other hand, when the jar is turned mouth upward, the gas escapes immediately. These facts may be shown by bringing the jars to a flame. The explanation is that hydrogen is much lighter than air. Anything tends to rise through fluids which are specifically heavier than itself and to fall through those which are lighter. Hence, water pours downward through air, but, if immersed in mercury, water will pour upward just as hydrogen does in air. Because of the tendency of hydrogen to rise through air, it is sometimes used to inflate balloons, but since coal gas is lighter than air and much cheaper than hydrogen, it is much oftener used for this purpose. Furthermore, hydrogen possesses remarkable ability to pass through the pores of other substances. This enables it to escape from vessels of certain materials, although they have no perceptible defects.

One liter of hydrogen under standard conditions weighs 0.0899 g. For all ordinary computations, the weight of a standard liter of hydrogen may be taken as 0.09 g. Since it is the lightest substance known, it is taken as the standard in determining the specific densities of other gases.* *The gas density of any substance is the specific*

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* Formerly the density of gases was often referred to air as a standard. Since the average density of air is 14.4 times as great as that of hydrogen,

density of its gas referred to hydrogen as 1; that is, the ratio between the weights of equal volumes of hydrogen and any second gas is determined, both being under standard conditions. Thus, oxygen is found to be about 16 times as heavy as an equal volume of hydrogen; the gas density of oxygen is about 16, therefore. In calculating gas densities the hydrogen is always considered as being under standard conditions.

By intense cold and pressure, hydrogen may be condensed to a colorless liquid that boils at – 252° and freezes at – 259°. At these temperatures all other substances have become liquid and solid with the single exception of the very rare element helium, which liquefies only at – 269.5°.

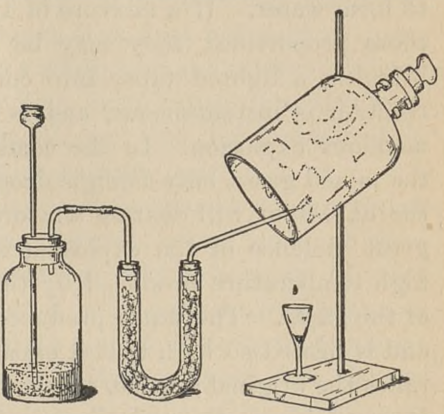

FIG. 14.

Chemical properties. Hydrogen burns in air with an almost invisible flame. If a considerable quantity of hydrogen is burned under a bell jar (Fig. 14) or some other cold surface, a mist appears in the jar, and soon drops of a colorless liquid trickle down the sides and may be collected and tested. The liquid proves to be water. The name hydrogen is derived from Greek words meaning "water former."

We have previously learned that combustion ordinarily

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the gas density of any substance may be calculated readily by multiplying the density referred to air by the factor 14.4. Thus, the specific density of oxygen referred to air is 1.105. Its gas density is $1.105 \times 14.4 = 15.9$.

consists in the combination of the burning substance with the oxygen of the air. Hydrogen combines chemically with oxygen, and the product is water. It will be remembered that in the electrolysis of water two volumes of hydrogen and one of oxygen collect at the poles. These are the proportions in which hydrogen and oxygen combine to form water. If a mixture of the two gases is made in these proportions, they may be caused to combine by bringing a lighted taper into contact with them. The reaction is instantaneous, and is accompanied by a tremendous explosion. In the combination of 100 ccm. of the mixed gases, only a single drop of water is formed, yet the explosion will shatter any ordinary container. The great violence of the explosion is due to the extremely high temperature produced by the chemical combination of the gases. The water produced is changed into steam and is heated so high that it expands and occupies many times the original volume, causing a pressure which bursts the container. For this reason only very small quantities of hydrogen and oxygen should ever be exploded.

Though colorless, the flame of hydrogen burning in air is very hot, the heat liberated being more than five times as great as that produced by burning an equal weight of coal. The heat may be intensified by causing the hydrogen to burn in an atmosphere of oxygen. The *oxyhydrogen blowpipe* is an apparatus for utilizing the great heat of combustion of hydrogen. As shown in Fig. 15, it consists of two tubes, one inclosed within the other. The inner tube is connected with a tank containing oxygen, while the outer tube leads to a similar tank containing hydrogen. While separated, the two gases cannot unite;

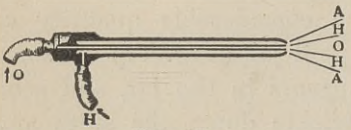

FIG. 15.

on issuing from the tubes, hydrogen, *H*, becomes mixed with oxygen, *O*, and air, *A*, and when set on fire they combine with the production of intense heat.

The oxyhydrogen blowpipe is used in operations requiring a high temperature, such as the melting of platinum, but it is now largely supplanted by the electric furnace. (See p. 202.) When the flame of the blowpipe is allowed to play upon some substance that does not melt or burn up, the latter is raised to a white heat and emits a brilliant light. Calcium oxid, or lime, being infusible at this temperature, is commonly used, and the light obtained is known as the *lime light* or *calcium light*.

Under ordinary conditions hydrogen is not an active element chemically, being without action on most substances. At high temperatures it may be made to react with many substances, but it is by no means as active as oxygen. In nature it exists almost entirely in combination, occurring most abundantly in water, but also in acids and minerals, as well as in many other substances. A study of the sun and of the fixed stars has shown that free hydrogen, though very rare on earth, is common in many other parts of the universe.

Oxidation and reduction. We have noted previously that many substances unite readily with oxygen, forming oxids. If these oxids are heated with hydrogen, in many instances reactions take place resulting in the formation of water, the elements previously united with oxygen being set free. Thus, copper, heated in the air, is converted into black copper oxid. If this substance is heated in a tube through which hydrogen is passed, water is formed, and metallic copper results.

$$\text{Copper} + \text{oxygen} \rightarrow \text{copper oxid.}$$

$$\text{Copper oxid} + \text{hydrogen} \rightarrow \text{copper} + \text{hydrogen oxid.}$$

The latter process is the opposite of oxidation and is called *reduction*. We shall find later that other elements act very similarly to oxygen, and still others behave as hydrogen does, hence the definitions of oxidation and reduction must be enlarged. In a broader sense, oxidation is the process of increasing the proportion of the non-metallic constituents in a compound. The reversal of this reaction, the process of reducing the proportion of the non-metallic constituents in a compound, is known as reduction.

The processes of oxidation and reduction always go on together and take place at the same time. For instance, in the experiment last cited, while copper oxid is reduced, hydrogen is oxidized. To reduce a compound, we make it act as an oxidizing agent and give up the whole or part of its non-metallic elements to some other substance which becomes oxidized. When oxidized, a substance takes on non-metallic elements which have been given up by some other substance which is in this way reduced. An oxidizing agent is any substance which will readily part with its non-metallic elements, and a reducing agent is one that will readily unite with non-metallic elements.

All non-metallic elements may act as oxidizing agents. Of these, oxygen, chlorin, and bromin, and substances which will liberate these elements, are most frequently used.

Hydrogen and carbon, and certain substances containing one or both of these elements, are the best reducing agents.

Nascent state. A peculiar action of hydrogen may be illustrated by the following experiments. Permanganates are purple-colored substances very rich in oxygen. When they give up their oxygen, substances having little color are formed, hence, when reduction takes place, the color is bleached. If through one portion of a solution of potassium permanganate mixed with sulfuric acid hydrogen gas from a generator is bubbled, bleaching action is noticed only when the action is long continued. If zinc be added to a second portion of the solution, hydrogen is set free by the action of the acid on the metal. But little gas escapes from the solution, however, for much of it is used in reducing the permanganate, a process which is taking place rapidly, as the bleaching of the solution indicates.

This action is not peculiar to any of these compounds. Other acids and other metals may be used and other substances reduced. At the instant in which hydrogen is liberated from its compounds, it exhibits much greater activity than it does later. Other elements show the same behavior. When in this especially active condition, they are said to be in the *nascent state*. The term *nascent* is derived from a Latin verb meaning "just being born." What the explanation of these facts may be, has not been settled as yet, but the action is well known.

SUMMARY

HYDROGEN

Preparation. When water containing a little salt or similar substance is electrolyzed, oxygen is given off at the anode and hydrogen in double the volume at the cathode. Hydrogen is also liberated from water by sodium and many other metals, but the most common method of preparation is to set it free from dilute acids by the action of metals. Sulfuric acid and zinc or iron are commonly used.

Physical properties. Hydrogen is a colorless, odorless, tasteless gas that burns, but does not support combustion. It is about $\frac{1}{14}$ as heavy as air, 1 liter weighing 0.09 g. It is the lightest substance known.

Chemical properties. Under ordinary circumstances hydrogen is not an active element, but heat increases its activity. Just at the instant in which it is liberated from its compounds, it shows an activity far beyond its ordinary properties and is said to be in the *nascent state.* Other elements exhibit the same behavior. Hydrogen burns in air or oxygen with an almost colorless flame that is very hot. The oxyhydrogen blowpipe produces the hottest flame known. The product of the burning is water. A mixture of oxygen and hydrogen explodes violently when ignited.

OXIDATION AND REDUCTION. Oxidation in a broad sense is the process of increasing the proportion of the non-metallic constituents in a compound. Reduction is the process of diminishing the proportion of the non-metallic constituents in a compound. Oxidation and reduction always go on together.

QUESTIONS

1. Contrast the chemical properties of oxygen with those of hydrogen.

2. Wax is a compound containing hydrogen. When the wax of a candle burns, what becomes of the hydrogen? (Hold a piece of cold glass above a candle flame for a few seconds.)

3. What objections would there be to the use of hydrogen as an illuminating gas; as a fuel?

4. How does the mixture of oxygen and hydrogen used in producing hydrogen explosions differ from water, which is composed of the same elements?

5. Light is produced by burning many different substances. The lime light is a very powerful source of illumination. Is it produced by burning lime? Explain.

6. Calculate the volume of 1 gram of hydrogen under standard conditions.

7. Calculate the volume of 1 gram of hydrogen at 20° and 750 mm.

8. Calculate tne volume of 1 gram of oxygen under standard conditions.

9. If a liter flask filled with hydrogen under standard conditions is warmed to 100°, how much of the hydrogen will be forced out if the stopper is loose? How much oxygen would escape under the same conditions? How much air?

10. If a balloon has a capacity of 1000 cubic meters and is filled with hydrogen, how much will the hydrogen weigh under standard conditions?

11. If 1 liter of air weighs 1.3 grams what is the lifting power of the hydrogen in the above balloon?

12. How could you prepare nascent hydrogen? When and how must it be used? Can you keep it?

13. Iron and tin ores are generally oxids. In obtaining the metals from these ores, what kind of a reaction is used?

CHAPTER VI

WATER

Of all the substances met with in the study of chemistry, water is by far the most common and the most important. It is absolutely essential for life, a large part of all living things consisting of it. Of the 150 pounds that make up the average weight of a man, 100 pounds are water. Our food is largely water. Of vegetables, three quarters or over is water. Meats are somewhat over and breadstuffs somewhat less than one half water. So universal is its occurrence either in chemical combination or present as moisture, that few substances are free from it.

Natural bodies of water cover about three quarters of the earth's surface. From these water is continually passing into the air in the form of vapor and is carried by the winds to all parts of the earth's surface. The quantity of water vapor that the atmosphere can hold depends on its temperature. When air is cooled, its capacity for holding water vapor is diminished. If the cooling proceeds far enough, a condition results in which the air contains all the water vapor it can hold. It is then said to be *saturated*. Any further cooling results in the separation of moisture in the shape of small drops. In nature this process gives rise to dew, fog, clouds, and rain, and, if the temperature is low, to frost and snow. The same effect is seen on a small scale when a water pitcher "sweats" or when frost forms on the pipes of a cold-storage plant.

Natural waters. After rain has fallen, it comes into contact with the ground, running off in streams or sink-ing into the soil, in the latter case usually to reappear at some other point in a spring. All soils contain substances that dissolve more or less in water, hence natural waters always contain an appreciable quantity of foreign material. The character of these waters depends on the character of the soil and the rock. Waters flowing through land containing limestone or gypsum dissolve small quantities of these substances, and are said to be *hard*. The water of springs sometimes comes from a considerable depth in the earth where it has been in contact with beds of salt or similar substances. In such cases the water has a decided smell or taste, and is called a *mineral water*. Some mineral waters are said to be beneficial to health, but this effect is probably due largely to the water itself rather than the material which it contains; for most of us drink too little water.

Fig. 16.—Cholera bacilli magnified 1000 times.

The mineral matter contained in water is not usually of such a character as to render it unfit for drinking, but it does interfere with its use in steam boilers. As the water is converted into steam, the mineral matter forms "boiler scale," which is a poor conductor of heat and so causes loss of fuel. Decaying animal and vegetable matter and the presence of germs, *i.e.* minute forms of animal and vegetable life, some of which cause disease (Figs. 16 and 17), often render the use of water for drinking purposes highly dangerous.

FIG. 17.—Typhoid bacilli magnified 1000 times.

Purification. Before we can tell the properties of water from an examination of natural specimens, it is necessary to purify them. Suspended matter, silt, etc., may be readily removed by filtering (Fig. 18). A circular sheet of filter paper, folded as shown in the figure, is placed in a funnel and the liquid is poured upon it. The process of *filtration* is merely a mechanical screening out of the larger particles. Ordinary filter paper is made of such a quality and thickness that it retains all matter not in solution. Dissolved substances cannot be removed by filtration, however, and resort must be had to the process of *distillation* (Fig. 19). This consists in heating up the solution until

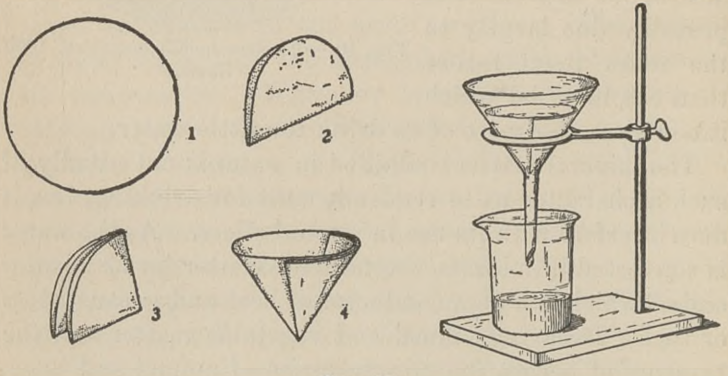

FIG. 18.

the liquid changes its state and becomes gaseous. In the case of aqueous solutions, water changes to steam which, passing out of the container, is cooled by means of a condenser. This consists of a tube surrounded by an outer tube through which water is kept flowing, the low temperature of which causes the steam to liquefy again.

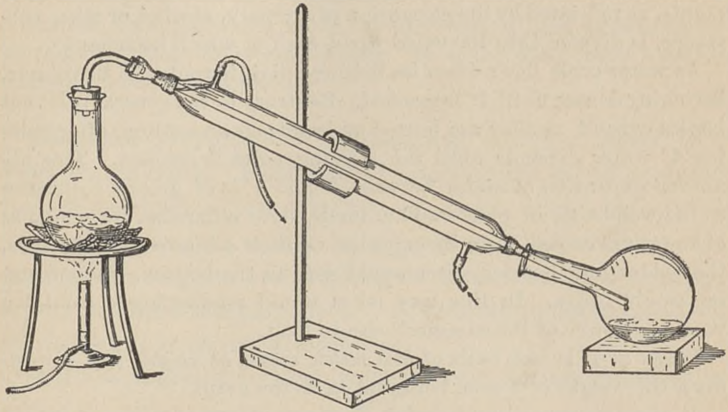

Fig. 19.

The condenser is inclined so that the portion of the liquid that distills over, known as the *distillate*, does not return to the boiling flask, but may be collected in a receiver. In this way any liquid may be separated from the non-volatile matter dissolved in it, for this remains behind in the distilling flask. Filtration through beds of sand is used extensively in purifying water for the use of cities, since germs as well as other suspended matter are largely removed. On board ship, sea water is distilled for drinking purposes and sometimes for use in the boilers. Rain is nature's distilled water.

Pure water is a colorless, odorless, tasteless liquid, the taste usually observed in drinking water being due to the presence of dissolved substances. In large quantities it has a bluish color, such as is seen in the ocean or on looking into a crevasse in a glacier.

Water is such a common substance and is so readily prepared in a state of purity that it is taken as a standard on which many systems of measurement are based. Its freezing point is taken as the zero of the *centigrade scale* of measuring temperature, its boiling point being considered as 100°. The range of temperature between these two points, as indicated by the expansion of mercury, alcohol, or other substance, is divided into 100 equal parts, each of which becomes 1°.

As water cools down from its boiling point, it contracts in volume, becoming denser until 4° is reached. Contrary to the general rule that bodies expand as they are heated and contract on cooling, after passing 4° water expands until the freezing point is reached. This abnormal expansion of water between 4° and 0° is of great significance to the well-being of plants and animals, since otherwise, when bodies of water are cooled down by exposure of their surfaces to cold winds, the colder and heavier water would sink to the bottom, where freezing would begin. In this way lakes would readily freeze solid, beyond the power of the summer's sun to melt.

Water at 4° is the basis of the *metric system of weights* (see Appendix), the weight of 1 ccm. being taken as the gram.

It requires more heat to raise the temperature of a given amount of water 1° than it does for the same amount of any other substance except hydrogen. On this account water is said to have a greater heat capacity than any other substance except hydrogen. Water is taken as the standard in determining *specific heat capacities.* The amount of heat necessary to raise 1 gram of water 1° is called a *calorie.* Whenever a substance changes its state from solid to liquid or from liquid to gas, heat is absorbed. In the reverse process, heat is liberated, as we have seen. The *heat of change of state* for water is greater than for any other known substance. In melting 1 gram of ice, 79 calories of heat are absorbed. This is known as the *heat of fusion.* To convert 1 gram of water at 100° into steam at 100° requires 540 calories of heat. This is called the *heat of vaporization.* These figures measure the differences in energy content between ice and water and between water and steam.

Because water possesses such a large heat capacity and great heat of change of state, large bodies of water act as regulators of temperature for the regions in proximity to them. Excessively hot days are prevented by the absorption of large amounts of heat without appreciable rise in temperature of the water. Conversely, excessive cold is modified by the liberation of the heat given out as the temperature of the water falls.

Should the water begin to freeze, for each gram that solidifies, 79 calories of heat are given out, thus tending to moderate excessively cold weather. Should very hot weather cause much water to evaporate, as it becomes gaseous it absorbs a very large amount of heat, thus tending to lower the temperature.

As has been previously noted (p. 6), water is used as a basis for the determination of *specific density*. In many other ways water is similarly used as a standard.

Chemical properties. In chemical conduct water is a very stable body. Heat tends to decompose all substances, but it requires a temperature of about 1800° before the decomposition of water takes place appreciably. Of course, the oxygen and hydrogen thus liberated combine again at lower temperatures. A reversible decomposition of this kind is called *dissociation.*

Although stable to heat, water is very active chemically, entering into reactions of a most varied character. It seems to be a universal catalytic agent, for experience indicates that no chemical reaction can take place without traces of water being present.

Composition by weight. We have seen that water is composed of two volumes of hydrogen to one of oxygen. Knowing the weight of a liter of these gases under standard conditions, the composition of water by weight may be calculated. This may be determined experimentally by passing hydrogen through a heated tube containing copper oxid (*C*, Fig. 20). Hydrogen from the generator, *A*, is dried while passing through the tube, *B*, which is filled with calcium chlorid or some other substance that will combine with water. When it enters *C*, it combines with the oxygen of the copper oxid to form water which is absorbed in a second tube, *D*, containing calcium chlorid.

The copper oxid tube and the second calcium chlorid tube are each accurately weighed before and after the experiment. The loss of weight of the copper oxid tube is the weight of oxygen. The gain in weight of the calcium chlorid tube is the amount of water formed. Subtracting the weight of oxygen from the weight of water, the weight of hydrogen which combines with this weight of oxygen is obtained. Water is found to have the composition of one part of hydrogen to approximately eight parts of oxygen by weight (1 : 7.9).

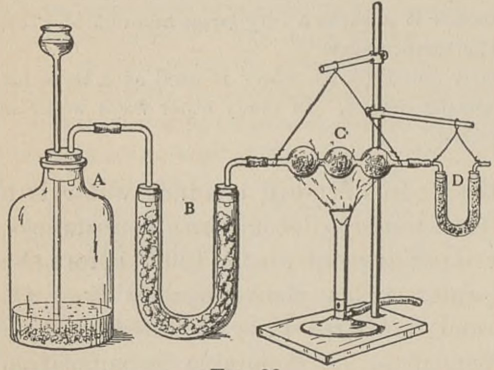

Fig. 20.

Water as a solvent. The property that above all others makes water indispensable is its power of dissolving other substances. When water is brought into contact with a solid such as sugar the latter disappears in the water, and the resulting liquid is called a *solution.* That the particles of a dissolved substance are in an extremely fine state of division is shown by the following experiment.

A gram of some intensely colored soluble substance is added to 1000 ccm. of water. As the dye dissolves, the color becomes uniformly distributed throughout the water, each cubic centimeter of which contains $\frac{1}{1000}$ of a gram of coloring matter. If 1 ccm. of the solution is removed and mixed with 999 ccm. of water, the whole solution becomes colored. Each cubic centimeter now contains $\frac{1}{1000}$ of $\frac{1}{1000}$ of a gram of dye. With a suitable substance, similar dilutions may be made once or twice again before the color vanishes, yet every particle of every drop of water contains coloring matter. Nevertheless, there are reasons for believing that the size of the particles of a dissolved substance is very much smaller than this method would lead one to suspect.

Solubility. As water is such a common liquid, solutions are of universal occurrence. Nothing is absolutely insoluble, though many things are so little affected by water that for practical purposes they are regarded as insoluble. Some liquids dissolve in water or in other liquids in almost any proportion. In the case of the great majority of substances, however, when a liquid is brought in contact with a solid, the latter continues to dissolve, and the solution becomes "stronger" or more concentrated until a certain definite proportion between the solid and the liquid is reached, after which no more will dissolve. Such a solution is said to be *saturated*, the meaning of the term being "completely full." *The ratio between the weight of the solid and the weight of the liquid required to make a saturated solution* is known as the *solubility* of that particular solid. It is different for each substance.

Effect of temperature. The solubility of a substance is affected by temperature, the general but not quite universal rule for solids being that *a rise in temperature causes an increase in solubility.* Thus a solution, saturated at a given temperature, will not become any more concentrated no matter how long the liquid and solid remain in contact, provided the temperature remains constant. If the solution is heated, however, it will become saturated at the new temperature, usually dissolving an additional amount of the substance. The increase in solubility varies greatly with different substances, as the following table shows:

VARIATION IN SOLUBILITY WITH TEMPERATURE

SUBSTANCE	GRAMS DISSOLVING IN 100 GRAMS OF WATER AT					
	0°	20°	40°	60°	80°	100°
Alum	4	15	31	67	135	358
Borax	3	8	18	40	76	201
Salt	35.7	36	36.6	37.3	38.4	39.8
Sodium nitrate	73	87	102	122	148	180
Saltpeter	13	31	64	111	172	247
Potassium chlorid	28	35	40	46	51	57
Sodium sulfate	5	19	48	45	44	42.5

A fall in temperature results in diminished solubility. In consequence, as a saturated solution is cooled, it immediately contains an excess of the dissolved substance. Usually this excess will at once separate from solution, but under proper conditions it may sometimes remain in solution for a considerable time. In such a case the solution is said to be *supersaturated*. The state of supersaturation is quite easily destroyed by vigorous shaking or by introducing into the solution bits of the same solid substance which was used in making the solution. When so treated, a supersaturated solution separates the *excess* of the substance that it contains. *Whenever a substance separates from solution, it is only the excess beyond the amount necessary for saturation that is removed. Whether the quantity left in solution is large or small, the remaining solution is always saturated.*

Crystalloids and colloids. In some cases, when a substance separates for any reason from what appears to be a solution, its particles take no definite form, but make a pasty or gummy mass. Glue, rubber, and gum are cases in point. Such substances are called *colloids*. In the majority of instances, however, the dissolved substance tends to form particles of a definite shape. Thus, a cooling salt solution forms cubes of salt, and an alum solution octohedrons of alum. These regular forms are called *crystals*, and the substances forming them *crystalloids.* Each crystalloid has crystal forms (frontispiece) that are peculiar to itself, and, if from a mixed solution two substances begin to crystallize at the same time, there usually result, not one kind of crystals containing both substances intermingled, but two different kinds of crystals, one for each substance.

Differences in solubility are often put to practical use in the laboratory, and also in factories where commercial products are purified. Thus, in manufacturing salt from sea water, the water is evaporated by artificial heat or by aid of the sun, until not enough water is left to retain all of the dissolved solids in solution. Salt is present in largest quantity and is less soluble than most other substances contained in sea water. Hence the solution becomes supersaturated with salt before it becomes saturated with any other substance, and the salt crystallizes out first. The salt crystals thus obtained contain a slight amount of impurity, but by dissolving them in fresh water and repeating the process of crystallization, the salt may be obtained in any desired degree of purity.

Solids that do not react with each other when in solution may usually be separated by repeated crystallization. No two substances are equally soluble at all temperatures, and the less soluble will tend to predominate in the mixed crystals, while the more soluble will accumulate in the "mother liquor" until it can itself be removed by crystallization. This process is called *fractional crystallization.*

Other things being equal, the size of the crystal is proportional to the length of time taken in producing it. If a solution evaporates slowly, large crystals will form. If it evaporates quickly or is rapidly cooled down from a higher temperature, the crystals will be minute.

When a substance is formed by a chemical reaction taking place in solution, the first portions formed serve to saturate the liquid. If the reaction product is but little soluble, supersaturation soon occurs, and the excess separates from solution as a *precipitate.* While precipitates may be *amorphous*, *i.e.* without crystal form, most precipitates are very finely crystalline.

Boiling points of solutions. Solutions boil at temperatures different from that of the pure solvent. If the substance dissolved boils higher than the solvent, then the solution generally boils higher also, and *vice versa.* The boiling point of a solution is not constant. As the solvent boils away, the solution becomes more concentrated, until it becomes saturated. Accompanying this change the boiling point rises until the saturated solution is reached. After this the temperature remains unchanged and the solid separates as the liquid distills.

The freezing point of a solution is always less than that of the pure solvent. When a solution begins to freeze, it is the pure solvent which freezes, and the remaining solution becomes more concentrated. Consequently, the freezing point of a solution is not constant. It falls steadily until a saturated solution is obtained, after which the solvent and the substance dissolved separate together.

Solutions of liquids. Some liquids "mix" with water; that is, they mutually dissolve each other. Other liquids, such as oil, do not mix with water, and are practically insoluble. Each liquid, like each solid, has its own solubility.

An increase of temperature has at first about the same effect as with solutions of solids. But if more heat be applied, the temperature finally reaches the boiling point of one of the constituents of the solution, and this liquid begins to pass off as vapor. At first the distillate may be nearly pure, but the boiling point gradually rises, and portions of the other liquid also distill. However, by changing the vessels that catch the distillate and redistilling the separate portions, a quite complete separation of the two liquids may often be obtained. The process is called *fractional distillation.* It is much used in the industries, as in the purification of alcohol, kerosene, etc.

Solutions of gases. All gases are soluble in water, though most of them dissolve only to a slight extent. One hundred volumes of water dissolve about four volumes of oxygen. At first thought this seems to be an insignificant quantity, yet on it depends the life of fishes and other aquatic organisms. Most gases do not dissolve in a much larger proportion than does oxygen. Some, such as ammonia gas, are very soluble, but in such cases chemical union is believed to have taken place.

The *effect of heat* on the solution of a gas in water or other liquid is opposite to its effect on a solution of a solid. When the solution of a gas is warmed, the gas begins to escape, and boiling usually expels it entirely.

If the *pressure* on a gas in contact with a liquid is increased, more of the gas will dissolve than if the pressure is less. *The weight of the gas which dissolves is directly proportional to the pressure on the gas*, and when the pressure is relieved, some of the gas escapes from solution. This effect is seen when soda water is drawn from a siphon. The water inside the bottle is saturated with the gas under two or three times the pressure of the atmosphere. When the liquid is drawn from the siphon, the pressure falls, and large quantities of the gas escape at once. If the siphon is taken from the ice, as the water warms up to room temperature, more of the gas escapes slowly, thus showing the effect of temperature on the solubility of a gas.

There is no essential difference between solution of solids, of liquids, and of gases, and, with the exception noted, what applies to one applies to all. It makes no difference whether ice, water, or water vapor be dissolved in alcohol; the resulting solutions are identical.

Water in crystals. Many crystalline substances that seem to be dry yield water when heated. Sometimes more than half of the weight of the crystal consists of water, but some crystals contain no water at all.

PERCENTAGE OF WATER IN COMMON CRYSTALS

SUBSTANCE	CHEMICAL NAME	PERCENTAGE OF WATER
Soda crystals	Sodium carbonate	62.9
Alum	Potassium aluminum sulfate	57.1
Glauber's salt	Sodium sulfate	55.5
Borax	Sodium tetraborate	47.1
Blue vitriol	Copper sulfate	36.0
Gypsum	Calcium sulfate	20.9
Salt	Sodium chlorid	00.0

Water thus held in crystals is often called "water of crystallization." Many other substances act in exactly the same way as the water does. We have no reason for believing that this water or other substance is present in any other way than in a comparatively unstable chemical combination which, for the most part, is broken up at the temperature of boiling water. The crystal possesses different properties from the substance that has been dried out, yet each is pure. They are simply two different chemical compounds. It seems preferable, therefore, to designate those crystals which contain water as crystalline **hydrates**. Any readily decomposed compound formed by the union of any substance with water is a hydrate.

Crystals that have lost their water crumble to pieces, but the powder will usually take up water again when moistened. The water in crystals is held with different degrees of firmness. Some crystals, such as Glauber's salt and soda, give up some of their water to the atmosphere and fall to powder merely on exposure to dry air. The process is the same as when crystals are heated, except that it is slower. Such substances are said to be *efflorescent.* Other substances, such as calcium chlorid and potash and soda lyes, retain their water with tenacity and, if deprived of it, will absorb water from the air and become more or less completely dissolved in it. Such substances are said to be *deliquescent.*

Desiccators. For the purpose of drying gases, substances which combine readily with water are used. Calcium chlorid, sulfuric acid, and phosphorus pentoxid absorb water vapor in the order named, the last being the best *drying agent.* In scientific work it is frequently necessary to keep a body for some time in a thoroughly dry condition. For this purpose a *desiccator* is prepared. This is usually a closed jar in which calcium chlorid or other drying agent is kept (Fig. 21).

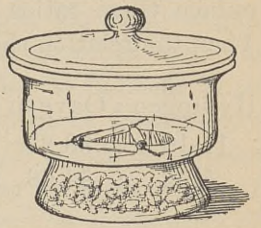

Fig. 21.

Hydrogen dioxid. When hydrogen burns, it unites with oxygen to form an oxid known as water. But the same two elements may be obtained in chemical combination in another substance called hydrogen dioxid. It is a colorless liquid usually sold only in aqueous solution under the name of "peroxid of hydrogen." It is an unstable substance, easily decomposing into water and oxygen. It is a good oxidizing agent, therefore, and on this account finds use as a bleaching and disinfecting substance.

Studies of the decomposition of hydrogen dioxid indicate that the oxygen and hydrogen are combined in equal volumes. In other words, in proportion to the hydrogen present, there is twice as much oxygen in hydrogen dioxid as in water. We shall find many instances of two or more elements combining in different proportions to form substances with entirely different properties.

In every instance of this kind *the amounts of the one ele-*

ment that unite with a definite amount of the second element stand to each other in very simple ratios, as 1 : 2, 1 : 3, 2 : 3, and so forth. Dalton was the first to perceive this relation and announce it to the world under the name of the law of **multiple proportions.** He discovered it by a lucky chance. It is customary to express the composition of substances in percentages. Thus, water contains 11.19 % hydrogen and 88.81 % oxygen, while hydrogen dioxid contains 5.92 % hydrogen and 94.08 % oxygen. Expressed in this way no significant relation between the amounts of either element is to be noted. Dalton's method is to reduce these ratios so that one term is always unity. Then the relation shown below becomes apparent at once.

Hydrogen : Oxygen :: Hydrogen : Oxygen
11.19 : 88.81 :: 1 : 8 in water
5.92 : 94.08 :: 1 : 16 in hydrogen dioxid

So also

Carbon : Oxygen :: Carbon : Oxygen
42.86 % : 57.14 % :: 1 : 1.33 in carbon monoxid
27.27 % : 72.73 % :: 1 : 2.66 in carbon dioxid

Although a hundred thousand new compounds have been prepared since this principle was first stated by Dalton nearly a hundred years ago, not an exception to it has yet been discovered.

Chemical reactions are often expressed in what are called **chemical equations.** Just as there is a symbol for each element, so a **formula** for each compound may be written. It consists of the symbols of the elements contained in a compound written together in a group like the letters in a word. The symbol for hydrogen is H; for oxygen, O. The formula for any compound of these elements will be HO. Water contains two volumes of hydrogen to one of oxygen, while hydrogen dioxid contains twice as great a proportion of oxygen as water does, *i.e.* two to two. In order to distinguish the formula for water from the formula for hydrogen dioxid, for the former we write H_2O and for the latter H_2O_2. The small figure written to the right of a letter and below the line affects only the symbol of the element immediately preceding it. Thus, in water there are two parts of hydrogen combined with one part of oxygen, but in hydrogen dioxid there are two parts of oxygen combined with the same amount of hydrogen. If we wish to indicate three parts of water, a large figure is written in front of the formula for the compound, as $3\,H_2O$. This multiplies the whole formula and signifies that in three parts of water there are six parts of hydrogen and three parts of oxygen.

Expressed in chemical symbols and formulas we may write equations indicating the reactions between hydrogen and oxygen as follows:

$2\,H + O \rightarrow H_2O$	$2\,H + 2\,O \rightarrow H_2O_2$
when water is formed.	when hydrogen dioxid is formed.

In chemical equations the arrow → means "goes into" or "forms."

How the correct formula for a chemical compound is determined must be left for future consideration.

The condition of substances entering into or produced by chemical reactions will be indicated hereafter when equations are written by printing solid substances in **black-faced type**, liquids and substances in solution in ordinary type, and gases in *italics*.

SUMMARY

WATER

In nature. Water is probably the most important of all compounds. Everything contains some water, and living things are more than half composed of it. Natural waters are always impure. Matter held in suspension may be removed by filtration, but substances in solution require distillation to separate them.

Properties. Water is an odorless, tasteless liquid, with a slightly bluish tinge. It is used as a standard for determining specific density, specific heat, etc., and the temperatures at which it freezes and boils are taken as the zero and 100° on the centigrade thermometer. The weight of 1 ccm. of water measured at 4° is taken as 1 g. Water has a greater heat of fusion and vaporization than any other substance except hydrogen. These facts, together with its abnormal expansion when cooled below 4° and when it freezes, carry important consequences for the welfare of all living things.

Chemically, water is a stable compound. When heated to high temperatures it begins to decompose into its elements, but these combine again on lowering the temperature. A reversible decomposition like this is called *dissociation*. Water is active chemically. It seems to be a universal catalytic agent, for apparently no reactions take place without, at least, traces of water being present. The composition of water is two volumes of hydrogen to one volume of oxygen, or one part, by weight, of hydrogen to eight (approximately) parts of oxygen.

In crystals. Though dry, many crystals yield, when heated, "water of crystallization." This water is held in loose chemical combination, and when it is lost, a new substance is left. Crystals that fall to powder, through the loss of their water by evaporation, at ordinary temperatures are *efflorescent*. Substances that absorb water from the air and dissolve in it are *deliquescent*.

SOLUTIONS

Of solids. Water is almost a universal solvent. A solution is *saturated* with a substance when it can dissolve no more of that substance. Different substances dissolve in different degrees, each substance having its own solubility. The *solubility* of a substance is expressed by the ratio of the weight of the substance to the weight of solvent necessary to form a saturated solution at any given temperature. A rise in temperature increases solubility, and a lowering of temperature diminishes it. Hence, when a saturated solution is cooled, it becomes *supersaturated*, and the *excess* of the dissolved substance separates out. If a substance separates out in crystal form, it is called a *crystalloid;* if in an amorphous condition, it is called a *colloid.* Differences in solubility are put to practical use in the purification of many substances.

Of liquids. Resemble solutions of solids at ordinary temperatures; but when the temperature of a solution is raised sufficiently, the boiling point of one constituent is reached, and that constituent begins to evaporate. By careful distillation a practical separation of the liquids may often be accomplished.

Of gases. Resemble solutions of solids and liquids; but (1) pressure increases the solubility, the weight of gas dissolved being directly proportional to the pressure, and (2) increase of temperature lessens the solubility and usually drives most of the gas out of the solution.

HYDROGEN DIOXID, like water, is a compound of hydrogen and oxygen, but contains just twice as much oxygen in proportion to its hydrogen. It is a liquid commonly known in solution as peroxid of hydrogen. It readily decomposes into water and oxygen, and is a good oxidizing agent.

Law of multiple proportions. In the case of water and hydrogen dioxid the ratio between the weights of oxygen that are combined with equal weights of hydrogen is 1 : 2. In other cases where two elements form more than one compound, similar simple ratios always exist. These facts were stated by Dalton in the law of multiple proportions: *If two elements unite with each other to form more than one compound, the weights of the one that combine with a fixed weight of the other stand in simple ratios to each other.*

QUESTIONS

1. Why is rain water the purest natural water?

2. Why does the chemist use distilled water rather than filtered water in making up his solutions?

3. Suggest as many reasons as you can why water extinguishes fire.

4. What kind of impurities interfere with the use of water (*a*) in steam boilers; (*b*) for drinking purposes?

5. What changes would take place in nature if water did not expand (*a*) when cooled below 4°; (*b*) when it freezes?

6. How could you determine whether a given solvent, such as water, contains anything dissolved in it?

7. Suggest a method for determining the amount of water in a substance. Try your method on bread, soap, meat, and fruit, and calculate the percentage of water.

8. How much water is contained in 10 pounds of fresh soda crystals?

9. If sold at the same price per pound, which would you purchase for laundry purposes, fresh bright soda crystals, or those which had crumbled to powder?

10. What becomes of the water in crystals when efflorescence takes place?

11. If given a solution of some known substance, how could you tell whether the solution was saturated, unsaturated, or supersaturated?

12. Explain why sugar crystals sometimes form in jams, jellies, and preserves, also in molasses, when no appreciable evaporation has taken place.

13. What is the cloud seen above the spout of a teakettle containing boiling water? How is it formed?

14. In a mixture of sand and sugar, how could you recover each substance?

15. The gas density of water vapor is about 9. Calculate the volume occupied by 1 gram of water when in the form of steam at 100°.

16. To what temperature must the steam in the above example be heated in order that its volume may be doubled?

17. Marsh gas has the composition: carbon 75%, hydrogen 25%. Ethane has the composition: carbon 80%, hydrogen 20%. How do these facts support the law of multiple proportions?

18. Two compounds have the following composition: (*a*) phosphorus 56.36%, oxygen 43.64%; (*b*) phosphorus 43.65%, oxygen 56.35%. Show whether or not the law of multiple proportions holds.

CHAPTER VII

HOW CHEMICAL REACTIONS TAKE PLACE

In a previous chapter mention was made of a method of preparing hydrogen by passing steam over red-hot iron. The iron is placed in a tube and heated in a furnace (Fig. 22). Into one end of the tube steam is passed, while from the other end hydrogen issues and may be collected over water, burned, or treated in any way desired. In this reaction hydrogen oxid (steam) is changed into iron oxid; that is, iron is substituted for hydrogen. This kind of reaction differs from either analysis or synthesis, and is called *substitution*. In this reaction the points essential for our purpose may be expressed by the equation*

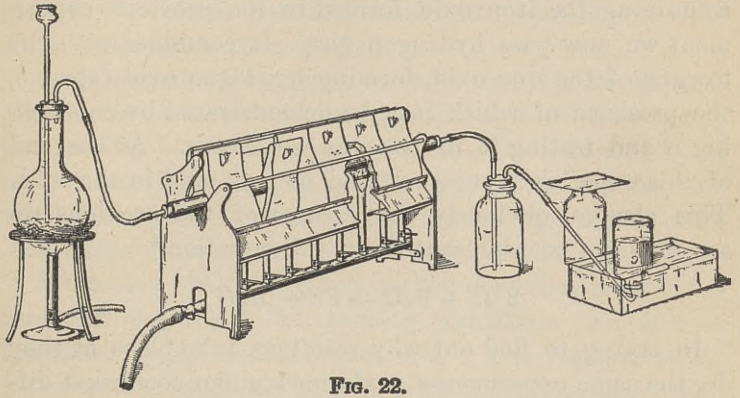

FIG. 22.

$$\mathrm{Fe} + H_2O \rightarrow 2\,H + \mathrm{FeO}.$$

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* The compound actually formed in this reaction contains a different proportion of oxygen and iron from that represented in the equation, which has been simplified for the present purpose.

It used to be customary to explain chemical reactions such as this by saying that the chemical affinity between iron and oxygen is greater than the affinity between hydrogen and oxygen. Hence, when iron is brought in contact with hydrogen oxid, the iron takes the oxygen from the hydrogen and the hydrogen is set free, just as a big dog meeting a small dog with a bone, takes the bone because he is stronger than the small dog. That such an explanation is incorrect is shown by experiments like the following.

After continuing the reaction for some time and converting the iron wholly or partially into iron oxid, let us change the experiment somewhat. Using the same furnace heated to the same temperature, into the same tube containing the iron oxid formed in the previous experiment we now pass hydrogen gas. It combines with the oxygen of the iron oxid, forming hydrogen oxid (steam), the presence of which may be demonstrated by condensing it and testing it in any way we choose. At the end of this experiment we shall find no iron oxid in the tube. This change, obviously the reverse of the previous reaction, may be represented by the equation*

$$2\,H + \mathrm{FeO} \rightarrow \mathrm{Fe} + H_2O$$

In trying to find out why reactions take place as they do, the same experiments performed under somewhat different conditions will be helpful. We may place iron and hydrogen oxid together in one sealed tube and equivalent amounts of iron oxid and hydrogen in another sealed tube and heat both tubes in the same furnace to the same temperature for the same time. Neither reaction runs to completion, no matter how long the heating is continued. Under the conditions of this experiment we can never make hydrogen decompose *all* of the

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* The compound actually formed in this reaction contains a different proportion of oxygen and iron from that represented in the equation, which has been simplified for the present purpose.

iron oxid, nor iron decompose *all* of the hydrogen oxid. In each tube there will always be a mixture of iron and iron oxid and of hydrogen and hydrogen oxid. Furthermore, *the proportions between the constituents will be the same in each case.*

The reaction in the second tube has gone in a direction opposite to that taking place in the first tube. *Apparently*, in each tube the reaction stops before all the material present has reacted, and the point at which the reaction stops is the same in each case. Yet we know that each reaction *can* take place, and we discover no reason why either reaction should not continue to take place when once it is started.

A more reasonable explanation is that a point of *equilibrium*, or balance, is reached, *a point at which the reaction goes as fast in one direction as in the other.* If this is so, no further change in the proportions of the constituents would take place, and the reaction would *apparently* stop. This supposition proves to be the true explanation.

A reaction that may go in either direction is called a *reversible reaction.* In writing equations this fact is indicated by the *double arrow*, $\longleftrightarrow$. The two preceding experiments illustrate such a reversible reaction, which may be expressed more correctly by the equation:

$$\mathrm{FeO} + 2\,H \longleftrightarrow \mathrm{Fe} + H_2O$$

Summing up the experience gained from this and many other reactions, chemists have come to believe that *under proper conditions practically all chemical changes can be reversed.* In each reaction a condition of equilibrium results. The most peculiar thing is, that in each reaction that has come to equilibrium, there are certain definite proportions between the reagents. These proportions may be determined in any reaction. If the reagents are brought together in proportions different from those necessary for equilibrium, a reaction takes place until the correct proportions are reached. Those substances which are present in too great a proportion react to form those which are present in too small a proportion.

When the reactions previously mentioned take place in sealed tubes, nothing escapes, and the equilibrium is soon reached and maintained. When steam is passed over iron heated in the open tube, the reaction endeavors to reach equilibrium, but this condition is disturbed by the fact that steam is continuously introduced and hydrogen continuously withdrawn. Consequently the reaction proceeds apparently in one direction only. When hydrogen is passed over heated iron oxid in an open tube, the same thing happens; for the proportion of hydrogen is continuously increased and the proportion of steam continuously lowered. Hence this reaction apparently goes in one direction only.

The proportions necessary for equilibrium in any reaction are modified by the conditions under which the experiment takes place. They vary with the temperature, pressure, and other factors, but once determined for any set of conditions, they remain constant for those conditions. In determining a condition of equilibrium, solids have little effect; for, unlike gases and liquids, reactions take place only on the exposed surfaces of solids and not all through the mass.

The condition of equilibrium in any reaction may be disturbed by increasing the proportion of one (or more) of the reagents, or by decreasing the proportion of one (or more) of the products formed in the reaction. The effect of these two actions is the same; for if the proportions of the substances on one side of an equation are increased, the proportions of the substances on the other side of the equation are made relatively smaller; and *vice versa.*

The effect of varying the proportions of the substances present in a reaction is known as **mass action.**

Mass action increases the speed of a reaction in one direction, and so disturbs equilibrium. As an illustration we may take the fact that substances burn more rapidly in pure oxygen than in air. In any volume of air there is only one fifth oxygen, while in the other case the proportion is five times as great. This method of increasing the speed of reactions is used quite as often as increase of temperature or the addition of a catalytic agent.

If any one of the substances produced in a reaction is removed as fast as formed, of course it cannot react with other products of the reaction to cause a reversal of the reaction. A condition of equilibrium cannot be brought about, and the reaction will proceed in one direction only. *Reactions go only in one direction whenever a gas or an insoluble substance is formed*, for these are removed from reactions as fast as formed. Provided such a reaction is possible, *we may predict that a gas or an insoluble substance will be formed as long as there is material present to form it.*

Gases. In the reaction of zinc on sulfuric acid (hydrogen sulfate), hydrogen, being a gas, escapes as fast as formed; hence the reaction goes only in the direction indicated by the equation:

$$\text{Zinc} + \text{hydrogen sulfate} \rightarrow \text{zinc sulfate} + \text{hydrogen}$$

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H$$

If the gas ceases to flow, we know that either the metal or the acid is used up. If hydrogen were not a gas and did not escape, there would be the possibility of hydrogen reacting with zinc sulfate to form hydrogen sulfate and the metal. This reversal of the reaction would cause equilibrium, and the liberation of hydrogen would cease soon after the reaction began, even though both acid and metal were present. Such is not the case.

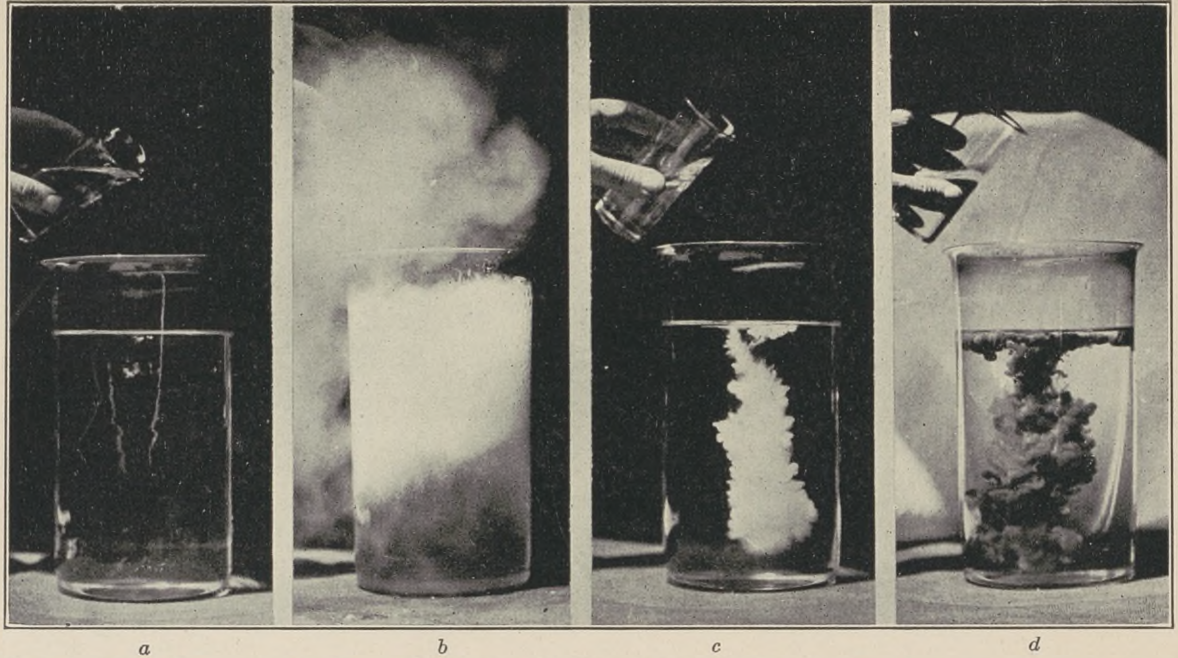
Insoluble substances. Many reactions take place only in solution, that between sodium carbonate and calcium chlorid being such a one. When these reagents are brought together in solution, the reaction takes place as shown in the equation:

$$Na_2CO_3 + CaCl_2 \rightarrow 2\,NaCl + \mathbf{CaCO_3}$$

Calcium carbonate is an insoluble substance and, as soon as formed, separates from solution as a precipitate. This reaction takes place only in solution, and calcium carbonate is not in solution; hence a reversal of the reaction is impossible. Even if the substance is so finely divided that it will float all through the liquid which entirely surrounds it, nevertheless it is not in solution and will not affect the reaction any more than a glass rod in a beaker. *In all reactions that take place in solution, if an insoluble substance is formed, equilibrium is impossible.* Fig. 23 shows some reactions running to completion; also one running to equilibrium, there being apparently no change taking place.

Other causes which prevent reactions from being reversible will be noted later.

The ideas of reversible reactions, equilibrium, and the effect of changing the proportions of the reagents lie at the very foundation of any understanding of chemical reactions. Yet the reactions with which one is most familiar do not seem to be reversible or to tend to run to equilibrium. On the contrary, they seem to go in one direction only, almost without exception. We must remember that it is generally desirable to transform all, not part, of a reacting substance. In the laboratory, in the home, and in the factory, therefore, such reactions are used as lead to the formation of gases or insoluble substances, thus making equilibrium impossible by preventing the reversal of the



a b c d

Fig. 23. — Chemical Reactions

(*a*) Reaction runs to equilibrium ; no gas or precipitate.
(*b*) Reaction runs to completion because gas is formed.
(*c*) Reaction runs to completion ; precipitate ($BaSO_4$) formed.
(*d*) Reaction runs to completion ; precipitate (HgI_2) formed.

processes. At ordinary temperatures the tendency for many reactions to reverse is practically zero, yet at high temperatures many of these same reactions are completely reversed.

SUMMARY

Reversible reactions. When steam (*i.e.* hydrogen oxid) is passed over heated iron, iron oxid and hydrogen are formed. When hydrogen is passed over heated iron oxid, iron and hydrogen oxid are formed. Reactions like this, which may go either forward or backward, are said to be *reversible*. In writing equations this fact is indicated by the double arrow $\longleftrightarrow$. Under proper conditions practically all reactions can be reversed to a certain extent at least.

Equilibrium. Reversible reactions tend to run to equilibrium. *Equilibrium is a condition which, when disturbed, tends to restore itself.* In each reaction the condition of equilibrium is characterized by certain definite proportions between the substances entering into and those formed by the reaction. If certain substances are present in proportions larger than what is necessary for equilibrium, the reaction takes place in such a direction as to lessen the amounts of these substances and to increase the amounts of those substances present in smaller proportion until equilibrium is reached. Then the reaction proceeds as fast in one direction as in the other. No change in the proportions of the substances takes place, and the reaction apparently stops. Equilibrium may be disturbed by increasing the amounts of the substances on one side of the reaction or by decreasing the amounts of the substances on the other. This is often called *mass action*.

If a substance is removed from a reaction as fast as it is formed, a reversal of the reaction is impossible. On this account reactions in which gases or insoluble substances are formed do not run to equilibrium. On the contrary, the gas or the insoluble substance is formed just as long as there is material present to form it. Most reactions of the arts and industries lead to the formation of gases or of insoluble substances, and do not run to equilibrium.

QUESTIONS

1. Are the reactions reversible by which (*a*) oxygen is obtained from potassium chlorate; (*b*) hydrogen from sodium and water; (*c*) water from oxygen and hydrogen? Why?

2. When dilute acid is poured on zinc, what causes the reaction to go in one direction only? If hydrogen dissolved abundantly in water, how far would the reaction go?

3. Is the burning of a candle a reversible reaction that runs to equilibrium? Why?

4. The reactions of baking powder and of a Seidlitz powder are much alike. Do they run to equilibrium? Why?

5. Is the rotting of wood a reaction that runs to equilibrium? Why?

CHAPTER VIII

CHLORIN

THROUGH an investigation of water, that most common of all substances, much of interest was learned. From this experience it will be well for the beginner in science to learn the lesson that nothing is so commonplace that it will not repay investigation. With a similar end in view, let us turn our consideration to another substance of everyday acquaintance — common salt.

Potassium chlorate was decomposed by heating it. We should find on trial that salt resists our efforts to break it down by this means, but is readily decomposed by electricity. This is a fact of general experience. *Electricity causes the decomposition of many substances that are not decomposed by any degree of heat that is easily reached.*

Electrolysis of salt. Under proper conditions salt in solution may be decomposed into its elements in the same way in which water was separated into oxygen and hydrogen. However, we may learn another point about the conditions under which electrolysis takes place if we heat the salt until it is melted and then pass a current of electricity through the molten material. Under these conditions a gaseous substance appears at the anode, and at the cathode a soft, waxy material which is so active chemically that it must be protected from the atmosphere. The gas is chlorin; the other material, sodium. Both are elements, and these are the only constituents of common salt. Since chlorin is similar in many respects to oxygen, it will be considered first.

For general laboratory purposes, another method for the **preparation of chlorin** will prove more satisfactory. If a mixture of manganese dioxid and hydrochloric acid is gently heated, an abundance of chlorin is evolved. We might collect it over water as we did oxygen and hydrogen, but since it dissolves quite readily, we would lose much of our gas. Of course we might collect it over hot water, for the solubility of all gases decreases as the temperature increases, but the method of *downward displacement*, as it is called, proves more satisfactory. In this case the exit tube from the gas generator reaches to the bottom of a tall cylinder or other container (Fig. 24). As the heavy chlorin enters, it remains at the bottom of the jar, displacing the lighter air which overflows at the top, just as mercury, introduced into a vessel of water, would cause the lighter liquid to overflow at the top.

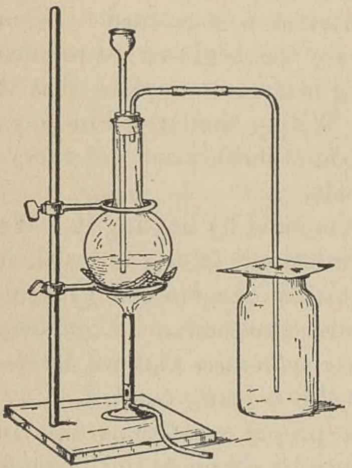


FIG. 24.

Physical properties. Chlorin is a pale, yellowish green gas with an unpleasant odor. It attacks the mucous membranes of the nose and throat, producing inflammation. In larger amounts it produces nausea and is quite poisonous. Inhaling ammonia or alcohol fumes counteracts its effect somewhat. Chlorin is nearly 2.5 times as heavy as air and about 35 times as heavy as hydrogen. When strongly cooled, it condenses to a yellow liquid which boils at −34°. Two volumes of the gas dissolve in one volume of water, forming a solution known as *chlorin water*.

Chemical properties. Chlorin is a most active element, only one other substance, the element fluorin, surpassing it in this respect. It unites with most other elements, forming compounds know as *chlorids.* It combines with hydrogen in the dark so slowly that the action is inappreciable. In ordinary daylight the reaction is moderate, but when the mixture is exposed to the direct rays of the sun, a violent explosion takes place. A jet of hydrogen burning in the air when placed in chlorin continues to burn with a peculiar, whitish flame. The ash or product of combustion is a colorless gas, which has a sharp odor and sour taste, turns blue litmus * paper red, and fumes in moist air. This gas is hydrogen chlorid.

Combustion in chlorin. A burning candle or gas flame introduced into a jar of chlorin burns with a very sooty flame. Besides soot, hydrogen chlorid is formed. Since soot is carbon, it follows that tallow, paraffine, and illuminating gas must contain hydrogen and carbon.

Chlorin is so energetic that it will often abstract hydrogen from compounds of the latter element simply on mixing the two substances. If boiling turpentine be poured over a filter paper which is then immersed in chlorin, a flash of flame shoots from the jar, accompanied by clouds of soot. Hydrogen chlorid can be detected among the reaction products here also, hence turpentine must be composed of hydrogen and carbon. The soot results from the fact that chlorin does not combine with carbon under these conditions.

In a similar way, thin copper foil and powdered anti-

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* Litmus is one of a number of substances, usually of a vegetable origin, which change color when treated with acids and some other chemicals. The coloring matter in red cabbage, radish skins, and many berries, and yellow turmeric, are substances of similar character. Carminic acid, extracted from the cochineal insect, is another. Such substances are known as **indicators.**

mony spring into spontaneous combustion. Sodium requires to be heated somewhat; then a brilliant flame accompanies the production of a white ash that proves to be common salt. Thus the composition of salt has been proved by analysis and by synthesis as well.

The preceding experiments demonstrate that chlorin supports combustion of many substances as well as, or better than, oxygen. The definition of combustion must be expanded, therefore. *Combustion is any chemical combination that proceeds with the evolution of heat and light.*

Hydrogen chlorid is one of the most important chlorids. Its preparation by direct combination of the elements is not a satisfactory method for general purposes. By heating any chlorid with sulfuric acid (hydrogen sulfate), hydrogen chlorid may be obtained in quantities. When common salt, the cheapest chlorid, is used, a double substitution is effected, and we obtain hydrogen chlorid and sodium sulfate.

Sodium chlorid + hydrogen sulfate → hydrogen chlorid + sodium sulfate

$$2\,NaCl + H_2SO_4 \rightarrow 2\,HCl + Na_2SO_4$$

Such a double substitution is known as *metathesis*.

Hydrogen chlorid is gaseous at ordinary temperatures; sulfuric acid boils at 330°. As ordinarily performed, this reaction runs to completion without any sign of equilibrium; for the reverse action, the interaction of hydrogen chlorid and sodium sulfate, is prevented by the fact that hydrogen chlorid is a gas.

If water solutions of salt and sulfuric acid are mixed, the reaction does not run to completion, for hydrogen chlorid is very soluble in water and the reaction reverses and comes to equilibrium. No difference in the properties of two solutions can be detected if one is made of sodium chlorid and hydrogen sulfate and the other of hydrogen chlorid and sodium sulfate, provided that the proportions are correctly taken. Each pair of reagents interacts, and the condition of equilibrium is the same in each case. Four different substances are present, and the proportions between them are identical in each solution. The two reactions given below are identical.

$$2\,NaCl + H_2SO_4 \longleftrightarrow 2\,HCl + Na_2SO_4$$
$$2\,HCl + Na_2SO_4 \longleftrightarrow 2\,NaCl + H_2SO_4$$

In the manufacture of hydrogen chlorid any other acid with a high boiling point might be used, but sulfuric acid is the cheapest.

Physical properties. Hydrogen chlorid is a colorless gas with a sour taste and a sharp odor. It does not burn or support combustion of ordinary substances. It is heavier than air and may be collected by downward displacement or over mercury, for it is very soluble in water and many other liquids. One volume of water at 0° absorbs more than 500 volumes of hydrogen chlorid, and the solution is known as *hydrochloric acid* or, frequently, *muriatic acid*. When the gas is brought in contact with moist air, it fumes strongly, the fumes being due to the fact that hydrogen chlorid unites with water vapor to form hydrochloric acid, which condenses in minute droplets to form a fog or cloud. Hydrogen chlorid may be condensed to a colorless liquid that boils at – 84°. The dry gas and the liquefied substance are remarkably inert. If, however, traces of moisture are present, they become very active. The aqueous solution of hydrogen chlorid is much more active than the gas or the liquid, and for this reason is generally used.

An aqueous solution saturated at ordinary temperatures contains about 450 volumes of hydrogen chlorid. It is known as **concentrated hydrochloric acid** and consists of something less than 40 % of hydrogen chlorid and something over 60 % of hydrogen oxid — water. When pure it is a colorless, fuming liquid, but the commercial article is somewhat yellow in color because of the presence of iron salts and other impurities. Gases being less soluble at high temperatures than at lower ones, when concentrated hydrochloric acid is heated, hydrogen chlorid gas passes off, and small amounts of it may be made in this way.

Hydrochloric acid is known as a *strong acid.* The meaning of this term is that it possesses the qualities known as **acid properties** to a greater degree than many another acid. Taking hydrochloric acid as a type, we may learn what is meant by acid properties.

1. *Any strong acid tastes sour* even in dilute solutions.

2. It *turns blue litmus red* and affects other indicators even in very dilute solutions.

3. *When brought in contact with many metals, the hydrogen of the acid is replaced by the metal and a compound of the metal with the acid radical (or element) is formed.* Such compounds are called *salts.* With hydrochloric acid, chlorids are formed, as the following equation shows :

$$\mathrm{Fe} + 2\,\mathrm{HCl} \rightarrow \mathrm{FeCl_2} + 2\,H$$

Iron + hydrochloric acid → iron chlorid + hydrogen

4. *Oxids of metallic elements react with solutions of strong acids forming water and a salt of the metal and the acid.* With hydrochloric acid, chlorids are formed.

$$\mathrm{CuO} + 2\,\mathrm{HCl} \rightarrow \mathrm{CuCl_2} + \mathrm{H_2O}$$

Copper oxid + hydrochloric acid → Copper chlorid + hydrogen oxid

5. *An acid neutralizes a base, and vice versa.*

To understand this last statement we must know what a base is, and something of its properties. *A base is a compound of a metallic element with oxygen and hydrogen*, such as sodium hydroxid, $NaOH$. A solution of a base has a bitter, soapy taste and slippery feeling, and turns red litmus blue. When a solution of a base is treated with an acid, the soapy taste and slippery feeling disappear. If the proportions are correctly taken, the sour taste and all other acid properties disappear also, and there results a solution which has a salty, brackish taste and does not affect litmus paper. The mutual action of an acid on a base accompanied by the disappearance of the properties of both, is what is meant by the statement that the one neutralizes the other. If the base is sodium hydroxid and the acid hydrochloric acid, on evaporation of the solution common salt is left.

$$\mathrm{NaOH} + \mathrm{HCl} \rightarrow \mathrm{NaCl} + \mathrm{H_2O}$$

Inasmuch as any acid when treated with any base gives rise to a substance more or less closely resembling salt in its properties, *all* compounds which may be formed by the neutralization of an acid with a base are called* **salts.**

Salts: how formed. Salts may be formed in various ways, for the same body results whether chlorin acts on zinc, or hydrochloric acid on the metal, the oxid or the hydroxid, as the following equations show:

$$\begin{gathered}\mathbf{Zn} + 2\,Cl \rightarrow \mathrm{ZnCl_2} \\ \mathbf{Zn} + 2\,\mathrm{HCl} \rightarrow \mathrm{ZnCl_2} + 2\,H \\ \mathbf{ZnO} + 2\,\mathrm{HCl} \rightarrow \mathrm{ZnCl_2} + \mathrm{H_2O} \\ \mathbf{Zn(OH)_2} + 2\,\mathrm{HCl} \rightarrow \mathrm{ZnCl_2} + 2\,\mathrm{H_2O}\end{gathered}$$

Test for chlorids. The silver salt of hydrochloric acid is very insoluble in water and also in nitric acid. The formation of this salt is used as a "test" for hydrochloric acid or any of its soluble salts. The solution to be tested is made acid with nitric acid, and silver nitrate is added. If a chlorid is present, a white precipitate, darkening in the sunlight, will form. Hydrogen chlorid or the chlorid of any metal will give this test, the reaction in any case being similar to the following equations:

$$\begin{gathered}\mathrm{HCl} + \mathrm{AgNO_3} \rightarrow \mathbf{AgCl} + \mathrm{HNO_3} \\ \mathrm{NaCl} + \mathrm{AgNO_3} \rightarrow \mathbf{AgCl} + \mathrm{NaNO_3}\end{gathered}$$

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* Water is one of the compounds formed by the action of any acid on any base, but this substance is not considered as a salt.

Hydrochloric acid is a stable body, that shows no appreciable tendency to decompose until a temperature of 1000° is reached. At ordinary temperatures combination between hydrogen and chlorin takes place with explosive violence, and the reaction runs to completion. Above 1000° the reaction runs to equilibrium, for the reverse reaction, the decomposition of hydrogen chlorid into its elements, takes place to an appreciable extent.

In dilute solutions hydrogen chlorid is more stable than when concentrated, for in the latter case strong oxidizing agents convert it into chlorin and hydrogen oxid.

Now that we know something of the character of hydrochloric acid, we may speak in somewhat more general terms of the **methods of preparing chlorin.** There are two general methods: first, *electrolysis of any chlorid;* second, *oxidation of hydrogen chlorid* either in solution or as a gas. The first method needs no further comment.

The oxidation of hydrogen chlorid by means of the oxygen of the air does not take place with sufficient rapidity at any temperature to be of service. In the presence of copper chlorid, which acts as a catalyzer, the reaction becomes available for the commercial production of chlorin at temperatures of about 400°. It is known as the Deacon process. The simple reaction would seem to be

$$2\,HCl + O \rightarrow H_2O + 2\,Cl.$$

The copper chlorid is found at the end of the process in the same quantity and condition in which it was introduced. *Apparently* it has not been changed during the process. This is a typical instance of catalysis.

If we examine this reaction carefully while it is in progress, however, we shall be able to detect the presence of another substance which is formed from copper chlorid and which gives us an entirely different idea of what catalysis is. Copper chlorid reacts first with oxygen to liberate half of its chlorin, and forms copper oxychlorid.

This substance then reacts with hydrogen chlorid to re-form copper chlorid and water.

$$\begin{aligned} 2\,\mathrm{CuCl_2} + O \quad &\rightarrow \mathrm{Cu_2Cl_2O} + 2\,Cl \\ \mathrm{Cu_2Cl_2O} + 2\,HCl &\rightarrow 2\,\mathrm{CuCl_2} + H_2O \end{aligned}$$

Although the catalytic agent at first sight appears to be inactive, we see in reality that the catalyzer is the most active substance present in a reaction. In many other instances we know that catalytic agents act in a similar manner, although we cannot as yet explain all their action. The explanation of catalysis often is that *the catalyzer unites with some of the reagents to form an unstable compound which decomposes into the catalyzer and some of the reaction products.* Thus the catalyzer is used up and re-formed over and over again, and a very small amount of a catalyzer is sufficient to transform much larger amounts of material.

Any strong oxidizing agent will serve to furnish the oxygen necessary to oxidize hydrogen chlorid. Manganese dioxid is such an oxidizing agent. Instead of treating the latter with hydrochloric acid, very often chlorin is prepared by heating a mixture of **manganese dioxid, salt, and sulfuric acid.** In this and most other cases of comparatively complex mixtures *complex reactions involving several different substances do not generally take place. Instead, several simple reactions take place at the same time.*

In the present case, sulfuric acid and salt interact to liberate hydrogen chlorid. As soon as formed, this reacts with manganese dioxid to produce manganese chlorid, water, and chlorin. Manganese chlorid reacts with more sulfuric acid to liberate hydrogen chlorid and form manganese sulfate. This hydrogen chlorid reacts with more manganese dioxid to form more chlorin and more manganese chlorid, and so on. The final products are manganese sulfate, sodium sulfate, and water.

$$\begin{aligned}
&2\,\mathrm{NaCl} + \mathrm{H_2SO_4} \rightarrow 2\,\mathrm{HCl} + \mathrm{Na_2SO_4}\\
&4\,\mathrm{HCl} + \mathbf{MnO_2} \rightarrow 2\,Cl + \mathrm{MnCl_2} + 2\,\mathrm{H_2O}\\
&\mathrm{MnCl_2} + \mathrm{H_2SO_4} \rightarrow 2\,\mathrm{HCl} + \mathrm{MnSO_4}\\
&4\,\mathrm{HCl} + \mathbf{MnO_2} \rightarrow 2\,Cl + \mathrm{MnCl_2} + 2\,\mathrm{H_2O}
\end{aligned}$$

Bleaching. One reaction of chlorin that is of great industrial importance has not yet been considered. Chlorin has a very marked bleaching action on vegetable substances. The material to be bleached must be moist, for very little action takes place in dry chlorin, even on long standing (See Fig. 25). The action of water in this case is well understood. For it is known that chlorin reacts with water to form hydrochloric acid and the hydroxid of chlorin which is known as *hypochlorous acid.*

$$2\,\mathrm{Cl} + \mathrm{H_2O} \rightarrow \mathrm{HCl} + \mathrm{HOCl}$$

Hypochlorous acid is composed of hydrogen, oxygen, and chlorin in equal parts by volume. It is a very unstable substance, and in order to learn much of its properties we must convert it into one of its salts, for *salts are usually more stable than the free acid.* By passing chlorin into an aqueous solution of sodium hydroxid, the sodium salt is obtained. The chlorin reacts with the water to form hydrochloric and hypochlorous acids just as before, but the base neutralizes each, as the equations show:

$$\begin{aligned}
2\,Cl + \mathrm{H_2O} &\rightarrow \mathrm{HCl} + \mathrm{HOCl}\\
\mathrm{NaOH} + \mathrm{HCl} &\rightarrow \mathrm{NaCl} + \mathrm{H_2O}\\
\mathrm{NaOH} + \mathrm{HOCl} &\rightarrow \mathrm{NaOCl} + \mathrm{H_2O}
\end{aligned}$$

Bleaching powder consists of a mixture of the calcium salts of these two acids made by passing chlorin over slacked lime (calcium hydroxid). Hypochlorous acid and all of

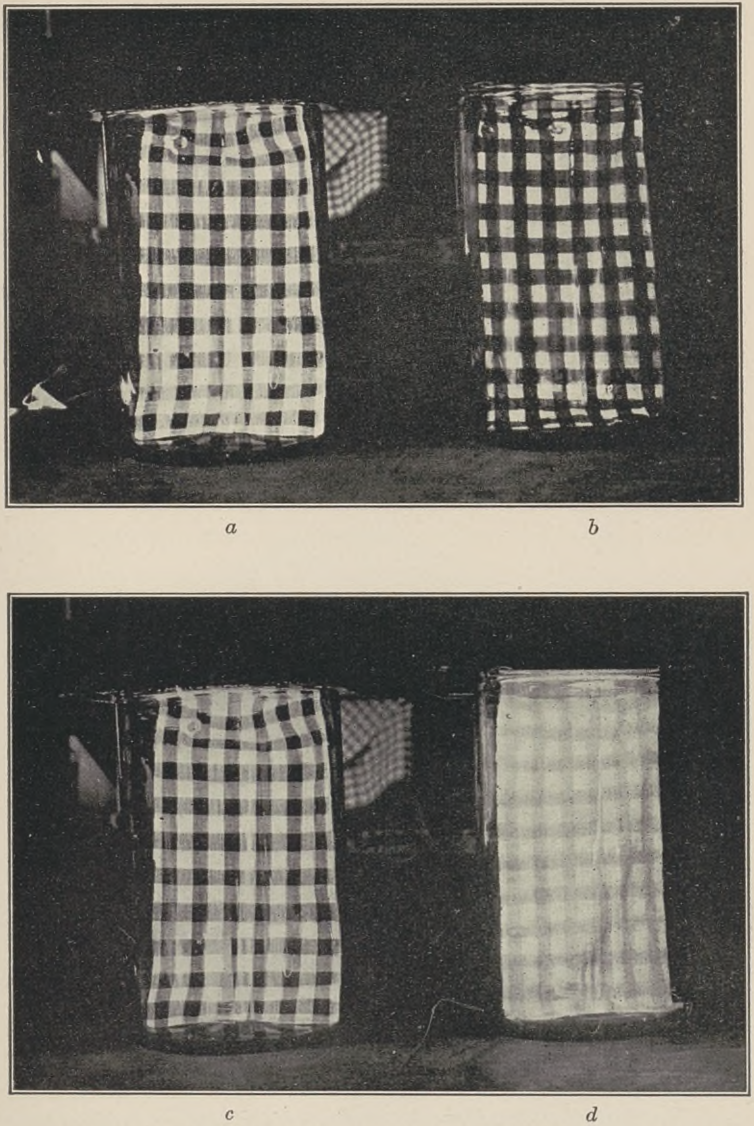

FIG. 25. — BLEACHING WITH CHLORIN

(*a*) Glass jar containing chlorin and dry gingham (red check).
(*b*) Glass jar containing chlorin and moist gingham (red check).
(*c*) Dry gingham and (*d*) moist gingham 15 minutes later.

its salts are unstable, and in the presence of any material that will absorb oxygen they readily liberate oxygen and break down into chlorids. This oxygen being in the nascent condition, attacks and burns up the coloring matter present, for dyes in general are very readily acted on by oxidizing agents.

Naming chemical compounds. Elements have been named because of some peculiarity that appealed to the discoverer, as we have seen. In naming chemical compounds, however, certain definite rules are followed. *All compounds consisting of two substances only are designated by the name of the metallic element, followed by the stem of the name of the non-metallic element to which the ending* "id" *is added*, as in zinc oxid, sodium chlorid, hydrogen chlorid, sodium hydroxid. In naming hydroxids, the hydrogen and oxygen contained in them are considered as one unit, for they often act as a unit, the hydrogen and oxygen remaining together throughout many reactions. *When a group of elements acts as a unit and remains together through numerous reactions, it is called a* radical.

If two bodies are composed of the same elements in different proportions, the one containing the greater proportion of the metallic element is designated by the ending "ous," *while the compound containing the smaller proportion of the metallic element is indicated by the termination* "ic." The ending "ous" means, here as elsewhere, "full of" and "ic" means "like." These endings are added to the stem of the name of the metallic element, the Latin name being used in preference to the English name. Thus, there are two chlorids of iron; the one containing the greater proportion of iron is called ferrous chlorid, its formula being $FeCl_2$. It is more "full of" iron than is the other compound "like" it, which is called ferric chlorid and has the formula $FeCl_3$. Similarly, we have stannous oxid, SnO, and stannic oxid, SnO_2. Sulfurous acid, H_2SO_3, is more "full of" sulfur than sulfuric acid, H_2SO_4.

When more than two compounds containing the same elements exist, they are further indicated by the prefixes "**per**" meaning "higher," and "**hypo**" meaning "lower."

Salts of acids ending in "ic" are indicated by the ending "**ate**" *while salts of the "ous" acids end in* "**ite**."

The following illustrative table of the compounds of chlorin will make this usage plain. Since hypochlorous acid consists of equal volumes of hydrogen, chlorin, and oxygen, let us indicate its composition by writing the formula HClO. There is no difference in the composition of the other compounds of chlorin except that they contain relatively larger amounts of oxygen. This we may indicate in the way given in the table. When an acid is converted into a salt, its hydrogen is substituted by a metal, as the table shows.

COMPOUNDS OF CHLORIN

FORMULA	ACID	SALT	FORMULA
$HClO$	**hypo**chlorous acid	sodium **hypo**chlor**ite**	$NaClO$
$HClO_2$	chlor**ous** acid	sodium chlor**ite**	$NaClO_2$
$HClO_3$	chlor**ic** acid	sodium chlor**ate**	$NaClO_3$
$HClO_4$	**per**chlor**ic** acid	sodium **per**chlor**ate**	$NaClO_4$

When **hypochlorites**, *i.e.* salts of hypochlorous acid, are heated in the absence of reducing matter, they undergo a peculiar decomposition by virtue of which a part of the material becomes more highly oxidized at the expense of the remainder, which is reduced. Hypochlorites decompose partly into chlorates and partly into chlorids. If we make use of the formulas previously given for each of these substances, we may indicate the change by the equation:

$$3\ NaClO \rightarrow 2\ NaCl + NaClO_3$$

This reaction takes place because both chlorids and chlorates are more stable than hypochlorites. The reaction is not peculiar to these substances; other instances of the same kind will be noted as the study proceeds.

Chlorates are good oxidizing agents, especially at high temperatures. Hence they are much used in fireworks. In the presence of reducing matter they give up all of their oxygen and break down into chlorids. When heated alone, however, they decompose in a way similar to hypochlorites. One third of the oxygen contained in a chlorate is liberated during the reaction. To express the change we may write the following equation:

$$2\ NaClO_3 \rightarrow NaCl + NaClO_4 + 2\ O$$

Perchlorates and chlorids are more stable than chlorates, hence the reaction takes place. If perchlorates are heated still higher, they liberate all of their oxygen and break down into chlorids.

$$NaClO_4 \rightarrow NaCl + 4\ O$$

The decomposition of potassium chlorate has already been used as a means of preparing oxygen.

Other compounds intermediate between hypochlorites and chlorates are known as **chlorites**, the salts of chlorous acid. No chlorites are of importance.

This series of compounds affords a beautiful illustration of the law of multiple proportions. Hypochlorous acid is composed of equal volumes of hydrogen, chlorin, and oxygen. Chlorous acid contains the same amounts of hydrogen and chlorin, but twice as much oxygen. Chloric acid has three volumes of oxygen, and perchloric acid four volumes of oxygen. One, two, three, and four volumes of oxygen are united with the same amounts of hydrogen and chlorin in each case.

SUMMARY

CHLORIN

Preparation. When salt is electrolyzed, sodium separates out at the cathode and chlorin at the anode. A more convenient method of preparation is to warm a mixture of manganese dioxid and hydrochloric acid, and collect the gas by downward displacement.

Properties. Chlorin is a pale, yellowish green gas with an unpleasant, irritating odor. It is about 2.5 times as heavy as air and dissolves in one half its volume of water. Chemically, it is second only to fluorin in activity. It unites with most other elements to form chlorids. The combination of chlorin with other substances is often accompanied by the evolution of heat and light exactly like combustion in oxygen. Hence the definition of combustion must be enlarged. Combustion includes all chemical union accompanied by the evolution of heat and light.

Bleaching with chlorin. Most animal and vegetable dyes are bleached rapidly in chlorin, but little action takes place when they are dry. Chlorin reacts with water to form hydrochloric and hypochlorous acids. The latter decomposes readily, yielding oxygen, which oxidizes the dye. Oxygen can accomplish this result only when in the nascent state.

HYDROGEN CHLORID is formed by the direct union of hydrogen and chlorin, but it is most conveniently prepared by the action of sulfuric acid on salt. As hydrogen chlorid is a gas under these conditions, the reaction runs to completion.

Properties. Hydrogen chlorid is a colorless gas with a sharp odor and a sour taste. It is heavier than air, and is exceedingly soluble in water. Its attraction for moisture causes it to fume in the air. The dry gas and the liquefied substance (not the solution) are not chemically active. The ordinary solution in water contains about 450 volumes of gas; *i.e.* about 40 % of hydrogen chlorid, and is known as concentrated hydrochloric acid, or muriatic acid. It is a colorless liquid that fumes because it liberates hydrogen chlorid. It possesses strong acid properties.

Oxidation of hydrogen chlorid. Hydrogen chlorid is oxidized fairly readily. The oxidizing action of the air is slow, but at 400°, in the presence of copper chlorid as a catalyzer, the reaction proceeds rapidly. Manganese dioxid acts as a ready oxidizer when warmed. Chlorin may be produced by the action of sulfuric acid on a mixture of salt and manganese dioxid, hydrochloric acid being liberated and oxidized at the same time.

Acid properties. Any strong acid (1) is sour in taste; (2) turns blue litmus red; (3) acts on many metals, giving up its hydrogen in exchange for the metal and forming a salt; (4) dissolves the oxids of metals, forming water and a salt of the metal and the acid; (5) neutralizes bases. *A base is the hydroxid of a metallic element.* Its solution has a soapy taste and slippery feeling, and turns red litmus blue. The products of the neutralization of a base by an acid are (*a*) water; (*b*) a salt.

Naming compounds. A compound containing only two substances is designated by the name of its metallic element followed by the stem of the name of its non-metallic element to which the ending "**id**" is added, as sodium chlorid. If two substances are composed of the same elements in different proportions, they are distinguished by the endings "**ous**" and "**ic**," added usually to the stem of the Latin name of the metallic element, as ferrous chlorid and ferric chlorid. "Ous" indicates the larger proportion of the metallic element, "ic" the smaller. Acids are designated similarly, and still higher and lower states of oxidation are shown by the prefixes "**per**" and "**hypo.**" Salts of "ous" acids end in "**ite**"; salts of "ic" acids end in "**ate.**"

Acids of chlorin. Hypochlorites are obtained by treating bases with chlorin. When heated, they yield a mixture of chlorids and chlorates. When chlorates are heated, they yield chlorids and perchlorates. Chlorites also exist. These compounds are the salts of hypochlorous, chlorous, chloric, and perchloric acids, which furnish an excellent illustration of the law of multiple proportions.

QUESTIONS

1. Why is chlorin not likely to occur in nature?

2. Compare chemically the burning of a candle in chlorin and in oxygen.

3. Mention all the acid properties which you know.

4. How many liters of hydrogen chlorid, measured under standard conditions, are used in making 1 kilo of concentrated hydrochloric acid? (1 liter of hydrogen chlorid weighs 1.63 grams.)

5. Thin layers of oxids form over the surfaces of most metals, making soldering impossible. The tinsmith makes firm joints by using acid or rosin when soldering. Explain the action.

6. What four different classes of reactions have we noted so far? State clearly the differences between them, and write a reaction illustrating each class.

7. Name the following compounds:

(*a*) The magnesium salt of chloric acid.
(*b*) The zinc salt of chlorous acid.
(*c*) The calcium salt of nitrous acid.
(*d*) The potassium salt of hypochlorous acid.
(*e*) The sodium salt of carbonic acid.
(*f*) The lithium salt of perchloric acid.
(*g*) The mercurous salt of nitric acid.
(*h*) The mercurous salt of nitrous acid.
(*i*) The mercuric salt of nitric acid.
(*j*) The mercuric salt of nitrous acid.

8. Name the following:

(*a*) The compound of zinc and oxygen.
(*b*) The compound of magnesium and sulfur.
(*c*) The compound of sodium and hydrogen.
(*d*) The compound of calcium and carbon.
(*e*) The compound of aluminum and silicon.
(*f*) The two compounds of iron and chlorin.
(*g*) The two compounds of tin and sulfur.
(*h*) The two compounds of copper and oxygen.

9. Name the following acids, the first in each column being the one that receives the termination *-ic*:

H_2SO_4
H_2SO_3
$H_2S_2O_8$

H_3PO_4
H_3PO_2
H_3PO_3

HNO_3
HNO_2
HNO

HIO_3
HIO_4

10. Name the substances having the following chemical formulas:

CaS
SnO
$ZnSO_3$
$HgCl_2$

ZnO
SnO_2
$KClO_3$
Hg_2Cl_2

KCl
$CuCl$
$NaClO$
$AgClO_4$

CaC_2
$CuCl_2$
FeO
$CaSO_3$

NaI
$ZnSO_4$
Fe_2O_3
KOH

CHAPTER IX

COMBINATION BY VOLUME AND BY WEIGHT

Up to this point attention has been directed largely to the preparation and properties of the substances which we have considered, without especial regard to the quantities of the elements that react together. A consideration of any subject which does not deal with the quantities involved is termed *qualitative*, but if the amounts of the reacting substances are determined, it is said to be *quantitative*. Thus, a decomposition of water into its elements would be a *qualitative analysis*, unless we weigh or measure the amounts of the reagents concerned. It becomes a *quantitative analysis* when we determine these amounts. **The quantities of hydrogen and oxygen which react together** may be determined in many ways, one of the most direct methods being as follows: Into an apparatus called a *eudiometer* (Fig. 26), hydrogen is introduced through the upper stopcock and its volume measured in the graduated tube *A* by bringing the mercury to the same level in

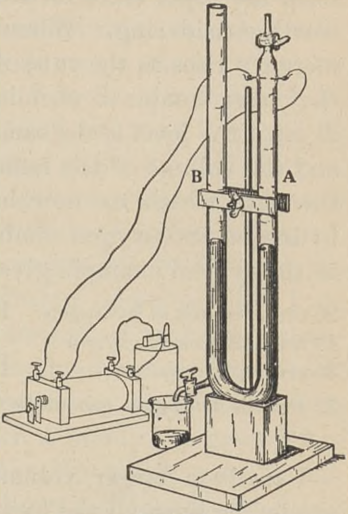

Fig. 26.

both arms *A* and *B*. After the volume of hydrogen has been noted, about the same number of cubic centimeters of oxygen is introduced and the volume noted after adjusting the mercury level once more. Mercury is now poured into *B* until a quantity is present greater than what is necessary to fill completely one side of the apparatus, and a cork is pressed into the open end of the tube *B*. Two pieces of platinum wire have been fused into the upper end of the tube *A*. These are now connected to a Ruhmkorff coil, and an electric spark is passed through the gases. An explosion results as the elements combine. The amount of water formed in the reaction condenses from the vapor state immediately and occupies no volume worth considering. When the cork is removed from *B*, mercury rises in the tube *A* to take the place of the gases that have combined chemically. Mercury is poured into *B* until the level is the same in each side of the apparatus, and the volume of the remaining gas is measured. From the data which we now have, the proportions in which hydrogen and oxygen combine may be calculated as shown in the typical example given.

20 ccm. volume of hydrogen	19 ccm. volume of oxygen introduced
19 ccm. volume of oxygen	9 ccm. volume of oxygen left over
39 ccm. total volume	10 ccm. volume of oxygen used

20 ccm. of hydrogen gas unite with 10 ccm. of oxygen gas to form water.

Usually a larger volume of oxygen is taken than is needed to burn all the hydrogen. Under these conditions the gas left in the apparatus is oxygen. If too large a volume of hydrogen is taken, the excess of hydrogen is left in the apparatus; but the proportion between the quantities of hydrogen and oxygen which have united is found to be exactly the same in either case. In the mixture of gases it makes no difference what amounts of hydrogen and oxygen are present; when they combine, 2 volumes of hydrogen invariably unite with 1 volume of oxygen under the conditions of this experiment.

Experiments like this enabled the French chemist, Proust, to demonstrate to the satisfaction of every one the law of definite proportions. For eight years (1799–1807) his fellow countryman, Berthollet, maintained that the proportions of the reagents present influenced the composition of the compound formed and that there was no law of constant composition and definite proportions. Proust showed that Berthollet was working with impure substances, *i.e.* with mixtures and not pure chemical compounds, and so won the day.

Combination by volume. The average result of all the most careful work that has been done by many different methods on the question of the composition of water indicates that the proportion by volume in which hydrogen and oxygen gases combine is 2 to 1. In this and in other ways it may be demonstrated also that 1 volume of hydrogen gas unites with 1 volume of fluorin, 1 of chlorin, 1 of bromin, 1 of iodin in the gaseous state; and that 2 volumes of hydrogen combine with 1 of sulfur, selenium, and tellurium when these elements are in the gaseous condition; and that 3 of hydrogen combine with 1 of nitrogen, or 1 of phosphorus, arsenic, or antimony gases, provided that these gases are measured under proper conditions of temperature and pressure. Gay-Lussac first determined the volumes in which a number of gases combine, and in 1808 announced the law which goes by his name. It may be stated as follows: *The volumes of any two gases which combine stand to each other in very simple ratios.* The volume of the product, if gaseous, also stands in a simple ratio to the volume of either constituent.

Several illustrations of this law are given in tabular form on the next page. Not all of these can be measured directly; some have been calculated from other data.

COMBINATION OF GASES BY VOLUME

COMPOUND	VOLUME OF HYDROGEN	VOLUME OF NON-METAL	FORMULA
Hydrogen fluorid	1	1	HF
Hydrogen chlorid	1	1	HCl
Hydrogen bromid	1	1	HBr
Hydrogen iodid	1	1	HI
Hydrogen oxid	2	1	H_2O
Hydrogen sulfid	2	1	H_2S
Hydrogen selenid	2	1	H_2Se
Hydrogen tellurid	2	1	H_2Te
Hydrogen nitrid	3	1	H_3N
Hydrogen phosphid	3	1	H_3P
Hydrogen arsenid	3	1	H_3As
Hydrogen antimonid	3	1	H_3Sb
Hydrogen carbid	4	1	H_4C
Hydrogen silicid	4	1	H_4Si

Gay-Lussac's law does not apply alone to those substances which are gases at ordinary temperatures. It holds for all substances, for under proper conditions of temperature and pressure, every substance can be made to exist in the gaseous state.

Combination by weight. Since a given volume of gas always has a definite weight, it follows that *substances unite in definite proportions by weight as well as by volume.*

Hydrogen was taken as the unit of weight, or 1, because it has been found that the weight of hydrogen which unites with a given amount of another substance is less than that of any other element which could take its place in the reaction. On this basis we find that:

1 part by wt. of H combines with 19 parts by wt. of F
1 part by wt. of H combines with 35.5 parts by wt. of Cl
1 part by wt. of H combines with 80 parts by wt. of Br
1 part by wt. of H combines with 127 parts by wt. of I

These ratios are determined from the facts that the volume of fluorin with which 1 volume of hydrogen combines weighs 19 times as much as the hydrogen, etc. By the results of analysis we learn also that 35.5 parts by weight of chlorin unite with 23 parts by weight of sodium, 39 parts of potassium, 108 parts of silver. These same weights of sodium, potassium, and silver unite without a remainder with 19 parts of fluorin, 80 parts of bromin, 127 parts of iodin. Furthermore, 23 parts of sodium or 39 parts of potassium unite with 1 part of hydrogen. These facts are shown graphically in the following diagram:

Parts by Weight		Parts by Weight
1 of H		19 of F
or		*or*
23 of Na		35.5 of Cl
or	combine with	*or*
39 of K		80 of Br
or		*or*
108 of Ag		127 of I

From the preceding facts it is seen that *from the results of the analysis of a few compounds, a number may be assigned to any element, and this number (or some multiple of it) will express the proportion by weight in which this element combines with all other elements.* Such numbers are known as **combining or reacting weights.** From the results of analysis and synthesis a combining weight has been chosen for each element.

The selection of the proper reacting weight for each element is not always so simple as in the cases just mentioned, and the earlier chemists were greatly puzzled in some instances to know which of several ratios was the correct one. The ratio between the weights of hydrogen and oxygen in water is 1 : 8. Another compound furnishes the ratio 1 : 16. Ordinarily we choose the smallest ratio, but in the case of water the volume composition, 2 : 1, suggests that possibly 1 : 16 is the correct ratio, since the second compound is composed of equal volumes of hydrogen and oxygen. To-day the question of selection is not often a serious one, for rules have been discovered which enable us to determine in most cases the proper ratio without difficulty. These will be considered somewhat later.

Significance of combining weights. The existence of these definite ratios between the weights of elements that combine points to the existence of particles of each element which have definite weights, and suggests that these particles of the elements act as units in chemical reactions. This supposition may be true or not; but each element, as it combines with others, acts exactly as though it were true. Chlorin, for instance, always unites with hydrogen in the proportion of 35.5 : 1, never 34, 33, 30, 75, 15, or any number other than 35.5. Furthermore, chlorin never unites with any other element in proportions which can not be represented by the number 35.5, unless it be some simple multiple of this number, as 71, 106.5, 142, etc. That these ratios exist inherent in the elements is an undisputed fact of which any one can obtain evidence. How we explain these ratios is hypothesis, and our explanation or theory may or may not be true.

The situation is closely analogous to what we might find in any city. Its buildings are composite structures differing greatly among themselves, yet on analysis they are found to be built up out of a very few building materials which may be called their elements. If we investigate in a quantitative manner one of these elements, brick, for instance, and examine the various heaps to be found about the streets, we should find these piles to weigh, respectively, 5000 pounds or a multiple of this number. If we should seek an explanation of this 5000-pound unit of bricks, we might make the hypothesis that bricks are sold by the thousand. If each individual brick weighs 5 pounds, the 5000-pound unit would be accounted for as a load, or 1000 brick. This hypothesis we should find correct. In selling brick this unit is not ordinarily divided. In other processes it may be divided into smaller units. In brick laying the unit is a thousand times smaller than the unit of brick selling, and the load is thus seen to be a composite unit.

Atomic theory. In explanation of the fact of combining ratios or weights, a hypothesis was put forth more than a hundred years ago by Dalton, an English schoolmaster, whose likeness is shown in Fig. 27. He assumed that in the case of each element certain minute particles of matter exist; that these particles have definite weights differing with different elements, but constant with each particular element; that chemical reactions take place between these particles, one particle of one element uniting with one, two, three, or four particles of a second element. All the evidence goes to indicate that in ordinary chemical reactions these particles are not divided. For this reason Dalton called them *atoms*, a term which means "not divided." The atoms of one element, so far as we know, are all exactly alike, but they are different from the atoms of every other element.

According to Dalton's theory, the reason why chlorin and hydrogen always combine in the proportions of 35.5 : 1 is as follows: Chlorin and hydrogen combine atom for atom; *i.e.* 1 atom of chlorin combines with 1 atom of hydrogen. The chlorin atom weighs 35.5 times as much as the hydrogen atom. In any amount of hydrogen chlorid there are equal numbers of chlorin and hydrogen atoms. Therefore, the proportion of chlorin to hydrogen must always be 35.5 : 1.

In the case of water the ratio found by analysis is 8 parts by weight of oxygen to 1 part of hydrogen. The oxygen atom weighs 16 times as much as the hydrogen atom. If 1 atom of oxygen combines with 1 atom of hydrogen, the proportions must be 16 : 1. But if one atom of oxygen combines with 2 atoms of hydrogen, the proportions must be 16 : 2; *i.e.* 8 : 1. We have reason to believe that the latter supposition is true. Hence, in any amount of water there must always be twice as many hydrogen atoms as oxygen atoms. Therefore, the ratio in which oxygen combines with hydrogen to form water must always be 8 : 1.

One atom of hydrogen, uniting with one atom of chlorin, forms the smallest amount of hydrogen chlorid that can exist and possess the properties of hydrogen chlorid. For the smallest amount of hydrogen and the smallest amount of chlorin that enter into chemical reactions are the atoms of hydrogen and chlorin, and the result must be the smallest particle of the compound. If we should attempt to divide it, we would no longer have a particle of hydrogen chlorid, but instead an atom of hydrogen and an atom of chlorin. *The smallest particle of a substance that can exist and possess the properties of that substance is a molecule. An atom may be defined as the smallest amount of an element that enters into chemical compounds.*

According to Dalton's theory, combining weights are simply the weights of the atoms of the different elements; *i.e.* the *atomic weights.* We should remember, however, that the idea of atomic weights is part of a theory only. If at some future time evidence should be found indicating that the atomic theory could not be true, we should no longer speak of atomic weights. That each element has a *reacting weight* is a fact, however, that will stand as long as there is any science at all.

In determining the relative weights of the atoms of different elements, the weight of the hydrogen atom was taken as 1. The weight of the hydrogen atom is often called a *microcrith.* The relative weights of the atoms of the other elements are given in the Appendix.

The atomic theory was published first as a hypothesis, like other new things of its class. In succeeding years, new evidence indicating its truth came to light, and it assumed the importance of a theory. Now after more than a century, having stood every test and not being disputed by any known facts, it is given almost as much credence as some of the laws of science. The actual size, shape, or

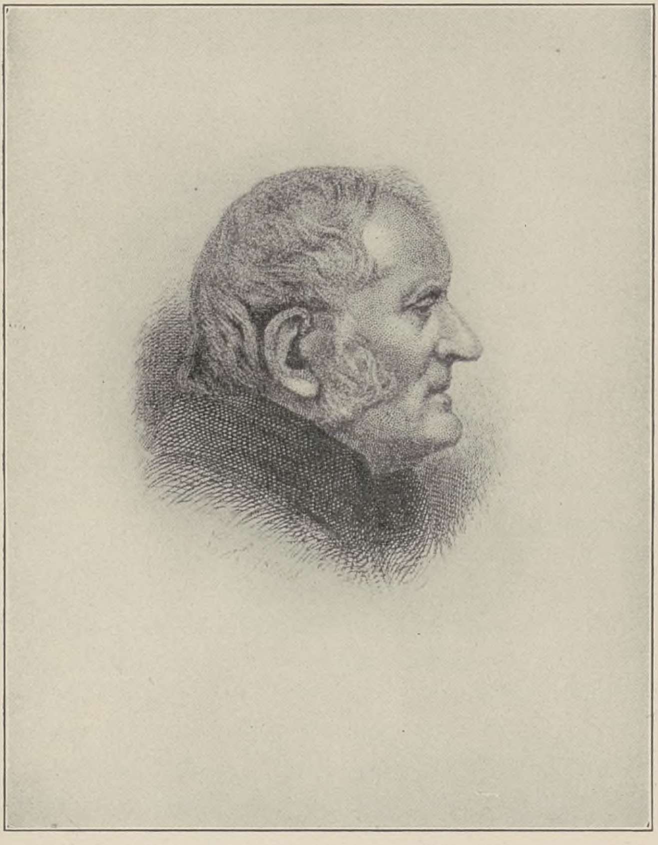

Fig. 27. — John Dalton (1766–1844)

An English schoolmaster who discovered the Law of Multiple Proportions and set forth the Atomic Theory.

weight of the atoms does not concern us. Whether they actually exist or not is a matter of little moment, for of this we are sure: *All elements behave exactly as if atoms do exist.* The theory is simply a picture or mind model to explain reactions, and it is, of course, a crude picture. Theory is the scaffolding by which we are helped in constructing our sciences; the building material is in every case facts.

Oxygen standard. Hydrogen was taken as the standard for combining weights because its combining weight is smaller than that of any other element; but when hydrogen is taken as 1, the combining weights of the other elements are almost invariably expressed by numbers containing decimal fractions. Then, too, hydrogen does not readily unite with many of the elements. Oxygen, however, readily unites with every element except fluorin and the argon group. On this account an international committee of chemists has recommended the use of oxygen as a more convenient practical standard. With hydrogen as a standard, the combining weight of oxygen is 15.879, but for the above-mentioned reasons in scientific work oxygen is usually taken as even 16.* This is simply to throw the decimal fraction on hydrogen, making it 1.0075. The ratios are not changed in the least; 1:15.879 expresses the same ratio as 1.0075:16, just as 1.5:3 expresses the same ratio as 1:2. When calculated on the basis of oxygen 16, the combining weights of many of the other elements come out nearly whole numbers.

As the result of analysis and synthesis, the combining weights of a number of elements were determined with considerable accuracy in the years previous to and directly

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* On the basis of oxygen 16, speaking accurately, we should have to define a microcrith as $\frac{1}{16}$ of the weight of the oxygen atom and say that the hydrogen atom weighs 1.0075 microcriths.

following Dalton's statement of the atomic hypothesis Experimenters were busy, also, in measuring all the physical properties of the elements, among others the heat capacity or specific heat. In 1818 Dulong and Petit noticed that when the specific heat of an element in the solid state is multiplied by the combining weight, the product is practically the same for all elements. Many elements were unknown in 1818 and have been discovered since, but the above relation has been found true for all of them, so that the rule is now known as the **law of Dulong and Petit.** It may be stated in the following way: *The product obtained by multiplying the combining weight of an element by its specific heat in the solid state approximates the constant* 6.4.

How close the approximation is to a constant quantity may be seen from the table, in which typical elements are given, chosen through the whole range of combining weights.

DULONG AND PETIT'S LAW

ELEMENT	COMBINING WEIGHT	SPECIFIC HEAT	PRODUCT
Bromin	80.0	0.084	6.72
Calcium	40.1	.170	6.80
Gold	197.2	.032	6.31
Iodin	127.0	.054	6.86
Iron	55.9	.112	6.26
Lithium	7.0	.940	6.58
Magnesium	24.3	.250	6.08
Mercury	200.0	.032	6.40
Phosphorus	31.0	.190	5.89
Potassium	39.1	.166	6.49
Sodium	23.0	.290	6.67
Sulfur	32.1	.178	5.71
Uranium	238.5	.0276	6.58
Zinc	65.4	.093	6.08

The law of Dulong and Petit is of service in determining combining weights, in this way: Let us suppose that the combining weight of iron is unknown. By the analysis of one or more compounds containing the metal, the ratio is determined in which iron combines with some other element, the combining weight of which is known. As a typical compound let us take iron chlorid, consisting of 34.46 % of iron and 65.54 % of chlorin. This ratio is then expressed in a proportion, one term of which is the combining weight of chlorin, *i.e.* 34.46 : 65.54 :: x : 35.5. The value of x from this proportion is 18.66. If this compound consists of one combining weight of iron united with one combining weight of chlorin, the combining weight of iron is 18.66. But it may be that two, three, or four combining weights of chlorin unite with one combining weight of iron, and that the ratio, in order to show this, should be expressed in one of the following ways: — 37.32 : 71, or 55.98 : 106.5, or 74.64 : 142. In other words, is the combining weight of iron 18.6, 37.3, 56, or 74.6? The third number is chosen, for the specific heat of the metal is 0.112, which, multiplied by 56, gives a product of 6.27. Evidence from other lines of investigation confirms the choice of 56 as the combining weight of iron.

SUMMARY

Qualitative analysis and synthesis deal only with the kinds of matter under consideration. **Quantitative** work considers both kinds and amounts.

Composition of water. Two volumes of hydrogen plus 1 volume of oxygen unite to form water.

Gay-Lussac's laws. *The volumes of any two gases which combine stand to each in very simple ratios.* The volume of the product, if gaseous, stands in a simple ratio to the volume of either constituent.

Since a given volume of gas always has a definite weight, it follows that substances unite in definite proportions by weight, also.

Combining weights. From the results of analysis and synthesis, a number has been assigned to each element. This number (or some multiple of it) expresses the proportions by weight in which this element combines with all other elements. Such numbers are called *combining* or *reacting weights.* Hydrogen was taken as the standard, or 1, because it is found that the amount of hydrogen that combines with any substance weighs less than any other element that can take its place in the reaction.

Atomic theory. Dalton's explanation of the facts of combination by weight is that the elements are composed of particles which have definite weights and which are not divided in chemical reactions. These particles he called *atoms*. Atoms unite into groups called molecules. A molecule is the smallest particle of a substance which can exist and possess the properties of that substance. According to the atomic theory the relative weights of the atoms are represented by the combining weights. The standard formerly used — hydrogen weighs 1 — has generally given place to the more practical one — oxygen weighs 16.

Dulong and Petit's law. *If the specific heat of an element in the solid state is multiplied by the combining weight, the product approximates the constant quantity* 6.4. The results of analysis and synthesis give the chemist a number for each element which is either its combining weight or a fraction of it. Application of the above law enables him to choose the correct combining weight.

QUESTIONS

1. If a standard liter of hydrogen weighs 0.09 gram, of oxygen 1.43 grams, and of steam 0.80 gram, calculate (*a*) how many parts by weight of oxygen unite with one part of hydrogen to form how many parts of steam; (*b*) how many cubic centimeters of steam are formed by the union of 2 ccm. of hydrogen with 1 ccm. of oxygen?

2. It was found in an experiment that 4.6 grams of sodium liberate 0.2 gram of hydrogen from water. Calculate the combining weight of sodium.

3. Experiment shows that 13.1 grams of zinc unite with 3.2 grams of oxygen to form zinc oxid. Calculate the combining weight of zinc.

4. Discuss the difference between an atom and a molecule.

5. Would it be proper to speak of an atom of (*a*) water; (*b*) chlorin; (*c*) hydrochloric acid; (*d*) mercury; (*e*) carbon dioxid; (*f*) nitrogen; (*g*) nitric acid?

6. Would it be proper to refer to a molecule of (*a*) hydrogen; (*b*) mercury; (*c*) water; (*d*) carbon dioxid; (*e*) nitric acid?

7. How would you state the rule applying in questions 5 and 6?

8. The specific heat of bismuth is 0.0308. What is its approximate combining weight?

9. It is found by experiment that 1.3 grams of zinc liberate 0.04 gram of hydrogen from dilute sulfuric acid. Calculate the apparent combining weight of zinc, and correct this by the use of Dulong and Petit's law, referring to page 108 for the specific heat of zinc.

10. One gram of aluminum acted on by acid yields 1230 ccm. of hydrogen under standard conditions. Calculate the apparent combining weight of aluminum, and correct this by the use of Dulong and Petit's law, the specific heat of aluminum being 0.22.

CHAPTER X

CHEMICAL FORMULAS AND EQUATIONS

In previous chapters we have made use of formulas and equations to express in "chemical shorthand" the changes taking place. We may now consider the method of determining the formula for any substance and the equations into which it enters.

In order to do this, we must know what elements enter into the composition of the substance and the proportions in which each is present.

Burning magnesium. When magnesium burns, we find that each gram of the metal produces 1.658 grams of ash. That is, magnesium oxid contains magnesium and oxygen in the proportion of 1.000 to 0.658.

In chemical literature it is customary to express the composition of substances in percentages; *i.e.* to state how many parts of each element are present in 100 parts of the substance. This is easily calculated from the figures given above. For, if in 1.658 grams of magnesium oxid there is 1.000 gram of the metal, in 100 parts of the oxid there will be 60.3 parts of magnesium. Similarly, if in 1.658 grams of magnesium oxid there is .658 gram of oxygen, in 100 parts of the oxid there will be 39.7 parts of oxygen. These figures are obtained by the solution of the proportions:

$$1.658 : 1.00 :: 100 : x \quad x = 60.3$$
$$1.658 : .658 :: 100 : x \quad x = 39.7$$

That there are 60.3 parts of magnesium and 39.7 parts of oxygen in 100 parts of oxid is usually expressed by the statement that magnesium oxid contains 60.3 % magnesium and 39.7 % oxygen. Now, whether these parts are grams, pounds, tons, or microcriths makes no difference; the proportions are the same. Let us consider these parts to be microcriths. In 100 mic. of magnesium oxid there are 60.3 mic. of magnesium and 39.7 mic. of oxygen. The atom of magnesium weighs 24.3 mic. Hence, in 60.3 mic. of magnesium there would be $60.3 \div 24.3 = 2.48$ atoms of magnesium. The atom of oxygen weighs 16 mic. Hence, in 39.7 mic. of oxygen there would be $39.7 \div 16 = 2.48$ atoms of oxygen.

The ratio between the number of atoms of magnesium and the number of atoms of oxygen in 100 mic. of magnesium oxid is 1 : 1.

The composition of magnesium oxid is always the same, however. If any specimen of magnesium oxid is composed of one atom of oxygen for each atom of magnesium, in any other amount of magnesium oxid there will be just as many atoms of magnesium as there are atoms of oxygen. We cannot tell the exact number of atoms until we know the weight of the molecule of magnesium oxid.

The molecule of magnesium oxid must weigh at least $24.3 + 16 = 40.3$ mic.; for it must contain at least one atom of magnesium and one atom of oxygen. But magnesium oxid may contain two atoms of each element, or five atoms of each. In the former case its molecular weight would be $2 \times 40.3 = 80.6$; in the second case $5 \times 40.3 = 201.5$.

Without knowing the weight of the molecule, we can determine only the ratio in which the atoms of each element are present. If the molecular weight is unknown, the simplest formula for any compound is always written.

How molecular weights are determined must be deferred for the present.

In writing formulas the symbol for an element stands for one atom of that element.

The ratio between magnesium and oxygen atoms in magnesium oxid is 1 : 1. The simplest formula that can be written is MgO, and the equation for its formation is

$$\mathrm{Mg} + O \rightarrow \mathrm{MgO}.$$

Calculation of quantities. Since the symbol stands for a definite amount, one atom, of each element, all chemical formulas and equations signify the proportions by weight in which the substances react. The equation for the burning of magnesium states that 24.3 parts of magnesium plus 16 parts of oxygen unite to form 40.3 parts of magnesium oxid. In making calculations it is well at first to write into the equations the relative weights that are always implied from the symbols and formulas present, as shown in the following equation:

$$\begin{array}{ccccc} \mathrm{Mg} & + & O & \rightarrow & \mathrm{MgO} \\ 24.3 & & 16 & & \underbrace{24.3+16}_{40.3} \end{array}$$

From this equation we may calculate the amounts of all of the substances used or produced in this reaction if the amount of any one substance is known.

Problem. How much magnesium will be required to combine with 8 grams of oxygen, and how much magnesium oxid will result?

Solution. Since 16 parts of oxygen require 24.3 parts of magnesium, 8 grams of oxygen will require magnesium in the same ratio:

$$16 : 24.3 :: 8 : x$$

$$x = \frac{24.3 \times 8}{16} = 12.15 \text{ grams. } \quad \textit{Ans.}$$

Since 16 parts of oxygen give 24.3 + 16 = 40.3 parts of magnesium oxid, 8 grams of oxygen will yield magnesium oxid in the same ratio.

$$16:40.3::8:y$$

$$y=\frac{40.3 \times 8}{16}=20.15 \text{ grams.} \quad \textit{Ans.}$$

Proof. According to the law of the conservation of matter, the amount of magnesium oxid after the change must be equal to the sum of the weights of the magnesium and the oxygen. The answers may therefore be proved by adding the weights of magnesium and oxygen and comparing the sum with the weight of the magnesium oxid.

12.15 grams magnesium + 8 grams oxygen = 20.15 grams magnesium oxid.

PROBLEMS. 1. How many grams of oxygen are required to combine with 10 grams of magnesium ribbon? 6.585 grams. *Ans.*

2. How many grams of magnesium oxid will result?

3. To combine with 40 grams of oxygen, how many grams of magnesium are required?

4. How many grams of magnesium must be burned to obtain 200 grams of magnesium oxid?

Decomposition of mercuric oxid. When mercuric oxid is heated, the products are mercury and oxygen. It has been found by quantitative methods that 27 grams of mercuric oxid give 25 grams of mercury and 2 grams of oxygen. The percentage composition is 92.6 % mercury and 7.4 % oxygen. In 100 mic. of mercuric oxid there would be 92.6 mic. of mercury and 7.4 mic. of oxygen. But the atom of mercury weighs 200 mic. In 92.6 mic. of mercury there would be .46 atom of mercury. In 7.4 mic. of oxygen there would be .46 atom of oxygen.

These numbers stand to each other in the ratio of 1 : 1. Therefore in any amount of mercuric oxid the number of mercury atoms is equal to the number of oxygen atoms. There must be at least 1 atom of mercury and 1 atom of oxygen, for nothing less than 1 atom of any substance is present in any compound. The weight of a molecule of mercuric oxid must be at least 216 mic., but it may be two, three, four, or more times heavier than this. However, the simplest formula for mercuric oxid is HgO, and the chemical change taking place when mercuric oxid is decomposed by heat may be represented by the equation:

$$\mathbf{HgO} \rightarrow \mathit{Hg} + \mathit{O}$$

The weight relations in this equation show that 216 parts of mercuric oxid yield 200 parts of mercury and 16 parts of oxygen.

$$\begin{array}{ccc} \mathbf{HgO} \rightarrow & \mathit{Hg} + & \mathit{O} \\ \underbrace{200+16}_{216} & 200 & 16 \end{array}$$

Problem. How much oxygen and how much mercury will be obtained by heating to complete decomposition 54 grams of mercuric oxid?

Solution. If 216 parts of mercuric oxid yield 16 parts of oxygen, 54 grams of mercuric oxid must yield oxygen in the same ratio.

$$216:16::54:x$$
$$x = \frac{16 \times 54}{216} = 4 \text{ g.} \quad \textit{Ans.}$$

Also, if 216 parts of mercuric oxid yield 200 parts of mercury, then 54 grams of mercuric oxid must yield mercury in the same ratio.

$$216:200::54:y$$
$$y = \frac{200 \times 54}{216} = 50 \text{ g.} \quad \textit{Ans.}$$

Proof. 54 grams of mercuric oxid = 50 grams of mercury and 4 grams of oxygen.

Problems. 5. How much oxygen and how much mercury will be obtained by heating 10 grams of mercuric oxid?

6. How much mercuric oxid must be heated to obtain 5 grams of oxygen?

How much mercury will be obtained at the same time?

Decomposition of potassium chlorate. From the results of analysis, potassium chlorate is found to have the composition: potassium, 31.89 %; chlorin, 28.96 %; oxygen, 39.15%. In every 100 mic. of potassium chlorate there are 31.89 mic. of potassium, 28.96 mic. of chlorin, and 39.15 mic. of oxygen. Dividing these weights by the weights of the respective atoms, we obtain the ratio in which the atoms are present in potassium chlorate.

ELEMENTS	WEIGHT	ATOMIC WEIGHT	NO. OF ATOMS	RATIO
Potassium	31.89	÷ 39.1 =	.82	1
Chlorin	28.96	÷ 35.5 =	.82	1
Oxygen	39.15	÷ 16 =	2.45	3

The simplest formula for potassium chlorate is therefore $KClO_3$, each molecule containing one atom of potassium, one atom of chlorin, and three atoms of oxygen. When potassium chlorate is heated until no further chemical change takes place, all its oxygen is given up and potassium chlorid, KCl, is left. The chemical equation and weight relations are

$$\underset{\underbrace{39.1+35.5+(3\times16)}_{122.6}}{KClO_3} = \underset{\underbrace{39.1+35.5}_{74.6}}{KCl} + \underset{\underbrace{3\times16}_{48}}{3\,O}$$

PROBLEM. How much oxygen and how much potassium chlorid will be obtained by heating to complete decomposition 61.3 grams of potassium chlorate?

Solution. If 122.6 parts of potassium chlorate yield 48 parts of oxygen, then 61.3 grams of potassium chlorate will yield oxygen in the same ratio.

$$122.6 : 48 :: 61.3 : x$$
$$x = 24 \text{ g.} \quad \textit{Ans.}$$

Also, if 122.6 parts of potassium chlorate yield 74.6 parts of potassium chlorid, then 61.3 grams of potassium chlorate will yield potassium chlorid in the same ratio.

$$122.6 : 74.6 :: 61.3 : y$$
$$y = 37.3 \text{ g.} \quad \textit{Ans.}$$

Proof. $61.3 = 37.3 + 24.$

Problems. 7. How much oxygen may be obtained by heating 30 grams of potassium chlorate?

8. How much potassium chlorate must be heated to obtain 5 grams of oxygen?

9. How much potassium chlorid would be formed (*a*) in problem 7; (*b*) in problem 8?

Problem. How many liters of oxygen will result from the heating of 61.3 grams of potassium chlorate?

Solution. From the problem explained above, it appears that 61.3 grams of potassium chlorate yield 24 grams of oxygen gas. Now, 1 liter of oxygen gas under standard conditions weighs 1.43 grams. Then

$$24 \div 1.43 = 16.78 \text{ liters of oxygen gas. } \textit{Ans.}$$

This solution gives the volume of oxygen under standard conditions.

Problems. 10. How many liters of oxygen will result from the heating of 10 grams of potassium chlorate?

11. 20 liters of oxygen are required for an experiment. How many grams of potassium chlorate must be taken?

12. What volume of oxygen gas will be consumed in the burning of 7 grams of magnesium?

13. How many liters of oxygen gas will be liberated in heating 100 grams of mercuric oxid?

Zinc and sulfuric acid. From investigations it is found that the chemical equation for the action of zinc on sulfuric acid is

$$\begin{array}{ccccc} Zn\ + & H_2SO_4 & \rightarrow & ZnSO_4 & +\ 2\,H \\ 65.4 & \underbrace{2 + 32.1 + 64}_{98.1} & & \underbrace{65.4 + 32.1 + 64}_{161.5} & 2 \end{array}$$

Problems. 14. (*a*) How much sulfuric acid would be required to react with 13.08 grams of zinc?

(*b*) How many grams of hydrogen would result?

(*c*) Under standard conditions how many liters would this gas occupy?

(*d*) How many liters of hydrogen would result at 20° and 750 mm., the gas being collected over water?

(*e*) How many grams of zinc sulfate, $ZnSO_4$, would be formed?

15. To obtain 2 liters of hydrogen under standard conditions, how much zinc must be treated with sulfuric acid? How much sulfuric acid must be used?

Chemical formulas and equations furnish a convenient method of expressing the composition of substances and the ways in which substances react. It must not be forgotten, however, that they cannot be mentally evolved like algebraic equations, but are in every case founded on the results of quantitative analysis or synthesis, as the following problems indicate.

Problems. 16. When sulfur burns in oxygen, it has been found that 1 gram of sulfur combines with 1 gram of oxygen to form 2 grams of the oxid of sulfur. Calculate

(*a*) the percentage composition of the oxid of sulfur;
(*b*) the relative numbers of sulfur and of oxygen atoms;
(*c*) the simplest formula for the oxid of sulfur;
(*d*) the simplest chemical equation for the burning of sulfur.

Ans. (*a*) 50 % sulfur; 50 % oxygen.
(*b*) 1 atom of sulfur to 2 atoms of oxygen.
(*c*) SO_2.
(*d*) $S + 2\,O \rightarrow SO_2$.

17. It has been found by experiment that 3.1 grams of phosphorus unite with 4 grams of oxygen. Make the calculations as enumerated above.

18. When iron burns, 21 grams of iron unite with 8 grams of oxygen. Make the similar calculations in this case.

QUESTIONS

1. A gasometer is capable of holding 20 liters of gas: how much zinc must be treated with acid, in order to fill the gasometer with hydrogen, the temperature being 20° and the atmospheric pressure 765 mm.?

2. Nitric acid is found by analysis to have the composition

Hydrogen 1.6 %, Nitrogen 22.2 %, Oxygen 76.2 %.

Calculate the simplest formula for the acid.

3. (*a*) 10 grams of sugar are dissolved in water. On evaporation of the liquid, how much residue will be obtained. (*b*) 10 grams of zinc are dissolved in hydrochloric acid. On evaporation of the liquid, how much residue will be obtained? (*c*) Explain the difference in (*a*) and (*b*).

4. How much potassium chlorate must be heated to furnish enough oxygen to consume 6 grams of sulfur? (Find a short method.)

5. 10 grams of sulfur are set on fire in a bottle containing the oxygen obtained by heating 15 grams of potassium chlorate. How much sulfur, if any, will remain unconsumed?

6. How many grams of hydrogen will be evolved from the action of acid on 100 grams of zinc, if the zinc contains 2 % of impurities?

7. To obtain 5 liters of oxygen gas, how much potassium chlorate containing as an impurity 3 % of potassium chlorid must be used?

8. If 10 grams of magnesium are heated in 10 grams of oxygen, what will result and how much?

9. How much hydrogen can be obtained by the action of 100 grams of zinc on 200 grams of sulfuric acid?

10. It has been found that when charcoal burns, 3 grams of carbon unite with 8 grams of oxygen to form oxid of carbon. Calculate

(*a*) the percentage composition of this oxid of carbon;
(*b*) the relative numbers of carbon and of oxygen atoms
(*c*) the simplest formula for this oxid of carbon;
(*d*) the chemical equation for the burning.

CHAPTER XI

SODIUM, A NOVEL METAL

By the electrolysis of molten salt the element sodium may be obtained, as we have seen. Sir Humphry Davy first prepared the element in 1807 by the electrolysis of fused "soda lye," or sodium hydroxid, NaOH. At this time the experiment attracted much attention because of the fact that "soda lye" had never before been decomposed and was considered to be an elementary substance. Moreover, the new element, sodium, is undoubtedly a metal, for it possesses a brilliant luster and conducts heat and electricity well. Nevertheless, its other properties are so very different from the metals commonly known at that time that much discussion arose.

No method of preparing sodium better than the electrolysis of sodium hydroxid is known. It is produced in this way at Niagara Falls and other places where electric power is cheap.

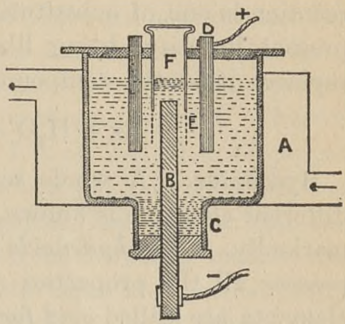

Fig. 28.

In Fig. 28 a steel cylinder, *A*, is shown, so placed in a flue that the neck, *C*, remains cool while the body of the cylinder is heated by hot gases from a furnace. *D* is a cylindrical carbon anode. Over the iron cathode, *B*, a collecting pot, *F*, is placed, from the bottom of which hangs a wire gauze, *E*, surrounding the cathode. When liberated on *B*, sodium floats up through the fused lye and collects in *F*, the wire gauze preventing its escape as it rises.

Sodium is a soft, silver-white, lustrous metal, melting at 96°. It is a very active element, uniting readily with non-metals to form compounds which are generally very stable. It is attacked by the water vapor in the atmosphere so rapidly that only a freshly cut surface shows its true luster, and this tarnishes almost instantly. For this reason the metal must be preserved under petroleum or in an atmosphere that will not attack it.

The action of the atmosphere on sodium is the same that takes place more rapidly when the element is brought in contact with water. The latter is decomposed and hydrogen is liberated, as we have seen. The sodium disappears in the water, giving to it a soapy taste and slippery feeling. Upon evaporation of the solution, sodium hydroxid, NaOH, is obtained. An investigation shows that the reaction is one of substitution, one half of the hydrogen present in water being liberated by the sodium which replaces it in the compound, as the equation indicates.

$$Na + H_2O \rightarrow NaOH + H$$

Hydroxids. A whole series of the hydroxids of the different elements is known, the properties of which differ markedly. *The hydroxids of non-metals* are acids* and possess all the properties of acids. Hence non-metallic elements are called *acid-formers.*

Hydroxids of the metals, however, give a bitter, soapy taste and slippery feeling to their solutions, turn red litmus blue, and affect other indicators similarly. They possess the power of destroying or neutralizing the properties of acids, as we have seen. *The hydroxids of metals are bases.* For this reason metallic elements are known as *base-formers.*

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* As we have seen (p. 87), certain non-metals form acids also by union with hydrogen alone, no oxygen being present in these compounds.

By the interaction of a base with an acid, a salt and water are produced, as was previously shown.

$$NaOH + HCl \rightarrow NaCl + H_2O$$

Just as we found a common factor present in every acid to which we could ascribe the properties which all acids possess, so in dealing with bases we say that the soapy taste, slippery feeling, and action on acids are due to the hydroxyl group; for no substance possesses these basic properties which does not contain at least one hydroxyl radical. But many substances containing hydroxyl groups do not act as bases, hence it must be that there is some peculiarity about the hydroxyl group in bases which is not characteristic of other substances containing oxygen and hydrogen. This we shall find is true.

The main points of difference between sodium and the metals of everyday acquaintance are its remarkable lightness and the formation by it of a soluble hydroxid possessing the properties of bases in an extreme degree. Whereas the specific gravity of iron is 7.8, of lead 11.4, of copper 8.9, of tin 7.3, of gold 19.3, the specific gravity of sodium is slightly less than 1. Experience has shown that the light metals (as distinguished from the heavy metals) are those in which the properties of bases are most strongly developed. Furthermore, most of the light metals form soluble hydroxids. The hydroxids of the heavy metals are so little soluble that, except for the fact that they neutralize acids readily, they do not show the properties of bases to any appreciable extent.

Soluble hydroxids. Metallic hydroxids that are soluble may be prepared by the action of the metals or their oxids on water, and also by special methods applicable in individual cases. *Potassium hydroxid*, KOH, is very similar to sodium hydroxid in all of its properties and is generally used interchangeably with it. These two substances are known as *alkalis* and are commonly called *caustic soda* and *caustic potash.* *Calcium hydroxid*, or *slacked lime*, $Ca(OH)_2$, is not so soluble and does not possess basic properties to quite so great a degree, but is much cheaper than either. It is much used in the industries. *Barium hydroxid*, $Ba(OH)_2$, resembles calcium hydroxid and finds use in the laboratory. The following are typical reactions:

$$\begin{aligned} K + H_2O &\rightarrow KOH + H \\ K_2O + H_2O &\rightarrow 2\,KOH \\ CaO + H_2O &\rightarrow Ca(OH)_2 \\ BaO + H_2O &\rightarrow Ba(OH)_2 \end{aligned}$$

Insoluble hydroxids may be prepared by adding a soluble hydroxid to a solution of a salt of the metal whose hydroxid is desired. The reaction runs to completion because of the insolubility of the desired hydroxid, which is formed as long as there is material present to produce it.

$$\begin{gathered} MgCl_2 + 2\,NaOH \rightarrow \mathbf{Mg(OH)_2} + 2\,NaCl \\ FeSO_4 + 2\,KOH \rightarrow \mathbf{Fe(OH)_2} + K_2SO_4 \end{gathered}$$

Spectroscope. When any sodium compound is introduced into the flame of a Bunsen burner, the flame is colored an intense yellow. Many other elements act similarly; potassium salts color a flame lavender; calcium, orange; barium, green, etc. Chlorids produce this effect more readily than other common compounds, hence by moistening a substance with hydrochloric acid and heating it in a Bunsen flame, some indication as to the elements it contains may often be obtained.

When sunlight is looked at through a prism of glass, it is separated into a series of colors — red, orange, yellow, green, blue, indigo, violet — known as the *spectrum* (Fig. 29). A *spectroscope* (Fig. 30) is an instrument depending on this principle, used to examine light and determine the different colors out of which it is blended. Light, entering the spectroscope through a narrow slit at *A*, passes through the prism, *P*, and is separated into a spectrum which, when viewed by the eye at *E*, appears spread out over considerable distance.

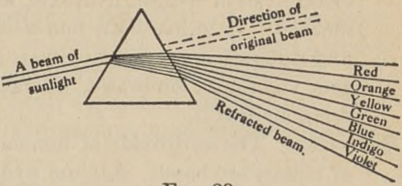

FIG. 29.

The light given by sodium compounds is yellow only. Viewed through a spectroscope, it appears as a single yellow line. Potassium gives a red and a blue line, calcium a red and a green line, barium a series of green lines, etc. Under proper conditions each element gives a series of lines of this character, by which it may be distinguished from every other element. Since mere traces of material are all that is necessary to give these indications, the spectroscope is one of the best means of analyzing a substance. To obtain the spectrum of many elements, however, temperatures higher than that of a Bunsen flame are frequently necessary, and the electric arc or other form of electrical discharge is often required.

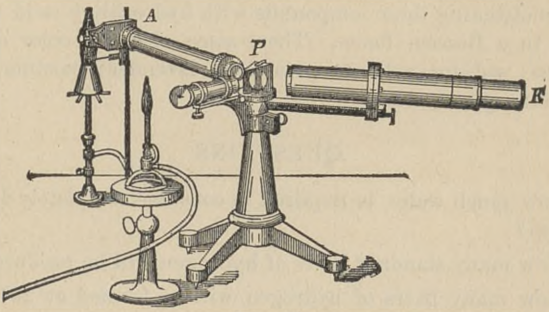

FIG. 30.

SUMMARY

Sodium was first prepared in 1807 by Sir Humphry Davy by the electrolysis of sodium hydroxid, and is still prepared by the same method. It unites with non-metals to form stable compounds, and differs from common metals mainly in being very light. It acts vigorously on water, liberating hydrogen and forming sodium hydroxid.

Hydroxids. The hydroxids of non-metals are acids. The hydroxids of metals are bases. Sodium hydroxid is a typical representative of the strong bases. Their solutions have a soapy taste and slippery feeling, turn red litmus blue, and neutralize acids. The hydroxids of the light metals are soluble and are the strongest bases. Insoluble hydroxids may be prepared by adding a soluble hydroxid to a solution of a salt of the metal whose hydroxid is desired.

The spectroscope is an instrument for determining what elements are present in a substance by means of the *spectrum* produced. Each element gives a series of lines different from every other element. Those elements which are the strongest base-formers require a lower temperature than others. Their spectra may be produced by moistening their compounds with hydrochloric acid and heating in a Bunsen flame. These same elements color a Bunsen flame: sodium, yellow; potassium, lavender; calcium, orange; barium, green, etc.

QUESTIONS

1. How much water is required to consume completely 4.6 grams of sodium?

2. How many standard liters of hydrogen will be produced?

3. How many liters of hydrogen will be formed at 20° and 750 mm. if it is collected over water?

4. How much sodium hydroxid will be formed in the reaction?

5. How much hydrogen chlorid would be required to neutralize this amount of sodium hydroxid?

6. How much sodium chlorid would be formed in the neutralization?

7. If this sodium chlorid were electrolyzed, how much sodium would be obtained?

8. If a solution of sodium chlorid, instead of fused salt, is electrolyzed, what becomes of the sodium?

9. A solution containing the magnesium chlorid formed from 2.4 grams of metal is treated with sodium hydroxid in sufficient quantity to precipitate all the magnesium as hydroxid. The filtered liquid is electrolyzed. What are the products formed at each electrode? Calculate the amount of soluble product formed at the kathode. How does this amount compare with the amount used to precipitate the magnesium hydroxid?

10. If both sodium and potassium hydroxids cost the same per pound, which would you use for neutralizing acids? If you were a manufacturer using 100 tons of sodium hydroxid per year, how much would you make (or lose) by substituting potassium hydroxid for sodium hydroxid?

CHAPTER XII

THE ATMOSPHERE AND NITROGEN

FROM previous experiments we have learned that air supports combustion because of the presence in it of oxygen which unites with the burning substance. When a combustible substance that forms a solid ash is set on fire in a volume of confined air, the flame goes out when about one fifth of the air has been absorbed. The remaining four fifths will not support combustion. This residual gas consists almost entirely of nitrogen, a name signifying "niter-former," for niter is an important compound of nitrogen.

Preparation. The method of obtaining nitrogen from the atmosphere by causing the oxygen to unite with some substance that will burn, such as phosphorus or copper, is slow and tedious and it does not give pure nitrogen. A better way is to heat a concentrated solution of ammonium chlorid to which a solution of sodium nitrite is gradually added from a dropping funnel. A metathesis takes place, forming ammonium nitrite, which decomposes into nitrogen and water according to the equations:

$$\mathrm{NH_4Cl + NaNO_2 \rightarrow NaCl + NH_4NO_2}$$
$$\mathrm{NH_4NO_2 \rightarrow 2\,\mathit{N} + 2\,H_2O}$$

Properties. Nitrogen (N—14) is a colorless, odorless, tasteless gas which at 194° below zero condenses to a colorless liquid much like water in appearance. It freezes at – 214°. Nitrogen is not poisonous, yet an animal placed in it drowns; *i.e.* dies from lack of oxygen just as if immersed in water. Slightly less than four fifths of the atmosphere is nitrogen.

When in the free state, nitrogen is one of the most inactive of elements. Compounds of nitrogen are relatively unstable; many of the simpler compounds are endothermic. These facts explain why most of the element is found free in the air instead of being locked up in compounds in the earth's crust. Under ordinary conditions nitrogen does not react with any other element, but under the influence of the electric spark it may be made to combine with oxygen to form oxids. It unites slowly with some other elements, also, at elevated temperatures, forming a class of compounds called *nitrids.* Thus, with red-hot magnesium it forms magnesium nitrid, Mg_3N_2. By the use of indirect means nitrogen may be obtained in combination with many elements with which it does not ordinarily unite.

Nitrogen and life. Nitrogen is an essential constituent of all living things. Animals appear to have no power of absorbing or using nitrogen or any other constituent of the atmosphere except oxygen. They must get their nitrogen from plants which they eat, or from other animals which have fed upon plants. In both plants and animals the nitrogen exists combined with carbon, hydrogen, oxygen, and sulfur in substances known as *proteids.* It was for a long time supposed that plants were dependent for their supply of nitrogen on compounds of this element existing in the soil. It has been found, however, that when certain peas, beans, and clovers are planted in soil that has been carefully analyzed, after growth the plants contain more nitrogen than was originally in the seed and the soil together. The inference is that such plants can in some way absorb the nitrogen of the air and cause it to enter into combination.

This power of assimilation does not reside in the plant itself, but has been shown to be due to the presence on its roots of certain bacteria, very minute forms of life, which absorb nitrogen from the air and convert it into compounds that are then taken up by the plant.

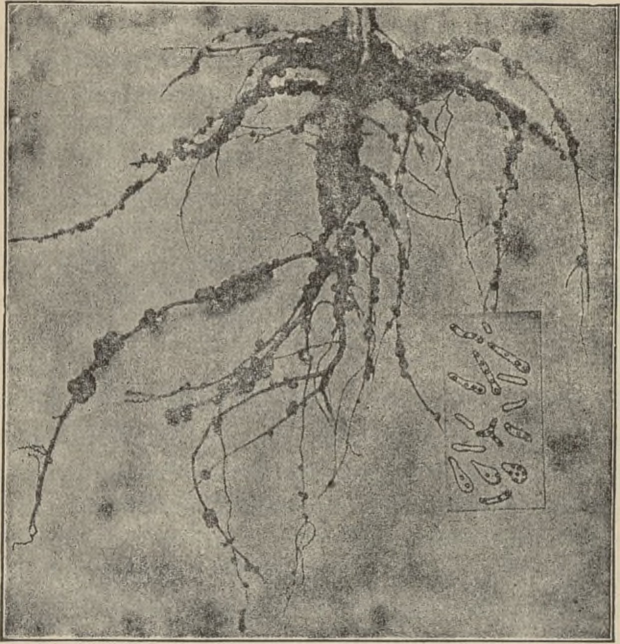

Fig. 31.

If one pulls up a clover plant, washes off the adhering soil from the roots, and examines them carefully, he will find small nodules (Fig. 31) in considerable numbers. These nodules are the abodes of the bacteria that absorb nitrogen. Farmers often sow clover, vetch, etc., on fields and orchard lands and then plow the crop under. The soil is thus enriched by the nitrogen absorbed from the atmosphere and held by these plants.

Decay. Most animal and vegetable substances contain the elements carbon, hydrogen, oxygen, and nitrogen in chemical combination. When they decay or are heated out of contact with air, decomposition into various simpler compounds of these elements takes place, such as water, H_2O, carbon dioxid, CO_2, marsh gas, CH_4, and ammonia, NH_3.

In the presence of certain bacteria, the decay of nitrogenous substances takes a different course. The nitrogen enters into combination, not with hydrogen alone, but with both hydrogen and oxygen, to form nitric acid, HNO_3. This manner of decomposition is favored by warmth and by the presence of something of a basic nature with which the acids can combine, for too much free acid kills the bacteria. Potassium nitrate, KNO_3, and sodium nitrate, $NaNO_3$, are thus formed and are common constituents of soils, especially in warm countries.

Ammonia and the compounds of nitric acid are in the main the materials from which other compounds of nitrogen are derived. These are obtained from animals and plants, and the latter derive them from bacteria. Hence it may be seen that the nitrogen compounds important in commerce and indispensable in the processes of life depend on the existence of these microscopic living things.

Other gases of the atmosphere. Besides oxygen and nitrogen, the following substances are present in the air:

1. *Water vapor* is present in the atmosphere in variable amount, the quantity depending on the temperature and on the proximity of natural bodies of water from which evaporation may take place. When the air contains about all the water vapor which it can hold, the atmosphere is said to be *humid*. When relatively little is present, the air is *dry*. The presence of "moisture" in the air is shown by the deliquescence of calcium chlorid and similar substances.

2. *Carbon dioxid* is another regular constituent of the air, its proportion being about 3 parts in 10,000 parts of air. Oxidation of carbonaceous matter, *i.e.* fires, decay, the breathing of plants and animals, and other natural processes, maintain the amount of carbon dioxid in the atmosphere.

3. *The argon group.* If air which has been freed from carbon dioxid and water vapor is passed repeatedly over red-hot magnesium, both oxygen and nitrogen combine with it, forming magnesium oxid and nitrid, both solid substances. Nevertheless a gaseous residue always remains. Nitrogen may be removed from air also by causing it to unite with oxygen under the influence of the electric spark, and the oxids of nitrogen thus formed may be absorbed in sodium hydroxid. After treatment in these and other ways that remove oxygen and nitrogen, about one per cent of the air always remains.

These processes were followed more than a hundred years ago by Cavendish, who did not realize that he had separated any new element. In 1894, however, two English chemists, Rayleigh and Ramsay, succeeded in separating this last fraction of the atmosphere into four distinct substances and proved that each was a new element. *Argon* constitutes about one per cent of the atmosphere; *neon*, *krypton*, and *xenon* occur in very minute quantities. Another element, *helium*, very abundant in the sun, is present in the atmosphere in small amount, together with traces of hydrogen, ammonia, and nitric acid.

Argon is so named from a Greek word meaning "lazy" or "inert," for no one has yet been able to make it unite with any other element. In this and in most other respects the other rare elements of the atmosphere resemble argon very closely.

Air a mixture and not a compound. The atmosphere is thus seen to be a complex mixture of several gases. That it is a mixture and not a compound is evident from several facts.

1. At different times or in different places the air varies in composition. Though slight, these variations are sufficient to show that air is not of constant composition and definite proportions.

2. When allowed to diffuse through a porous partition, the gas that first passes through is not of the same composition as the later portion or as the original air; for the lighter ingredients in the mixture diffuse through more rapidly than the heavier ones. If a compound is treated in a similar way, each particle that passes through has the same composition as those particles that are left behind.

3. When air dissolves in water, it does not dissolve as a compound does. A certain oxid of nitrogen is readily soluble in water and has the composition 63% nitrogen and 37% oxygen. When this gas is obtained again on boiling the solution, its composition is unchanged. On the other hand, when air dissolves in water, oxygen dissolves in larger proportion than nitrogen. When the water is heated, the gas that comes off is about two volumes of nitrogen to one of oxygen instead of four of nitrogen to one of oxygen.

4. When air is liquefied, it acts like a mixture and not a compound. Nitrogen boils at 79° and oxygen at 90° absolute temperature. Consequently nitrogen boils away more rapidly than oxygen, until the last portion left contains less than 10 per cent of nitrogen. In this way oxygen is prepared commercially.

Liquid air. Since air is the commonest of all gases, it has been liquefied in large quantities. When a gas is compressed, it grows hot; if allowed to expand, it grows cold. Air, compressed to a pressure of 3000 pounds, is cooled down by running water, and thus a large portion of its energy is removed. This cooled compressed gas is then allowed to expand. The liquefier is so arranged that the escaping air circulates around the pipes which hold the compressed air, thus cooling it down gradually until so low a temperature is reached that a portion of the compressed gas condenses to the liquid state. In appearance liquid air resembles water, but it is exceedingly cold, its boiling temperature being somewhere between – 194° and – 183°, the boiling points of nitrogen and oxygen, respectively.

At this temperature most things are frozen solid, and many substances undergo considerable change in properties. Flowers, vegetables, and meat, all largely composed of water, instantly change to ice; mercury and alcohol solidify; and a tallow candle may be powdered between the fingers. A tin dipper must be handled with care lest it break, and rubber becomes as brittle as glass.

Liquid air has little practical use save in the production of intense cold and the manufacture of oxygen. Since the ordinary temperature, about 20°, is more than 200° hotter than the temperature of liquid air, it constantly boils away. If the attempt were made to seal it up and prevent its evaporation, it would burst any container, just as water heated to 300° would burst a boiler. No way of preserving it is known except to insulate it well and prevent heat from getting to it, for no liquid can change to a gas except by the absorption of heat or some other form of energy.

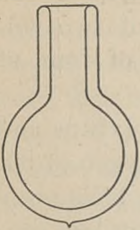
FIG. 32.

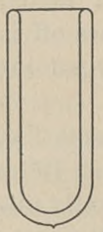
FIG. 33.

The most satisfactory method of insulating liquid air and other liquids of low boiling point is by the use of Dewar flasks, so named from the man who originated them. A double-walled flask is made of glass, one flask being blown inside the other (Fig. 32). The space between the walls is silvered like a mirror, and then the air is pumped out. Glass is a poor conductor of heat, convection is prevented by removing the air between the walls, and light and other forms of radiant energy are reflected by the mirror surface. In this way the access of heat by conduction, convection, and radiation is prevented. Thermos bottles are made on the same principle (Fig. 33).

SUMMARY

NITROGEN.

Preparation. Nitrogen may be prepared

1. In an impure condition by removing the oxygen from air.
2. In pure form by decomposing ammonium nitrite by heat.

Properties. It is a colorless, odorless, tasteless gas. Chemically it is very inactive, but it may sometimes be induced to combine with other elements to form nitrids and other compounds which are comparatively unstable.

In living things. Nitrogen is an essential constituent of living things. It is not absorbed directly from the air, except by bacteria. They cause nitrogen to enter into chemical compounds which plants can utilize. Animals derive their nitrogen from plants.

Compounds of nitrogen are formed in nature by the decay of the remains of living things. In this process the nitrogen may form

1. Nitrates, when the proper bacteria are present, together with a basic substance to neutralize the nitric acid first formed.
2. Ammonia, when the above conditions are absent.

THE ATMOSPHERE.

Contains other gases. Besides nitrogen and oxygen,

1. *Water vapor* is present in variable amounts.
2. *Carbon dioxid* forms about $\frac{3}{10000}$ and is formed by the oxidation of carbonaceous matter.
3. *Argon* and similar inert gases form about one per cent.

Air is a mixture, not a compound, because

1. It varies in composition, while compounds do not.
2. It diffuses like a mixture, not like a compound.
3. It dissolves like a mixture, not like a compound.
4. Liquid air evaporates like a mixture.

QUESTIONS

1. Calculate the weight of 1 liter of nitrogen, its specific gravity to air being 0.97 and the weight of 1 liter of air being 1.293 grams. What is the gas density of nitrogen?

2. Compare the weight of a liter of nitrogen with the weight of a liter of hydrogen. What is the ratio? Compare this ratio with the ratio between their atomic weights. What relation exists?

3. Compare similarly chlorin with hydrogen.

4. Compare similarly oxygen with hydrogen.

5. Of what use is the nitrogen in the air? If it were absent what changes would take place?

6. How may the water vapor be removed from a body of air, leaving it in a dry condition?

7. Why was the recognition of argon so long delayed?

8. On standing, liquid air turns blue. Why?

9. Why is nitrogen found more commonly in substances of animal and vegetable origin than in minerals?

10. How much nitrogen by weight and by volume can be obtained from 10 grams of ammonium nitrite?

11. Supposing that the air contains four volumes of nitrogen to every one volume of oxygen, calculate the composition of the mixture of air and hydrogen that will explode and leave no residue of oxygen.

12. Ice placed in liquid air makes it boil violently. Why? At the same time the ice grows very cold. Why?

CHAPTER XIII

NITRIC ACID AND THE OXIDS OF NITROGEN

UNDER the name of "aqua fortis," as early as the ninth century nitric acid was known to the alchemists, who prepared it by heating niter with certain other substances. Nothing was known of its composition until Cavendish produced it by passing electric sparks through a mixture of hydrogen, oxygen, and nitrogen. To-day the acid is prepared by heating sodium nitrate with sulfuric acid. Two reactions may take place, the second one requiring temperatures higher than ordinary.

$$NaNO_3 + H_2SO_4 \leftrightarrow NaHSO_4 + HNO_3$$
$$2\ NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2\ \mathit{HNO_3}$$

Exactly the same principles govern these reactions as apply in the manufacture of hydrochloric acid. In solution the reaction runs to equilibrium, but at higher temperatures nitric acid is volatile. Hence it distils out of the mixture, thus preventing a reversal of the reaction.

Pure nitric acid is a colorless, oily liquid that fumes in the air because its vapor unites with water vapor and condenses in minute drops to form clouds. It is 1.5 times as heavy as water and boils at 86°. As it boils it is partially decomposed into water, oxygen, and oxids of nitrogen. The last-named substances are brown gases that dissolve in the acid and give it a yellow color. If the acid be distilled repeatedly, this decomposition continues until a distillate results which has the composition HNO_3

68% and H_2O 32%. This product is fairly stable and boils at 120.5°. It is known as "**concentrated nitric acid,**" the pure product — 100% HNO_3 — never being found on the market.

Properties. In its chemical properties nitric acid combines the qualities of a strong acid and a good oxidizing agent. The first depend upon the compound as a whole, the latter upon its breaking down into unstable decomposition products.

Acting as an acid, nitric acid attacks metals and dissolves all oxids and hydroxids of metals, forming salts called *nitrates*, all of which are soluble. Although nitrates are among the products of the ordinary decomposition of animal matter, no large deposits are found except in rainless regions. Potassium nitrate, known as *niter* or *saltpeter*, comes from India and Peru. Sodium nitrate is found in large deposits in Chili and is known as *Chili saltpeter*. It is in great demand for the manufacture of nitric acid and for use as a fertilizer. Since it takes up water and deliquesces, it is not used for explosives as niter is.

The acid properties of nitric acid are best observed in dilute water solutions, for under these conditions its oxidizing action is least. Conversely, just in proportion as nitric acid is freed from water, it loses its acid properties and acts to best advantage as an oxidizing agent. We shall find this true of all acids which are also oxidizing agents.

Acting as an oxidizing agent, nitric acid stains the skin yellow, destroys vegetable and animal fabrics, and, if the action is sufficiently long continued, may oxidize wood and similar materials entirely.

It dissolves silver, copper, and mercury, metals which are not attacked by the strongest acids unless they possess some oxidizing properties. Gold and platinum alone resist its action.

When nitric and hydrochloric acids are mixed (best proportions 1 to 3), the former oxidizes the latter, forming *nitrosyl chlorid*, $NOCl$, an unstable substance, and liberating chlorin in the nascent condition.

$$HNO_3 + 3\ HCl \rightarrow NOCl + 2\ H_2O + 2\ Cl$$

This mixture containing nascent chlorin reacts with many substances which resist the action of any single acid. Since gold is acted on by chlorin, this mixture dissolves the "king of metals" and hence was named **aqua regia**, "the royal water." By the action of "aqua regia," chlorids are formed.

To the oxidizing action of nitric acid and its salts are due many of their industrial uses. *Gunpowder* is an intimate mixture of charcoal, sulfur, and niter. Its explosive action depends on the fact that potassium nitrate converts the carbon into oxids that are gaseous and under normal pressure occupy many times as great a volume as the gunpowder. Consequently a tremendous pressure develops which causes the explosion.

Nitrates are decomposed only at fairly high temperatures, salts being always more stable than the corresponding acids. Hence nitrates are used as oxidizing agents in fireworks, explosives, and the like.

When nitric acid acts on wood or cotton, under proper conditions, complete oxidation does not take place, but a derivative of nitric acid and the substance is formed. Cotton fibers consist mostly of a material called *cellulose*, and the product of the action of nitric acid on cellulose is cellulose nitrate, commonly called *gun-cotton*. If glycerine, another organic substance, be used in place of cotton, glycerine nitrate, or *nitroglycerine*, is obtained. These compounds of nitric acid are combustible, and, as they contain within themselves sufficient oxygen for complete combustion, they are capable of burning in closed spaces.

The composition of gun-cotton is expressed by the formula $C_{12}H_{14}N_6O_{22}$, each molecule of the substance containing more oxygen than is sufficient to convert all of the carbon present into carbon monoxid CO, and all the hydrogen into water. When the equilibrium of such a substance is disturbed by heat or by a shock, the material is completely converted into gases, the expansion of which causes the explosion (Fig. 34).

The oxidizing action of nitric acid and its salts depends primarily on the decomposition of the acid with the liberation of oxygen. How much oxygen will be set free depends on many circumstances, such as temperature, dilution, and the nature of the reducing agent present. The dioxid is the oxid of nitrogen most frequently produced; for, in the presence of reducing agents, it is more stable than any of the higher oxids of nitrogen. Hence, the following equation expresses a typical reaction:

$$2\,HNO_3 \rightarrow H_2O + N_2O_2 + 3\,O$$

The fact that nitric acid is such a good oxidizing agent complicates the reaction of this acid with metals. When zinc or iron is brought in contact with sulfuric or hydrochloric acid, hydrogen is liberated.

When nitric acid acts on metals, hydrogen is not obtained. The primary reaction is doubtless the same in each case. Since hydrogen, especially in the nascent state, is a powerful reducing agent, as soon as it is set free from one molecule of acid it interacts with the rest of the acid. A mixture of substances is usually formed in this reaction. Any one of the following reaction products is theoretically possible, and most of them can be detected practically as the conditions of the experiment are varied:

Photo by J. N. Le Conte

FIG. 34. — NITROGLYCERINE EXPLOSION UNDER WATER

The removal of Arch Rock, San Francisco harbor.

$2\,HNO_3 + 0\,H \rightarrow 1\,H_2O + N_2O_5$	Nitrogen pentoxid
$2\,HNO_3 + 2\,H \rightarrow 2\,H_2O + N_2O_4$	Nitrogen tetroxid
$2\,HNO_3 + 4\,H \rightarrow 3\,H_2O + N_2O_3$	Nitrogen trioxid
$2\,HNO_3 + 6\,H \rightarrow 4\,H_2O + N_2O_2$	Nitrogen dioxid
$2\,HNO_3 + 8\,H \rightarrow 5\,H_2O + N_2O$	Nitrogen monoxid
$2\,HNO_3 + 10\,H \rightarrow 6\,H_2O + N_2$	Nitrogen
$2\,HNO_3 + 12\,H \rightarrow 6\,H_2O + N_2H_2$	Diimid*
$2\,HNO_3 + 14\,H \rightarrow 6\,H_2O + N_2H_4$	Hydrazine*
$2\,HNO_3 + 16\,H \rightarrow 6\,H_2O + (N_2H_6) = 2\,NH_3$	Ammonia

The first equation shows that nitric acid may be considered as the pentoxid of nitrogen, N_2O_5, plus water. *Any oxid that may be formed by the separation of water from an acid is known as an* **anhydrid**; hence nitrogen pentoxid is known as nitric anhydrid.

All of the compounds of nitrogen given as reaction products in the preceding equations may be considered as reduction products of the pentoxid, N_2O_5. Conversely, all may be considered as oxidation products of ammonia, NH_3. So far as the oxids are concerned, this is obvious.

That **the removal of hydrogen is equivalent to the addition of oxygen**, and *vice versa*, may not be self-evident. This point may be best shown by the consideration of a concrete case. If ammonia is oxidized, we may consider that the oxygen attaches itself directly, forming a compound NH_3O. If this new compound subsequently decomposes into NH and H_2O, this does not lessen the fact that NH is an oxidation product of NH_3 as well as H_2O. Yet NH is simply NH_3 from which hydrogen has been removed. Further oxidation may remove all the hydrogen and later add oxygen. *The removal of hydrogen is as truly an instance of oxidation as is the addition of oxygen;*

---

* Diimid, N_2H_2, is entirely unknown, but derivatives of it have been prepared. Hydrazine, N_2H_4, is a colorless liquid quite similar to ammonia in some of its properties.

and conversely *the addition of hydrogen is reduction quite as much as is the removal of oxygen or any other non-metallic element.*

The **oxids of nitrogen** have the composition given in the table.

COMPOSITION OF THE OXIDS OF NITROGEN

NAME	PERCENTAGE RATIOS		SIMPLE RATIOS	RATIOS BY VOLUME	FORMULA
	N	O	N : O	N : O	
Nitrogen monoxid	63.70	36.30	[*]28 : 16	2 : 1	N_2O
Nitrogen dioxid	46.74	53.26	28 : 32	2 : 2	N_2O_2
Nitrogen trioxid	36.91	63.09	28 : 48	2 : 3	N_2O_3
Nitrogen tetroxid	30.49	69.51	28 : 64	2 : 4	N_2O_4
Nitrogen pentoxid	25.98	74.02	28 : 80	2 : 5	N_2O_5

This series affords one of the most beautiful illustrations of the law of multiple proportions known to science. Since these substances are of interest in themselves, they will be briefly considered.

Nitrogen pentoxid, N_2O_5, may be produced by heating the pentoxid of phosphorus with nitric acid. The pentoxids of both nitrogen and phosphorus are acid anhydrids, but phosphoric acid is much more stable than nitric acid. If a mixture of the two pentoxids is treated with just enough water to convert one anhydrid into its acid, phosphoric acid will be formed rather than nitric acid. Hence when nitric acid is treated with phosphoric anhydrid, phosphoric acid is formed and nitric anhydrid, as the equation indicates:

$$2\,HNO_3 + P_2O_5 \rightarrow 2\,HPO_3 + N_2O_5$$

Nitrogen pentoxid is a colorless, crystalline solid decomposing very readily into the tetroxid and oxygen. If nitric acid be considered as nitrogen pentoxid plus water, since water is neither an oxidizing nor a reducing agent,

---

[*] Exact figure 28.08.

the oxidizing action of nitric acid must be due to its anhydrid.

It has been found by experience that *the character of the anhydrid determines the character of the acid and of the salts formed from it* to a large extent. If the anhydrid is unstable, so will the acid be, and the salts also to a less degree. If the anhydrid is an oxidizing agent, so will the acid and its salts be also. If the anhydrid be volatile, the acid will be volatile or else it will tend to decompose into water and the anhydrid, both volatile. In this case the salts will be more stable, but not so stable as the salts of an acid the anhydrid of which is not volatile. By learning the character of the anhydrid, therefore, we get the best key to the behavior of acids and their salts.

Nitrogen tetroxid, N_2O_4, or *peroxid,* as it is often called, may be prepared by heating lead nitrate, when the decomposition indicated by the equation takes place.

$$\mathrm{Pb(NO_3)_2} \rightarrow \mathrm{PbO} + O + N_2O_4$$

Such a decomposition is not confined to this particular salt, but is quite general for the nitrates of metals when they are heated without the presence of any reducing matter. The reaction is probably due to a primary decomposition into nitric acid anhydrid and an oxid of the metal corresponding to the oxid of hydrogen formed when hydrogen nitrate decomposes; for, as we have previously stated, the pentoxid of nitrogen readily decomposes into the tetroxid and oxygen.

Nitrogen tetroxid is a brown gas that condenses to a yellow liquid and freezes to a white solid. As the temperature increases above its melting point, the color becomes continually darker until at 150° the gas is almost black. Investigation of this phenomenon shows that at this temperature the gas occupies about twice as great a volume as it should if it expanded from ordinary temperatures to 150° according to Charles' law. The explanation is that as the temperature rises, each molecule of the tetroxid dissociates, but as the temperature falls the two parts reunite as the equation indicates.

$$N_2O_4 \longleftrightarrow 2\,NO_2$$

Nitrogen tetroxid is a strong oxidizing agent, readily giving up half of its oxygen to a reducing agent and breaking down into the dioxid. The dioxid unites with oxygen from the atmosphere to form the tetroxid again. Bodies of this nature are said to be "carriers" of oxygen, for by their agency many substances may be indirectly oxidized by the air which are not oxidized directly without their aid. A "carrier" is simply a catalytic agent whose action is well understood. These two oxids of nitrogen are employed in the manufacture of sulfuric acid, as we shall see later.

When an electric discharge takes place through air, oxygen and nitrogen combine to form the tetroxid. This may be absorbed in some strong base, as sodium hydroxid, when the following reaction takes place:

$$2\,NaOH + N_2O_4 \rightarrow NaNO_3 + NaNO_2 + H_2O$$

In places where cheap electric power may be obtained nitrates are manufactured according to this reaction, the nitrites being converted into nitrates by the use of nitric acid. The electric arc is much enlarged by being blown by a blast of heated air between heavy copper electrodes (Fig. 35a) until the flame reaches three or four feet in length. In this way a cheap method of making nitric acid and its salts from the atmosphere has been perfected.

This commercial process is very similar to what takes place in nature during thunder storms. The lightning flash is the original electric spark causing oxygen and

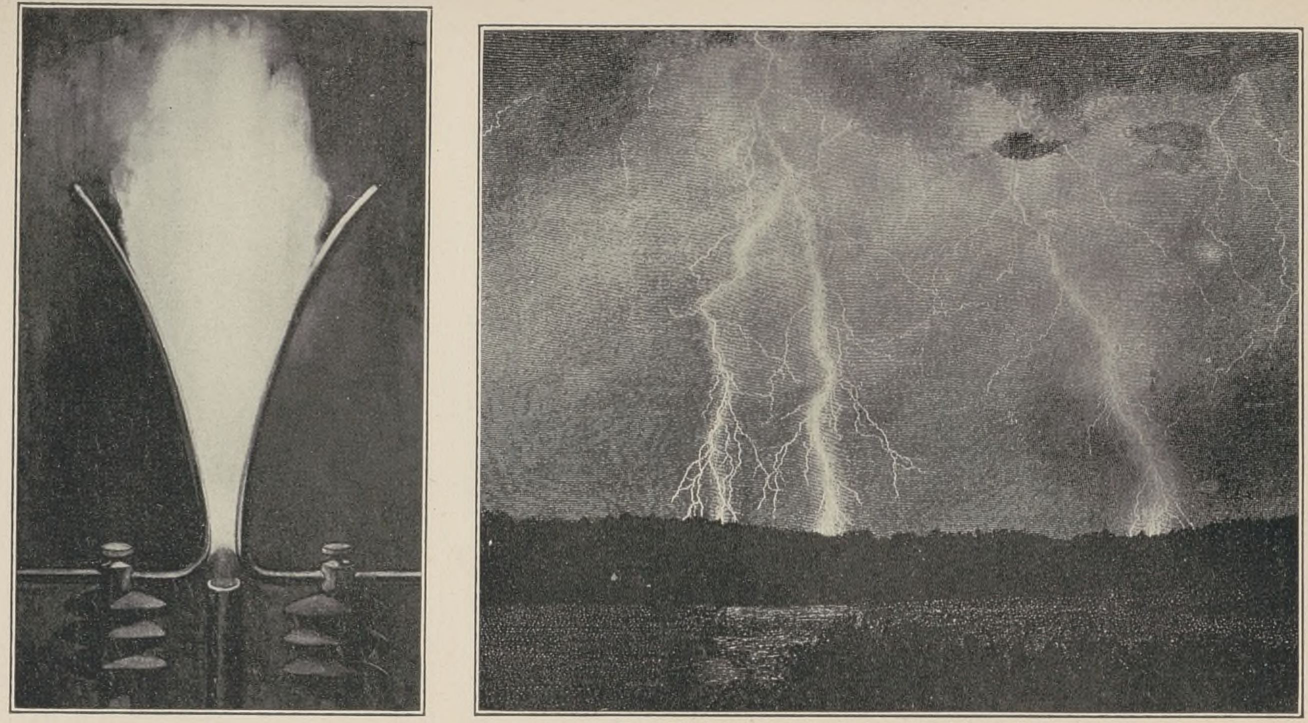

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FIG. 35. — NITRATES FROM THE ATMOSPHERE

(*a*) In the industries. (*b*) In nature.

nitrogen to combine. The rain, uniting with the oxid of nitrogen, forms nitric and nitrous acids which are carried down to the soil. It has been calculated that 20 pounds of nitric acid is added to each acre of land in this way every year. Since salts of nitric acid are among the most valuable plant foods, this world-wide action is very significant.

Nitrogen trioxid, N_2O_3, may be obtained as a blue liquid at low temperatures. At zero or below it decomposes into a mixture of dioxid and tetroxid, and hence has no existence at ordinary temperatures.

$$2N_2O_3 \rightarrow N_2O_2 + N_2O_4$$

Nitrogen trioxid is the anhydrid of *nitrous acid*, HNO_2, an unstable compound that has never been obtained free and exists to a slight extent only in solution. Its salts, the *nitrites*, are stable, and may be obtained by gently heating nitrates with mild reducing agents. The nitrate gives up one third of its oxygen, as the equation shows.

$$KNO_3 + Pb \rightarrow KNO_2 + PbO$$

On adding acid to a solution of a nitrite, the nitrous acid set free decomposes into water and the anhydrid.

$$KNO_2 + HCl \rightarrow KCl + HNO_2$$
$$2HNO_2 \rightarrow H_2O + N_2O_3$$

Being so unstable, nitrous acid may give up its oxygen or take on oxygen. It acts either as an oxidizing agent or as a reducing agent. Oxidizing agents convert it into nitric acid, each molecule of nitrous acid absorbing one atom of oxygen. On the other hand, reducing agents are oxidized by it, two molecules of nitrous acid giving up one atom of oxygen and breaking down into nitrogen dioxid and water. Substances that are neither oxidized as high as they may be, nor reduced as low as they may be, frequently act either as oxidizing or reducing agents under different conditions.

Nitrogen dioxid, N_2O_2,* or *nitric oxid*, as it is commonly called, may be obtained by treating copper with nitric acid. Since copper is a metal not appreciably attacked by strong acids, it is probable that the first action is not the liberation of hydrogen but rather the oxidation of the metal to the oxid. The oxid of the metal then dissolves in the acid to form a nitrate, as represented in the following equations:

$$2\,HNO_3 \rightarrow H_2O + \mathit{N_2O_2} + 3\,\mathit{O}$$
$$3\,Cu + 3\,\mathit{O} \rightarrow 3\,CuO$$
$$3\,CuO + 6\,HNO_3 \rightarrow 3\,Cu(NO_3)_2 + 3\,H_2O$$

Nitrogen dioxid is a colorless gas which on exposure to the atmosphere readily takes up oxygen and is converted into the brown tetroxid. It parts with its own oxygen less readily than any other oxid of nitrogen and therefore is the decomposition product most frequently formed when more highly oxidized compounds, such as nitrates and nitrites, break down.

Substances like phosphorus that burn vigorously in air continue to burn in nitrogen dioxid. The temperature of the flame in these cases is sufficient to decompose the dioxid into its elements, and there results a mixture of nitrogen and oxygen much richer in oxygen than air is. Substances that burn less energetically in air are extinguished in nitrogen dioxid, for the compound does not support combustion and the temperature is not high enough to decompose the latter and liberate its oxygen.

---

* Nitrogen dioxid seems to be completely dissociated at ordinary temperatures into two molecules of NO. At extremely low temperatures it may be that the substance N_2O_2 exists, but the only body that we know is NO. The proportion of oxygen to nitrogen is the same in either molecule, and hence we may call the substance nitrogen dioxid to avoid possible confusion.

Nitrogen monoxid, N_2O, *nitrous oxid*, is most readily obtained by heating ammonium nitrate, when the following reaction takes place:

$$\mathbf{NH_4NO_3} \rightarrow 2\,H_2O + N_2O$$

This reaction calls to mind the similar decomposition of ammonium nitrite with the formation of nitrogen gas instead of nitrogen monoxid.

$$NH_4NO_2 \rightarrow 2\,H_2O + 2\,N$$

Now that we have learned that nitric and nitrous acids are oxidizing agents, to explain these reactions we need simply state that ammonia is a mild reducing agent. The acid part of these salts oxidizes the ammonia part, the reaction so to speak taking place inside the molecule.

Nitrogen monoxid is a colorless gas with a sweet taste and odor and is somewhat soluble in water. By pressure and cold it is easily condensed to a liquid and in this form comes on the market enclosed in iron cylinders. Its most important use is as an anæsthetic. When inhaled in pure form, it produces insensibility; and, if one breathes it too long, death results. Mixed with air and taken into the lungs, it produces a kind of intoxication that gives it its common name of "*laughing gas.*" As the intoxication is accompanied by insensibility to pain, the gas is largely used in minor surgical operations. For this purpose it needs to be specially purified.

At ordinary temperatures nitrous oxid is quite stable, neither taking on more oxygen nor giving up its own. At higher temperatures it decomposes into its elements, the mixture containing a larger percentage of oxygen than air does. Hence, it supports combustion better than air.

SUMMARY

NITRIC ACID

Preparation. Nitric acid may be made from its elements, but is prepared in quantity by heating sodium nitrate with sulfuric acid.

Properties. It is a colorless, fuming liquid, heavier than water, boiling at 86° with partial decomposition. Concentrated nitric acid consists of 68% HNO_3 and 32% H_2O. It is colored yellow by its own decomposition products. Chemically it combines the properties of a strong acid with those of a good oxidizing agent.

1. *As an acid* it attacks the common metals, sometimes first oxidizing them. The nitrates thus formed are all soluble. Nitric acid shows its acid properties best in dilute solutions, but its oxidizing action is greatest in concentrated solutions, or in the absence of water. These statements hold true for other acids.
2. *As an oxidizing agent,* it oxidizes most organic substances, though it sometimes unites with them to form organic nitrates which are explosive. *Aqua regia,* a mixture of nitric and hydrochloric acids, is a powerful solvent because it evolves nascent chlorin and oxygen.

Reduction products. The oxidizing action of nitric acid depends on its decomposition with the formation of nitrogen pentoxid. Theoretically a complete series of reduction products is possible, ranging from N_2O_5 to NH_3. NH_3 is a reduction product of HNO_3, for the addition of hydrogen is equivalent to the removal of oxygen, and *vice versa.*

OXIDS OF NITROGEN

N_2O_5, nitrogen pentoxid, or *nitric anhydrid,* is obtained by removing the elements of water from nitric acid. A substance obtained by the abstraction of the elements of water from a compound is an *anhydrid.* The character of the anhydrid determines to a large extent the character of the acid, and, to a less extent, that of its salts.

N_2O_4, nitrogen tetroxid, is obtained by heating lead nitrate. It is a gas that condenses to a yellow liquid that freezes to a white solid. When heated its color grows darker, and its molecules are found to have dissociated into NO_2. The gas is used as a "carrier" of oxygen.

N_2O_3, nitrogen trioxid, exists only at a low temperature. It is the anhydrid of *nitrous* acid.

N_2O_2, nitrogen dioxid, or *nitric oxid*, is obtained by treating copper with nitric acid. It readily absorbs oxygen and is converted into the tetroxid.

N_2O, nitrogen monoxid, or *nitrous oxid*, is obtained by heating ammonium nitrate. It is used as an anæsthetic. At the kindling temperature of most substances it decomposes, and so is a good supporter of combustion.

QUESTIONS

1. How much nitric acid should be obtained from 1 ton of sodium nitrate?

2. Which yields a larger proportion of nitric acid when treated with sulfuric acid — sodium nitrate or potassium nitrate? Why?

3. Describe the chemical changes that come to equilibrium when concentrated sulfuric acid is poured upon sodium nitrate. Why is no nitric acid given off until heat is applied? To what temperature must the mixture be heated to make this reaction run to completion?

4. State two reasons why hydrochloric acid cannot be used to prepare nitric acid from its salts.

5. Why cannot nitric acid be used in the preparation of hydrogen?

6. Why cannot nitric acid stains be removed from clothing?

7. How many grams of oxygen gas would be absorbed when 1 liter of nitrogen dioxid oxidizes to the tetroxid?

8. With what volume of air must 1 liter of nitrogen dioxid be mixed to oxidize it completely? What contraction in the total volume of the gases will occur?

9. How many grams of nitrogen monoxid should be obtained from 20 grams of ammonium nitrate?

10. What is an acid anhydrid? What is the anhydrid of sulfuric acid, H_2SO_4; of carbonic acid, H_2CO_3; of chloric acid, $HClO_3$; of hydrochloric acid, HCl?

CHAPTER XIV

AMMONIA

Ammonia, NH_3, is formed in the natural decay of animal and vegetable substances, especially when the conditions for the formation of nitric acid are lacking. It is obtained in large quantities when coal, a vegetable product, is heated in retorts either to convert it into coke or for the manufacture of illuminating gas. To free it from impurities which would produce ill-smelling and injurious products when burned, the gas is bubbled through water in which the ammonia and some of the impurities dissolve. When this "gas liquor" is mixed with slacked lime and heated, the ammonia distills out and is absorbed in dilute sulfuric acid.

Preparation. Ammonia may be most readily prepared by treating ammonium chlorid, often called *sal ammoniac*, with a strong base. If potassium hydroxid is used, the reaction may be expressed by the equation

$$NH_4Cl + KOH \rightarrow KCl + H_2O + \mathit{NH_3}.$$

Slacked lime is often heated with ammonium chlorid, both reagents being in the solid state. The equation is

$$2\,NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2\,\mathit{H_2O} + 2\,\mathit{NH_3}.$$

Ammonia may be made in the laboratory by the direct union of nitrogen and hydrogen under the influence of the electric spark. The reaction comes to equilibrium when only 2 % of the mixture has combined to form ammonia, although 98 % of the mixed gases still remain uncombined. This fact indicates that ammonia must be quite an unstable body, for although present only to the extent of 2 % in the mixture of gases, as much ammonia decomposes into its elements as is formed from the 98 % of nitrogen and hydrogen present. The only way in which a given amount of nitrogen and hydrogen can be entirely converted by this method into ammonia is by absorbing the latter in acid as fast as it is formed. In this way the proportion of ammonia is kept continually below what is necessary for equilibrium. Hence the reaction goes in the direction to establish equilibrium, *i.e.* to form ammonia. For practical purposes the reaction is without value.

The relation of ammonia to nitric acid is shown by the fact that ammonia can be obtained by the complete reduction of the acid.

Properties. Ammonia is a colorless gas with a characteristic pungent odor and bitter taste. It does not support combustion nor does it burn in air, but it burns in oxygen, forming water and nitrogen. It is a little more than half as heavy as air. By pressure and cold it may be condensed to a colorless liquid boiling at – 33°. The heat of vaporization of ammonia is large and when it evaporates intense cold results. This fact is utilized in refrigeration and in the manufacture of artificial ice.

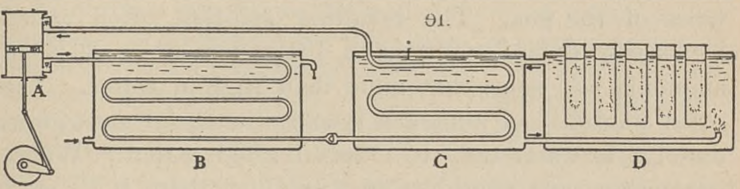

FIG. 36.

In an ice plant ammonia gas is compressed to about 10 atmospheres by means of a compressor, A (Fig. 36). The hot gas is cooled by passing through pipes immersed in water, B, or else having water trickling over them. Thus energy is taken from the gas and it condenses to the liquid state. The liquid ammonia is allowed to flow through pipes that pass back and forth in a large tank of salt water, C, from which it takes up heat and boils, thus being converted into gas again. After this it returns to the condensing pumps once more. The "brine" is cooled much below 0°, but does not freeze, for the freezing points of saturated solutions of sodium chlorid and of calcium chlorid, the two salts oftenest used, are – 21° and – 35° respectively. For refrigerating purposes the cold "brine" is conducted in pipes all about the building which it is desired to cool. In making ice, the "brine" is pumped into a second tank, D, in which are set rectangular cans of fresh water which loses heat to the "brine" and presently is frozen. Sometimes the second "brine tank" is done away with, and the cans of water are placed in C between the pipes carrying the liquid ammonia.

Ammonia gas is very soluble in water, 1 volume of the latter at ordinary temperature absorbing about 800 volumes of the gas. The resulting solution, often called "*ammonia water*," contains a little less than 30 % of ammonia and somewhat more than 70 % of water. The great solubility of ammonia is exceptional, for most gases dissolve in water only to a very limited extent. Where gases show any considerable solubility, there is in most cases evidence of chemical action between the water and the gas. In the present instance certain facts point toward the conclusion that when ammonia gas dissolves in water, these two substances unite according to the equation:

$$NH_3 + H_2O \longleftrightarrow NH_4OH$$

Ammonium hydroxid is the name given to the compound NH_4OH. It resembles in its chemical properties sodium and potassium hydroxids. It tastes soapy and feels slippery; it has the power to change red litmus to blue; it neutralizes acids and forms salts. It is a very unstable substance, readily decomposing into ammonia and water and existing only in solution.

When ammonium hydroxid is neutralized, the compounds formed resemble the compounds of sodium and potassium. In them the radical NH_4 appears to play the part of a metal, as may be seen by comparing the formulas of the compounds given below. Since the ending *-ium* signifies the possession of metallic properties, the group NH_4 is called *ammonium.*

HYDROXIDS	CHLORIDS	NITRATES	SULFATES	CARBONATES	SULFIDS
$NaOH$	$NaCl$	$NaNO_3$	Na_2SO_4	Na_2CO_3	Na_2S
KOH	KCl	KNO_3	K_2SO_4	K_2CO_3	K_2S
NH_4OH	NH_4Cl	NH_4NO_3	$(NH_4)_2SO_4$	$(NH_4)_2CO_3$	$(NH_4)_2S$

Ammonium. Considerable effort has been expended in the endeavor to isolate the ammonium radical and study its properties. Attempts in this direction have followed the methods by which sodium may be obtained from its compounds. Thus, when an aqueous solution of sodium chlorid is electrolyzed, the metal goes to the negative pole and the chlorin to the positive pole. Under the conditions of this experiment, sodium cannot be separated as a metal, however, for it reacts with water to form sodium hydroxid and liberates hydrogen. Similarly when an aqueous solution of ammonium chlorid is electrolyzed, the ammonium radical goes to the negative pole, where reactions take place, forming ammonium hydroxid and liberating hydrogen.

By using mercury as the cathode in the electrolysis of salt, the action of water on sodium is prevented; for the sodium dissolves in the mercury and is protected from the water. Mercury possesses the property of dissolving metals readily, forming solutions which, as they become concentrated, form crystalline solids. They are called *amalgams.* Sodium amalgam is solid and crystalline if it contains more than 2 % of sodium. By distilling off the mercury under the proper conditions we may obtain the sodium.

If a solution of ammonium chlorid is electrolyzed with a mercury cathode at low temperatures, a crystalline amalgam is obtained. Hence the radical is sufficiently like a metal to form an amalgam. As soon as the amalgam warms, however, decomposition into hydrogen and ammonia ensues.

If sodium amalgam is poured into a saturated solution of ammonium chlorid, ammonium amalgam may be formed, as the equation shows.

$$\mathbf{Na \cdot Hg} + NH_4Cl \rightarrow \mathbf{NH_4 \cdot Hg} + NaCl$$

Its decomposition liberates large quantities of ammonia and hydrogen within the mercury, which swells up and becomes so light that it will float on water. All the hydrogen finally escapes, leaving only mercury, and ammonia dissolved in the water. No one has ever been more successful in isolating the ammonium radical than these experiments indicate.

That the **composition of ammonia** is such as the formula NH_3 indicates may be shown by the electrolysis of ammonia water in which salt has been dissolved. Three volumes of hydrogen collect at the cathode and 1 volume of nitrogen at the anode.

The reaction is more complex than it would seem at first thought, for it is the salt which is electrolyzed. Sodium separates at the cathode and chlorin at the anode. Sodium, reacting with water, liberates hydrogen and forms sodium hydroxid. Chlorin attacks ammonia, forming hydrochloric acid and nitrogen. By the interaction of hydrochloric acid and sodium hydroxid, salt is formed again in the original quantity. In this experiment salt acts as a catalyzer, its action being clearly understood, as the equations indicate. Though many reactions have taken place, the final outcome is only the decomposition of ammonia.

$$3\,NaCl \rightarrow 3\,\mathbf{Na} + 3\,\mathit{Cl}$$
$$3\,\mathbf{Na} + 3\,HOH \rightarrow 3\,\mathit{H} + 3\,NaOH$$
$$3\,\mathit{Cl} + NH_3 \rightarrow 3\,HCl + \mathit{N}$$
$$3\,NaOH + 3\,HCl \rightarrow 3\,NaCl + 3\,HOH$$

Ammonia and acids. When ammonia is brought in contact with hydrogen chlorid, interaction takes place with the formation of clouds of a white solid that proves to be ammonium chlorid. Similar action takes place whenever acids are brought in contact with ammonia. The gas is absorbed and direct combination takes place as is indicated by the equations.

$$NH_3 + HCl \rightarrow NH_4Cl$$
$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$
$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

Ammonium salts are formed exactly as though ammonium hydroxid had been neutralized by these acids. Experiment has shown that if ammonia and hydrogen chlorid gases are thoroughly dried before they are brought together no reactions occur. In this, as in many other reactions, water acts as a catalyzer without whose presence the action is inappreciable. It may be that its action in the present instance is to form ammonium hydroxid, which is then neutralized by the acids.

SUMMARY

AMMONIA is formed in the decay of organic substances containing nitrogen and is obtained on the large scale when coal is dry distilled. It is best prepared by heating ammonium chlorid with slacked lime.

Properties. Ammonia is a colorless gas with a characteristic odor. It is readily condensed to a liquid by pressure and cold and is used in cold storage and in making ice.

Composition. Electrolysis of ammonia water (containing a little salt) yields 3 volumes of hydrogen and 1 volume of nitrogen.

AMMONIUM HYDROXID. 1 volume of water is capable of dissolving about 800 volumes of ammonia at ordinary temperature. The solution resembles in properties a solution of sodium hydroxid and so is believed to contain the compound NH_4OH, which is known only in solution. Its salts are the ammonium compounds, in which the ammonium radical plays the part of a metal. When isolated from its compounds, ammonium immediately decomposes into ammonia and hydrogen.

QUESTIONS

1. Write an equation showing how ammonia can be obtained by the action of nascent hydrogen on nitric acid.

2. In preparing 20 grams of ammonia how much ammonium chlorid must be used?

3. How many liters of ammonia should be produced from 25 grams of ammonium chlorid? (1 liter of ammonia weighs 0.77 gram.)

4. Can the preparation of ammonia by the interaction of solid ammonium chlorid and dry slacked lime be carried through to completion? Why? How is the result affected if a considerable volume of water is added to the mixture at ordinary temperature?

5. Concentrated sulfuric acid is frequently used as a drying agent. Could it be used for drying ammonia? Why?

6. Name some familiar instances where the evaporation of a liquid produces cold.

7. 5 grams of water, saturated with ammonia at ordinary temperature, contain how many liters of ammonia?

8. If an electric current is passed through an ammonia solution until 1 liter of nitrogen (weighing 1.26 grams) has been collected, 3 liters of hydrogen will have been evolved at the same time.

(*a*) How many grams of ammonia have been decomposed?

(*b*) What would be the volume of this weight of ammonia, if it were in the form of gas?

(*c*) Fill in the blanks in this statement: — volumes of ammonia when decomposed yield — volumes of nitrogen and — volumes of hydrogen.

CHAPTER XV

A THEORY AND ITS USES

Facts. Attention has previously been called to the fact that solids and liquids do not behave uniformly when subjected to changing conditions of temperature and pressure, but that each substance expands and contracts independently of all others. In every case, however, as soon as the temperature rises above the boiling point and the substance passes into the gaseous condition, all expand and contract uniformly. It is certainly a surprising fact that substances as diverse in character as hydrogen, oxygen, nitrogen, ammonia, and hydrogen chlorid should act uniformly in the gaseous condition. Some of these gases are elementary, others compound; some are heavy, others light; some are stable, others unstable; some acidic in properties, others basic in reaction. The character of the substance is evidently without influence. There must be some property of the gaseous state itself that makes "all gases behave alike," which property does not belong to the liquid and the solid states.

Hypotheses. No sooner is such a relation discovered than the question "Why" is at once asked. Hypotheses are put forward and tested by experiment, and all but the most satisfactory discarded. Previous considerations have forced us to believe that gases are composed of small particles which are called molecules. If we now make the additional assumption that, provided temperature and pressure conditions are uniform, equal volumes of all gases contain equal numbers of molecules, it would seem to offer an explanation of why gases expand and contract alike. For, on this assumption, if at any definite temperature we compress equal volumes of gas, we are crowding equal numbers of particles into equal spaces. This would seem to require equal pressures, just as is found to be the case.

Avogadro's theory. In 1811 Avogadro, an Italian physicist, first put forward the hypothesis that *at the same temperature and pressure equal volumes of all true gases contain equal numbers of molecules.* For some years but little attention was paid to it, but since that time it has been recognized that it is quite as important as the atomic theory. For nearly a century it has been rigorously tested by experiment, and not a fact is known to-day which is inconsistent with it. It is regarded as one of the most firmly established theories of the scientific world. Hypotheses and theories are formulated in the hope that they may be of assistance in directing scientific investigation. That hypothesis is best which is most helpful. Viewed in this light, Avogadro's theory is one of the very best, for it has been most helpful.

Difference between atoms and molecules. Avogadro's theory served to emphasize the difference between the terms *atom* and *molecule.* It is an experimental fact that 1 liter of hydrogen combines with 1 liter of chlorin to form 2 liters of hydrogen chlorid; *i.e.* after the reaction the hydrogen chlorid which is formed occupies the same volume that the hydrogen and chlorin did before the reaction. According to Avogadro, the number of molecules on one side of the equation equals the number on the other side, since there is no change in volume. A liter of hydrogen contains x molecules and a liter of chlorin contains the same number, or x molecules; and the two liters of the compound contain $2x$ molecules. We may write, therefore,

x molecules of H $+ x$ molecules of Cl $= 2x$ molecules of HCl.

Dividing this expression by x, we have

1 molecule of H $+$ 1 molecule of Cl $=$ 2 molecules of HCl.

Hydrogen chlorid is all the same, however. Every particle of it is just like every other particle. Hence the two molecules of hydrogen chlorid must contain equal amounts of hydrogen. Neither molecule can contain less than one atom of any element, for the atom is the unit which is not divided in chemical reactions. Hence there must be at least two atoms in the molecule of hydrogen, for what was in one molecule before the reaction took place is now in two molecules.

The same reasoning applies to the chlorin molecule, and shows that the atom and the molecule cannot be alike in the case of either hydrogen or chlorin.

Interpreted in a similar way the results of numerous experiments indicate that under proper conditions *the* **molecules of non-metallic elements** *contain two atoms* while *the* **molecules of the metals** *contain but one atom.* That is, in the case of metals, the atom and the molecule are the same, and with non-metals they are different. Some diagrammatic representations of these facts are given in Fig. 37.

Avogadro's theory, supplemented by deductions similar to the preceding, offers an explanation of certain facts in relation to the gas densities of elementary substances. For those elements which have been considered in the preceding pages, the gas densities are directly proportional to the reacting weights. Under standard conditions a liter of hydrogen weighs 0.09 gram; of nitrogen, 1.25 grams; of oxygen, 1.43 grams. The ratios 0.09 : 1.25 :

1.43 are the same as 1 : 14 : 16.* Standard liters of these gases contain equal numbers of molecules. Since each molecule contains the same number of atoms in these

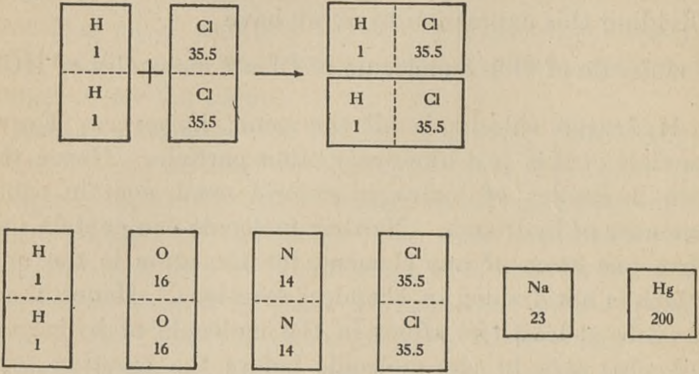

Fig. 37.

cases, the gas density is equal to the atomic weight. In the diagram above these ideas are represented.

Determination of molecular weight. Accepting Avogadro's theory as true, we are furnished with a method of determining the weight of the molecule of any gaseous substance. A standard liter of water vapor weighs about 9 (8.94) times as much as a standard liter of hydrogen. If we are weighing the same number of molecules in each case, it follows that each molecule of water must weigh about 9 times as much as the hydrogen molecule. In weighing molecules, we retain the same standard as in weighing atoms. The hydrogen molecule contains 2 atoms; its molecular weight is 2,† therefore. The molecule of water weighs 9 times as much, so its molecular

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* It should not be forgotten that the ratios are not expressed exactly by the whole numbers 1 : 14 : 16, but by the decimals 1.0075 : 14.01 : 16. The approximations are used for the sake of brevity and clearness.

† More exactly 2 × 1.0075 = 2.015.

weight is 9 × 2 = 18 (8.94 × 2.015 = 18.015). Hydrogen chlorid weighs 18.1 times as much as hydrogen, so its molecular weight is 36 approximately (18.1 × 2.015 = 36.5).

The gas density of any substance is the comparison of the weight of a given volume of its gas with the weight of an equal volume of hydrogen. According to Avogadro, since the volumes are equal, the numbers of molecules are equal. If x molecules of oxygen are 16 times as heavy as x molecules of hydrogen, 1 molecule of oxygen must be 16 times as heavy as 1 molecule of hydrogen. It follows, therefore, that gas density is the comparison of the weight of the molecule of one gas with the weight of the molecule of hydrogen. The weight of a molecule of hydrogen is 2.* Hence, to find the molecular weight of a substance, multiply its gas density by 2.*

Mole. *Whenever* 1 *gram of a substance is taken for each microcrith in its molecular weight, the amount taken is called a mole or gram-molecular weight.* To ascertain the mole of any substance, multiply its molecular weight by 1 gram. A mole of hydrogen is 2 grams; of oxygen, 32 grams; of water, 18 grams; of hydrogen chlorid, 36.5 grams.

If the numbers 2, 32, 18 and 36.5 represent the relative weights of single molecules of hydrogen, oxygen, water, and hydrogen chlorid, as long as we keep this proportion between the weights of these substances, we will have the same number of molecules of each substance. In other words, *a mole of any substance contains the same number of molecules as a mole of any other substance.*

According to the hypothesis of Avogadro, in the gaseous state a mole of any substance should occupy the same volume as a mole of any other substance. The facts agree closely with the theory, for, under standard conditions, a mole of any gas occupies 22.4 liters. Hence we may

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* More exactly 2 × 1.0075 = 2.015.

determine the weight of a liter of any gas by dividing the gram-molecular weight by 22.4. Thus the mole of oxygen is 32 grams; that is, 22.4 liters of oxygen weigh 32 grams. By dividing 32 by 22.4 we obtain the weight of a standard liter of oxygen; *i.e.* 1.43 grams.

In the liquid state the molecules are packed much closer than in the gaseous state. All those gases which are easily liquefied are not true gases, and they show considerable variation from this and all other gas laws. This is due to the fact that, to a certain extent, they show the properties of liquids, and their molecules are packed more closely than Avogadro's theory would indicate.

Freezing point and boiling point methods. It has been found by experience that whenever a mole of any substance that is not an electrolyte is dissolved in water * and made into a liter of solution, the boiling point of such a solution is always 0.52° higher than the boiling point of pure water. These same solutions freeze 1.89° below the temperature at which pure water freezes. By taking advantage of these facts we may derive another method of determining the molecular weights of substances, for we have only to prepare a water solution of such strength that it freezes at $-1.89°$. Such a solution contains a mole of the dissolved material. When 60 grams of urea are contained in a liter of solution, the latter freezes at $-1.89°$ and boils at 100.52°. Sixty grams is the mole of urea, and the molecular weight of urea is 60. Similarly, when 342 grams of cane sugar are dissolved in 1 liter of solution, the solution freezes at $-1.89°$ and boils at 100.52°; 342 grams make a mole of cane sugar, and the molecular weight of cane sugar is 342.

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* Similar results are obtained with other solvents. The rise of the boiling point and the lowering of the freezing point differ with the solvent, but are constant for each particular solvent. The action of electrolytes is somewhat different from non-electrolytes, and this will be considered later. (See p. 257.)

In practice we do not need to make a large number of solutions testing the freezing and boiling points of each until the proper concentration is found, for the following proportion holds: If a mole of any substance in a liter of solution causes the freezing point of the solution to fall 1.89° below zero, a fraction of a mole will cause a proportional depression. Hence, when we find that 34.2 grams of cane sugar in a liter of solution freezes 0.189° lower than pure water freezes, since the depression noted is $\frac{1}{10}$ of that caused by a mole, the amount in solution must be $\frac{1}{10}$ of a mole. Hence the mole of sugar must be 342 grams, and the molecular weight 342.

Correct formulas. By determining the gas density of a substance, or by experimenting with the freezing point and boiling point of its solutions, therefore, we can determine the molecular weight of most substances without difficulty. As soon as we have determined the weight of the molecule, we can determine the correct formula — a formula that expresses not only the ratios between the number of atoms of the different elements in the compound, but also the actual number of atoms of each element in the molecule.

We have noted previously (p. 113) how the simplest formula for a compound is determined. If we know the molecular weight, we may determine whether the simplest formula is the correct one. To illustrate: Hydrogen peroxid contains 94.1 % of oxygen and 5.9 % of hydrogen. Its molecular weight is 34. If in 100 parts of hydrogen peroxid there are 94.1 parts of oxygen, 34 microcriths of the compound will contain oxygen in the same ratio. $100 : 94.1 :: 34 : x = 32$. If in 100 parts of hydrogen peroxid there are 5.9 parts of hydrogen, 34 mic. of the substance will contain hydrogen in the same ratio, $100 : 5.9 :: 34 : x = 2$. 2 mic. of hydrogen means 2 atoms of hydrogen, and since the atom of oxygen weighs 16 mic., 32 mic. of oxygen means 2 atoms of oxygen. The formula for hydrogen peroxid is H_2O_2 therefore. But HO would express the proportion between hydrogen and oxygen as well as H_2O_2, and, furthermore, it is simpler. However, 34 is the molecular weight of hydrogen peroxid. The molecule of HO would weigh only 17. It requires 2 atoms of hydrogen and 2 atoms of oxygen to make up the molecular weight 34, and the correct formula must be H_2O_2.

Since it is very desirable that we know the correct formulas for the substances with which we are working, it is obvious that these and other methods of determining molecular weights are of prime importance.

Correct equations. That the molecules of hydrogen and the non-metallic elements consist of two atoms each has been indicated previously. The correct formulas for these substances are H_2, Cl_2, O_2, and N_2, rather than H, Cl, O, and N, as they have been written previously. We know, therefore, that the equation

$$H + Cl \rightarrow HCl$$

does not express the actual chemical change that takes place when hydrogen and chlorin unite. These gases consist of the molecules H_2 and Cl_2, whereas the equation given represents the chemical change as taking place between atoms of hydrogen and chlorin. As the smallest available portions of hydrogen gas and chlorin gas are the molecules H_2 and Cl_2, the correct equation must represent the change as taking place between these molecules, thus:

$$\begin{array}{ccccc} H_2 & + & Cl_2 & \rightarrow & 2\,HCl \\ \text{1 vol.} & & \text{1 vol.} & & \text{2 vols.} \end{array}$$

In a similar manner it appears that the correct equation for the formation of water by the union of hydrogen and oxygen is

$$\begin{array}{ccccc} 2\,H_2 & + & O_2 & \rightarrow & 2\,H_2O \\ \text{2 vols.} & & \text{1 vol.} & & \text{2 vols.} \end{array}$$

Further, the correct equation for the formation of ammonia by the union of hydrogen and nitrogen is

$$\begin{array}{ccccc} 3\,H_2 & + & N_2 & \rightarrow & 2\,NH_3 \\ \text{3 vols.} & & \text{1 vol.} & & \text{2 vols.} \end{array}$$

Other equations given in the preceding pages should be corrected in a similar way.

Why substances do not always react. It is possible that the reason why these and other substances do not interact readily as soon as they are brought together is because the molecules have to be broken up into atoms before appreciable reaction can take place. It is probable that the action of heat, light, electricity, etc., is to cause some kind of a decomposition of this nature and that on this account chemical activity is increased. One explanation of why elements in the nascent state are more active than they ordinarily are is that they are liberated from their compounds as atoms. The atoms soon unite together to form molecules, however, and in this condition are less active.

The **volume relations** which experience has shown to hold have been inserted in the previous equations. In dealing with gases, an inspection of a correctly written equation enables one to predict whether any change of volume will take place during a reaction. For, according to Avogadro's theory, *a molecule of any gas occupies the same space as a molecule of any other gas.*

Considering the equations on the preceding page, since there is the same number of molecules on each side of the first equation, there will be no change in volume, for 2 molecules of hydrogen chlorid occupy exactly the same space as a molecule of hydrogen and another of chlorin. In the last equation 3 molecules of hydrogen and 1 of nitrogen occupy twice the volume that 2 molecules of ammonia do. Hence when hydrogen and nitrogen, mixed in the proper proportions, combine to form ammonia, the volume of the compound formed will be one half that of the elements.

In reactions between gases, if the interaction causes a decrease in the number of molecules, there will be a decrease in volume; if there is an increase in the number of molecules, there will be an increase in volume; and if the same number of molecules appear on each side of the equation, there will be no change in volume.

PROBLEM. How much oxygen will be required for the combustion of 10 liters of marsh gas, CH_4, and how many liters of steam and of carbon dioxid will be formed?

The correct equation representing the burning of marsh gas is

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O.$$

The formula CH_4 represents 1 volume. It makes no difference whether we specify 1 molecule, liter, or some other volume, so long as we keep the same measure throughout. The formulas O_2, CO_2, and H_2O each represent 1 volume. Two volumes of oxygen are required to unite with 1 volume of marsh gas and there result 1 volume of carbon dioxid and 2 volumes of steam. If we start with 10 liters of marsh gas, 20 liters of oxygen will be required, 10 liters of carbon dioxid will be formed and 20 liters of water vapor. If the temperature be maintained above the boiling point of water, there will be no change in volume as the reaction takes place.

SUMMARY

Avogadro's theory. The fact that all gases, no matter how diverse their character, behave uniformly during changes of temperature and pressure suggests that they possess some common property that is the basis of the uniformity. Avogadro advanced as an explanation the hypothesis that *at the same temperature and pressure equal volumes of gases contain equal numbers of molecules.*

Applications of the theory. Avogadro's theory emphasizes the difference between the terms *atom* and *molecule.* Hydrogen, chlorin, oxygen, and nitrogen and similar *non-metallic elements in the gas-*

eous condition have 2 *atoms in the molecule*, but *molecules of the metallic elements in the gaseous state contain* 1 *atom.*

Moles. *When* 1 *gram of a substance is taken for each microcrith in its molecular weight, the amount so taken is called a mole or gram-molecular weight.* Moles of all substances contain equal numbers of molecules. In the case of gaseous substances 1 mole occupies 22.4 liters under standard conditions.

Molecular weights may be determined

1. by the *gas density method.* The molecular weight is twice the gas density. Mol. wt. = gas dens. × 2.
2. by the *freezing point* and *boiling point methods.* When a mole of any non-electrolyte is dissolved in enough water to make a liter of solution, the boiling point of the solution is 0.52° above the boiling point of pure water and the freezing point of the solution is 1.89° below the freezing point of pure water. By utilizing this fact it is possible to obtain the molecular weight of any substance that will go into solution.

Correct chemical formulas may be determined for all substances whose molecular weights can be found; *i.e.* for any substance that may be obtained in gas form or in solution. To get the formula for any such substance

(*a*) find its molecular weight;

(*b*) from the percentage composition calculate the number of microcriths of each element in the molecule;

(*c*) determine the number of atoms of each element present by dividing the number of microcriths of each element by the reacting weight of that element;

(*d*) write the formula, showing the number of atoms of each element in the compound.

The volumes of gases used or produced in chemical reactions are easily determined if one remembers that the ratios between the numbers of molecules are the same as the ratios between their volumes.

QUESTIONS

1. Why are the gas densities and specific gravities of the elementary gases thus far studied proportional to their atomic weights?

2. 10 ccm. of hydriodic acid when decomposed yield 5 ccm. of hydrogen and 5 ccm. of iodin vapor. Deduce the correct formula for the molecule of iodin vapor.

3. The gas density of sodium vapor is 11.5. Calculate the numbei of atoms in a molecule of sodium vapor.

4. What explanation can be given of the fact that hydrogen and oxygen do not at once unite when they are mixed?

5. Write correctly the equations for
(*a*) preparing oxygen from potassium chlorate;
(*b*) hydrogen from zinc and sulfuric acid;
(*c*) hydrogen from sodium and water;
(*d*) chlorin from manganese dioxid and hydrochloric acid;
(*e*) nitrogen from ammonium nitrite.

6. How much does a mole of sulfuric acid weigh; of potassium chlorate; of ammonium chlorid?

7. 180 grams of grape sugar in 1 liter of water solution boils 0.52° higher than pure water. What is the molecular weight of grape sugar? What will be the freezing point of the same solution?

8. Why do chemical changes between gaseous bodies always take place between definite volumes?

9. What volume of ammonia gas unites with 1 liter of hydrogen chlorid? Can the same reasoning be applied to determine the volume of the product?

10. How many cubic feet of oxygen are required to burn 100 cubic feet of carbon monoxid, CO? How many cubic feet of carbon dioxid, CO_2, result? The equation is $2\,CO + O_2 \rightarrow 2\,CO_2$.

11. Gas engines often use hydrogen or marsh gas, CH_4, as fuel. How much air will be required to burn 100 cubic feet of each gas? The equation for marsh gas is $CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$.

12. A gaseous compound of hydrogen and carbon is found to contain 12 parts by weight of carbon to 1 part of hydrogen. Its gas density is 13. What is its formula?

13. Another compound of hydrogen and carbon of exactly the same percentage composition has the gas density 39. What is its formula?

CHAPTER XVI

VALENCE AND EQUIVALENT WEIGHT

IN previous chapters we have noted that one volume of chlorin, of oxygen, and of nitrogen unite respectively with one, two, and three volumes of hydrogen. Passing from volume relations to the consideration of weights, we have seen that

1 react. wt. of Cl holds in combination 1 react. wt. of H.
1 react. wt. of O holds in combination 2 react. wt. of H.
1 react. wt. of N holds in combination 3 react. wt. of H.
1 react. wt. of C holds in combination 4 react. wt. of H.

These facts are summarized in the formulas for the substances formed by the combinations of these elements, as HCl, H_2O, H_3N, and H_4C. These formulas indicate that the atoms of carbon, nitrogen, oxygen, and chlorin unite with 4, 3, 2 and 1 atoms of hydrogen respectively.

Considered from the standpoint of either volumes, or weights, or atoms, it is evident that *different elements have different capacities for holding other elements in combination.* Thus, one reacting weight (or we may say atom) of carbon is capable of holding in combination four times as much hydrogen as one reacting weight (or atom) of chlorin can. Combination with other elements than hydrogen brings out the same difference in holding power, as the following formulas for well-known compounds of chlorin show: HCl, OCl_2, NCl_3, CCl_4.

The measure of the ability of an element to hold in combi-

nation other elements is known as its **valence.** The valence of hydrogen is taken as the standard, for its holding power seems to be invariable and is as small as that of any other element. Hydrogen is said to have a valence of 1. If 1 reacting weight of an element unites with 1 reacting weight of hydrogen, that element has a valence of 1 also. If 1 reacting weight of an element unites with 2, 3, or 4 reacting weights of hydrogen, that element has a valence of 2, of 3, or of 4, respectively.

The valence of elements is often indicated by the prefixes "mono" or "uni" signifying one, "di" meaning two, "tri" meaning three, and "tetra" meaning four. Thus carbon is tetravalent, nitrogen trivalent, oxygen divalent, chlorin monovalent or univalent.

Determination of valence. In order to ascertain the valence of an element it is only necessary to determine how many grams of hydrogen unite with 1 reacting weight of the element. Thus, 1 reacting weight of iodin unites with 1 gram, *i.e.* one reacting weight of hydrogen. Therefore the valence of iodin is 1. One reacting weight of arsenic combines with 3 grams of hydrogen. Therefore the valence of arsenic is 3.

There are, however, many metals that do not combine with hydrogen or that do so only with difficulty. Chlorin unites with all metals and in so doing shows the same valence as hydrogen. Hence by noting how many reacting weights of chlorin unite with one reacting weight of a metal we may determine the valence of the latter. Thus 71 grams of chlorin unite with 207 grams of lead; *i.e.* two reacting weights of chlorin unite with one reacting weight of lead. The valence of lead is 2, therefore.

Variation in valence. While a great many elements appear not to vary in valence at all, others exhibit more than one holding power. Thus, phosphorus forms with hydrogen the compound PH_3, in which it acts as a trivalent element. At the same temperature it unites with chlorin to form the compound PCl_5, thus being pentavalent or showing a valence of five. In accordance with the tendency of all substances to dissociate when heated, we find that higher temperature tends to decrease valence. Thus, phosphorus pentachlorid decomposes when heated into phosphorus trichlorid and chlorin, and only when they are cooled does combination take place again.

$$PCl_5 \longleftrightarrow PCl_3 + Cl_2$$

Valence told by formulas. When the valences of a few elements have once been learned, the valence of others may be found by an inspection of the formulas of their compounds. Thus, thallium forms the chlorid, TlCl, which being similar to HCl indicates that in thallium chlorid the metal is doing precisely what hydrogen is doing in hydrogen chlorid. Each is holding in combination one reacting weight of chlorin and each is univalent, therefore.

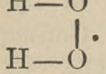
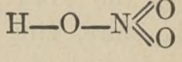
It has previously been stated that zinc acts upon sulfuric acid according to the equation:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

In this reaction one reacting weight of zinc replaces and does the work of two reacting weights of hydrogen. Therefore, zinc has a valence of two. Consequently, the formula for zinc chlorid must be $ZnCl_2$.

The conception of valence was first introduced into chemistry by Kekule in 1858. Previous to this time few questions had been raised as to the way in which atoms are united together within the molecule. Investigation of the compounds of carbon often reveals the existence of two or more substances having the same percentage composition and the same molecular weight, yet possessing unlike properties. Kekule asserted that there must be a different structure within the molecule to account for the difference in properties. Kekule's hypothesis has been of great help and has been widely extended. A photograph of Kekule is shown in Fig. 38.

From a study of the way in which a compound reacts with other substances or decomposes when alone, it is believed that something of the structure within the molecule may be learned. Based upon such investigations, so-called **structural formulas** may be written for many substances, which are intended to indicate the way in which these compounds react. These formulas show the valence for each element and suggest what seems to be the structure within the molecule; for all the evidence indicates that certain elements are often more closely united together than others in the same compound are.

In writing structural formulas the valence of an element is indicated by short lines or "**bonds**" attached to its symbol. The number of the lines denotes the valence, and their arrangement shows which elements are directly connected with each other. Thus, the valence of hydrogen and of chlorin is shown by the symbols H– and Cl–. Oxygen has a valence of two as the symbol –O– or O= indicates. Nitrogen is written N≡ or =N– or in any other way that shows three bonds. Carbon is =C= or C≣. The structural formula for water is H—O—H; for hydrogen dioxid,  $\begin{array}{l} \mathrm{H—O} \\ \quad\;\, | \\ \mathrm{H—O} \end{array}$. The structural formula  $\mathrm{H—O—N} \begin{array}{l} \nearrow \mathrm{O} \\ \searrow \mathrm{O} \end{array}$ for nitric acid, represents hydrogen with a valence of 1, oxygen 2, and nitrogen as pentavalent or having a valence of 5. The formula indicates also the fact which experience has demonstrated, viz. that hydrogen is not attached to the nitrogen directly; nitric acid is a hydroxid of nitrogen. Structural formulas are of great service in chemistry, and

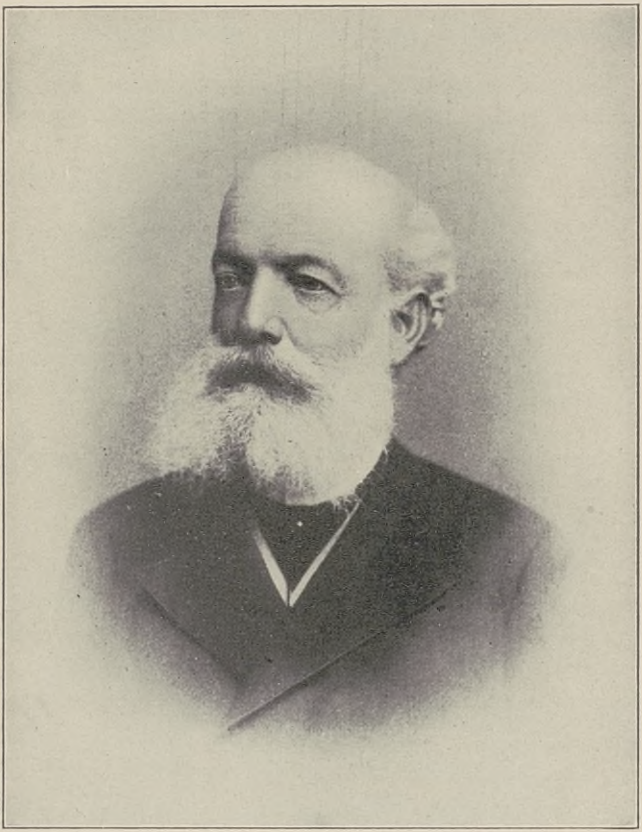


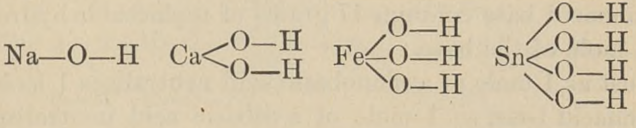
Fig. 38. — Friedrich August Kekule (1829–1896)

A German who worked out and developed the idea of the valence of the different elements and of the structure within the molecules of compound substances.

in understanding the complex compounds of carbon they are absolutely essential.

The student of chemistry should keep constantly in mind that the lines or bonds used in structural formulas are only conventional symbols to indicate the way in which substances react. Of the manner in which atoms are held together in the molecule we know absolutely nothing. We say that chemical affinity causes elements to combine, but this is merely giving a name to something of the exact nature of which we are in ignorance.

In dealing with bases we find that they have different capacities for combining with acids. Thus 1 mole of the hydroxids of sodium, calcium, ferric iron, and stannic tin combine respectively with 1, 2, 3, and 4 moles of hydrochloric acid. This is directly due to the fact that these metals have valences of 1, 2, 3, and 4, as the following formulas indicate:

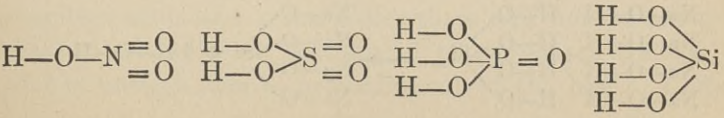


$$\mathrm{Na{-}O{-}H} \qquad \mathrm{Ca}<\begin{matrix}\mathrm{O{-}H}\\ \mathrm{O{-}H}\end{matrix} \qquad \mathrm{Fe}\begin{matrix}\diagup\mathrm{O{-}H}\\ -\mathrm{O{-}H}\\ \diagdown\mathrm{O{-}H}\end{matrix} \qquad \mathrm{Sn}\begin{matrix}\diagup\mathrm{O{-}H}\\ \diagup\mathrm{O{-}H}\\ \diagdown\mathrm{O{-}H}\\ \diagdown\mathrm{O{-}H}\end{matrix}$$

Instead of saying that these bases are mono-, di-, tri-, and tetravalent, we frequently state that they are *monacid*, *diacid*, *triacid*, and *tetracid* bases.

In dealing with acids we note that they also have different combining capacities. Thus 1 mole of nitric, of sulfuric, of phosphoric, and of silicic acids require respectively 1, 2, 3, and 4 moles of sodium hydroxid to neutralize them, and they are said to be *monobasic*, *dibasic*, *tribasic*, and *tetrabasic* acids respectively.

The structural formulas for these acids are:



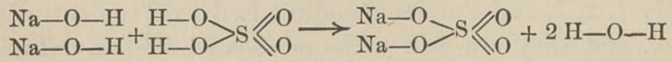
$$\mathrm{H{-}O{-}N}\begin{matrix}=\mathrm{O}\\ =\mathrm{O}\end{matrix} \qquad \begin{matrix}\mathrm{H{-}O}\\ \mathrm{H{-}O}\end{matrix}>\mathrm{S}\begin{matrix}=\mathrm{O}\\ =\mathrm{O}\end{matrix} \qquad \begin{matrix}\mathrm{H{-}O}\diagdown\\ \mathrm{H{-}O}-\\ \mathrm{H{-}O}\diagup\end{matrix}\mathrm{P}=\mathrm{O} \qquad \begin{matrix}\mathrm{H{-}O}\diagdown\\ \mathrm{H{-}O}\diagdown\\ \mathrm{H{-}O}\diagup\\ \mathrm{H{-}O}\diagup\end{matrix}\mathrm{Si}$$

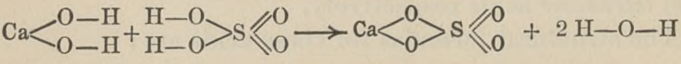
From these formulas it will be seen that the question as to whether an acid is mono-, di-, or tribasic, etc., depends on the valences of the elements composing the acid and the arrangement of the atoms within the molecule. Thus, in nitric acid the valence of nitrogen is 5 and of oxygen 2. These elements are so arranged that the nitrate radical, *i.e.* nitric acid minus hydrogen, has a valence of 1.

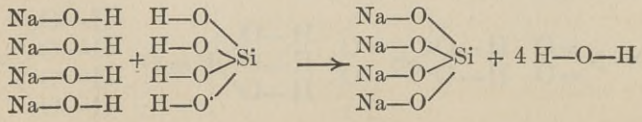
In sulfuric acid the sulfur shows a valence of 6. The four oxygen atoms are so joined to the sulfur that the resulting sulfate radical has a valence of 2. Similarly the phosphate and the silicate radicals have valences of 3 and 4 respectively.

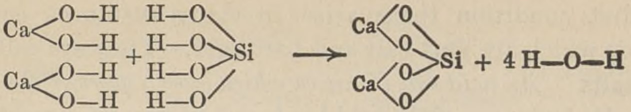
We may define a monobasic acid and a monacid base as follows: *A monobasic acid is one which contains* 1 *gram of replaceable hydrogen in a mole of the acid. A monacid base is one which neutralizes a monobasic acid mole for mole.* A monacid base contains 17 grams of replaceable hydroxyl in a mole of the base.

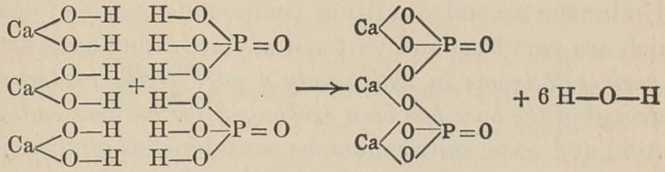
Just as 1 mole of a monobasic acid neutralizes 1 mole of a monacid base, so 1 mole of a dibasic acid neutralizes 1 mole of a diacid base, etc. 1 mole of a tetrabasic acid requires 2 moles of a diacid base for complete neutralization. 3 moles of a diacid base react with 2 moles of a tribasic acid without a remainder, and *vice versa.* The following equations represent typical reactions between acids and bases of different combining capacities.

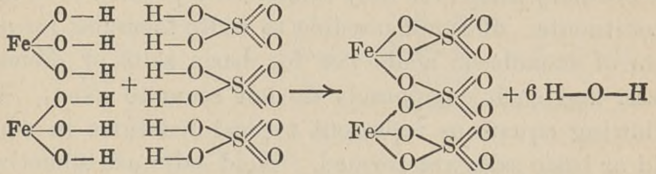


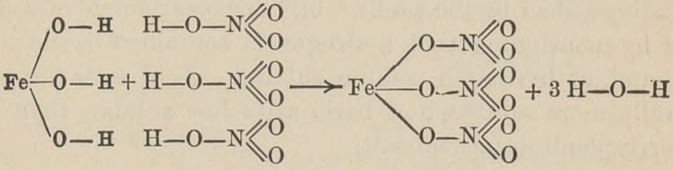










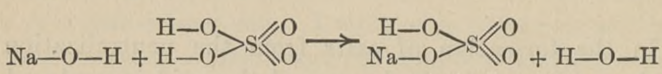


In the formation of salts from the neutralization of acids and bases, the hydrogen of the acid is replaced by metal, and for the hydroxyl of the base an acid radical is substituted. If acids and bases are mixed in the proper proportions, **normal salts** result. *A normal salt is one in which all the replaceable hydrogen of the acid has been exchanged for metal and all the hydroxyl of the base replaced by an acid radical.* All of those indicated in the preceding equations are normal salts.

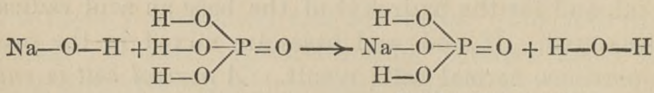
If the correct proportions are not observed in bringing together acids and bases, either there will not be enough base to neutralize all of the acid properties, or there will not be enough acid to neutralize all of the base. Under the first condition there arise in many instances compounds which are part salt and part acid. They are called **acid salts.** *An acid salt is one in which only a part of the replaceable hydrogen of the acid has been exchanged for a metal.*

Under the second condition compounds may be formed which are part base and part salt and are called **basic salts.** *A basic salt is one in which only a part of the replaceable hydroxyl of the base has been exchanged for an acid radical.*

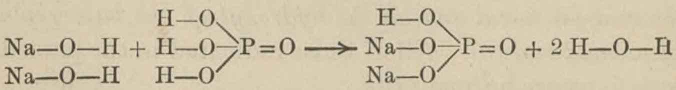
Acid and basic salts cannot be considered as mixtures in the ordinary sense, for they cannot be separated into their constituents. It is not possible to write formulas for acid salts of monobasic acids nor for basic salts of monacid bases, and such compounds do not seem to exist. The following equations represent typical reactions in which acid or basic salts are formed. Acid salts are sometimes distinguished by the prefix "bi," as "bicarbonate of soda," or by mentioning that hydrogen is contained in the compound, as hydrogen sodium sulfate. Acid salts are generally more soluble, and basic salts less soluble, than the corresponding normal salt.



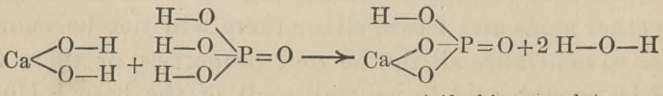
Acid sodium sulfate



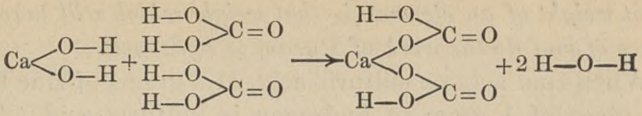
Diacid sodium phosphate



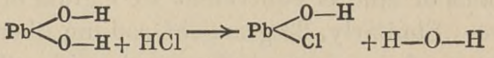
Acid disodium phosphate



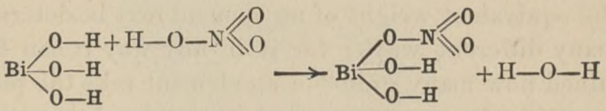
Acid calcium phosphate



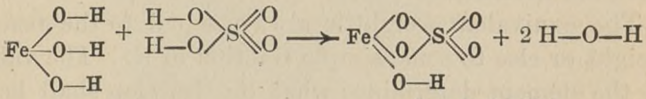
Acid calcium carbonate



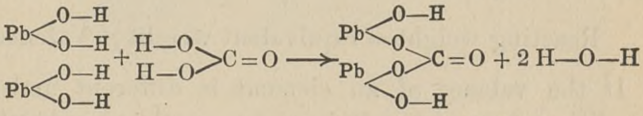
Basic lead chlorid



Dibasic bismuth nitrate



Basic ferric sulfate



Basic lead carbonate

Equivalent weights. From the preceding formulas and equations it will be seen that when an element is substituted for hydrogen in a compound, 1 reacting weight of some elements replaces 1 reacting weight of hydrogen, while 1 reacting weight of other elements replaces 2, 3, 4, etc., reacting weights of hydrogen. That is, 1 reacting weight of some elements is equivalent to 1 reacting weight of hydrogen. One reacting weight of other elements, however, is equivalent to 2, 3, 4, etc., reacting weights of hydrogen. The conception of equivalent weights of the different elements is important in chemistry. *The equiv-*

alent weight of an element is that weight which will take the place of and do the work of 1 *gram of hydrogen.*

When zinc acts on sulfuric acid, 31.5 grams of zinc take the place of 1 gram of hydrogen in sulfuric acid. The hydrogen is liberated and the zinc forms zinc sulfate. 31.5 grams of zinc is equivalent to 1 gram of hydrogen, therefore. Similarly, 23 grams of sodium liberate 1 gram of hydrogen from water or from any acid. 23 grams is the equivalent weight of sodium.

The equivalent weight of an element may be determined in many different ways; for if in any way it can be ascertained how many grams of an element take the place of 1 gram of hydrogen, the equivalent weight of that element has been determined.

The equivalent weight is always equal to the reacting weight or else to some simple fraction of it. The valence of the element determines what the fraction shall be, for the following relation holds between these quantities:

$$\text{Reacting weight} = \text{Equivalent weight} \times \text{Valence.}$$

If the valence of an element is different under one condition from what it is under another condition, the equivalent weight will differ in the two cases. *One equivalent of an element always unites with one equivalent of any other element*, provided that a reaction between the elements is possible.

In electrolysis (*a*) *the amount of decomposition is always proportional to the amount of electricity passed through the substance;* and (*b*) *the amounts of the different elements set free from their compounds by a given amount of electricity are always proportional to the equivalent weights of these elements.* That is, if a given amount of electricity liberates 1 equivalent weight of one element, the same amount of electricity will liberate 1 equivalent weight of any other

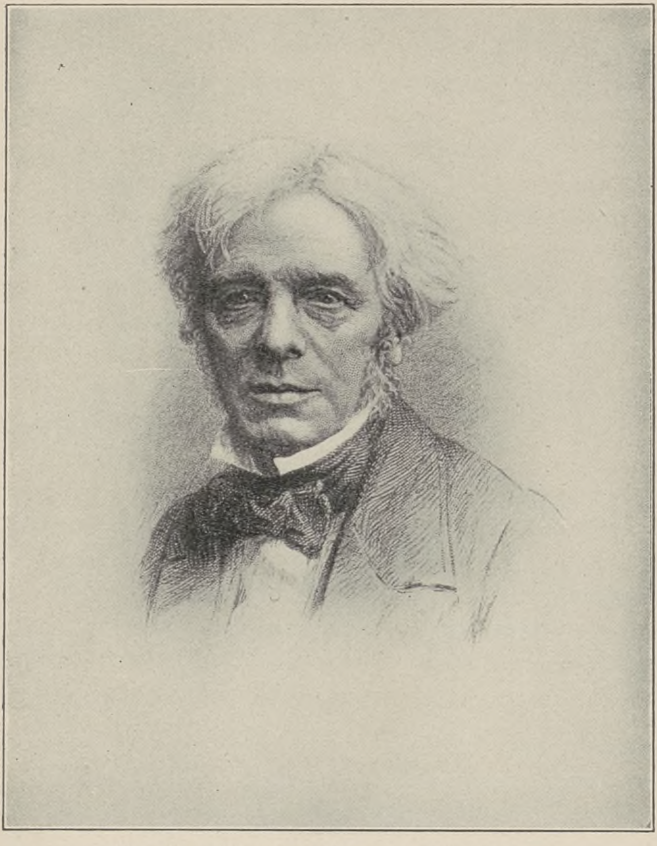


FIG. 39.—MICHAEL FARADAY (1791–1867)

The son of a poor blacksmith who became assistant to Sir Humphrey Davy and afterwards President of the Royal Society of England. A pioneer and experimental genius in many lines of scientific work. He laid the foundations of electrochemistry by discovering Faraday's Laws and wrote a most interesting book on "The Chemistry of a Candle."

element; 96,540 coulombs of electricity will liberate 1 equivalent weight of any element.

The statements given in the preceding paragraph are known as **Faraday's laws of electrolysis.** A portrait of Faraday is shown in Fig. 39. Based on Faraday's laws we have a very simple method of determining equivalents.

In the apparatus shown in Fig. 40, the equivalent weights of several different elements may be determined at the same time. Into each beaker a pair of suitable electrodes is placed and the whole series connected to a dynamo or other source of electricity in such a way that whatever electricity passes through one solution will pass through all. Compounds of different elements are placed in the different beakers and the current turned on. When sufficient electricity (96,540 coulombs) has passed to liberate 1 gram of hydrogen in any solution, 1 equivalent weight of each of the other elements has been set free also, as the following results indicate:

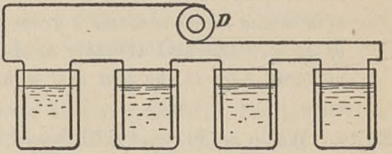


FIG. 40.

COMPOUND DECOMPOSED	ELEMENT LIBERATED	AMOUNT SET FREE	EQUIVALENT WEIGHT	×	VALENCE	=	REACTING WEIGHT
H_2O	H	1 g.	1	×	1	=	1
H_2O	O	8 g.	8	×	2	=	16
NaCl	Na	23 g.	23	×	1	=	23
NaCl	Cl	35.5 g.	35.5	×	1	=	35.5
NH_3	H	1 g.	1	×	1	=	1
NH_3	N	4.67 g.	4.67	×	3	=	14

SUMMARY

Valence. The ability of elements to hold in combination other elements varies greatly. *The measure of the capacity of an element* *to hold in combination other elements is known as valence.* The valence or holding capacity of hydrogen is taken as 1. When 1 reacting weight of an element unites with 1 reacting weight of hydrogen, the element has a valence of 1. If 1 reacting weight of an element combines with 2, 3, or 4 reacting weights of hydrogen, the element has a valence of 2, 3, or 4. Some elements seem to have a constant valence; with others the valence varies under different conditions.

Because of the different valences possessed by different metals, bases combine with different amounts of acids, and similarly different acids unite with different amounts of bases. *A monobasic acid is one which contains* 1 *gram of replaceable hydrogen in* 1 *mole of acid.* Di- and tribasic acids, etc., are similarly defined. *A monacid base is one that will unite with a monobasic acid mole for mole.*

Salts. When acids react with bases, if all of the replaceable hydrogen of the acid is exchanged for metal and all of the replaceable hydroxyl of the base is exchanged for an acid radical, the salt resulting is a *normal salt.* An *acid salt* is one in which part only of the replaceable hydrogen of the acid has been exchanged for a metal. The resulting compound is part salt and part acid. A *basic salt* is one in which part only of the replaceable hydroxyl of the base has been exchanged for an acid radical. A basic salt is part salt and part base.

Structural formulas are endeavors to express graphically not only the number and kind of atoms that form a molecule, but also the manner in which these atoms are arranged. To accomplish this, the valence of each element is indicated by short lines or "*bonds*" attached to its symbol, and by means of these bonds the symbols are joined together so as to indicate which atoms are directly attached to each other.

Equivalent weights. *The equivalent weight of any element is the amount of that element which will take the place of and do the work of* 1 *gram of hydrogen.* The equivalent weight always equals the reacting weight or else is some simple fraction of the reacting weight. What this fraction is, is determined by the valence; for *equivalent weight* × *valence* = *reacting weight.* The equivalent weight of an element may be determined in many ways, electrolysis being a very satisfactory method.

Faraday's laws of electrolysis state that (*a*) *the amount of decomposition* *is always proportional to the amount of electricity passed through the substance*, and (*b*) *the amounts of different elements set free by a given amount of electricity are always proportional to the equivalent weights of these elements.*

QUESTIONS

1. What is the valence of S in H_2S; of Br in HBr; of Si in SiH_4? Why?

2. What is the valence of Mn in $MnSO_4$; in $MnCl_2$; in MnO_2? Why?

3. What is the valence of Cu in cupric oxid, CuO? What must be the formula for cupric chlorid; for cupric nitrate; for cupric sulfate; for cupric carbonate?

4. What is the valence of iron in ferric chlorid, $FeCl_3$? What must be its valence in ferrous chlorid, $FeCl_2$? What must be the formula for ferric nitrate; for ferric sulfate; for ferrous nitrate; for ferrous sulfate?

5. What is the valence of tin in stannous oxid, SnO; in stannic oxid, SnO_2? What must be the formula for stannous chlorid; for stannic chlorid; for stannous hydroxid; for stannic hydroxid; for stannous sulfate; for stannic sulfate?

6. When hydrogen sulfid, H_2S, and lead chlorid, $PbCl_2$, are mixed in solution, the hydrogen and the lead exchange places. Write the equation for the reaction, giving each element its proper valence.

7. When hydrogen sulfid and arsenic chlorid, $AsCl_3$, are mixed in solution, the hydrogen and the arsenic exchange places. Write the equation.

8. Write the equation for the action of hydrogen sulfid on arsenic pentachlorid; on stannic chlorid.

9. When silver nitrate and aluminum chlorid are mixed in solution, silver chlorid is precipitated. Write the equation, giving silver a valence of 1 and aluminum a valence of 3.

10. Correct these equations so that the elements have their proper valences and no matter is created or lost:

$$KCl + H_2SO_4 \rightarrow KSO_4 + HCl$$
$$Ba(OH)_2 + NH_4Cl \rightarrow BaCl + H_2O + NH_3$$
$$NH_4OH + H_2SO_4 \rightarrow NH_4SO_4 + H_2O$$

11. Write the equation expressing the chemical change when sulfuric acid is treated with just enough potassium hydroxid for neutralization.

12. Write the equation expressing the chemical change when sulfuric acid is treated with just half of the amount of potassium hydroxid necessary for neutralization. Name the compounds formed.

13. Write the equations expressing the chemical changes when phosphoric acid is treated with one, with two, and with three moles of sodium hydroxid for each mole of the acid. Name the compounds formed.

CHAPTER XVII

CARBON

CARBON (C—12) is an important element because of the great number and complexity of the compounds into which it enters. The free element is not found in nature to any great extent. Combined with oxygen it occurs in the atmosphere as carbon dioxid, which is the anhydrid of carbonic acid. The calcium and magnesium salts of carbonic acid are common rocks, often forming whole mountain ranges. In combination with hydrogen and oxygen, and usually with nitrogen also, carbon forms the many compounds that are found in the bodies of plants and animals.

When animal or vegetable matter is heated out of contact with air, it usually decomposes and leaves a residue of carbon. The other constituents generally unite with hydrogen and escape as gaseous products. Of these water, ammonia, and marsh gas, CH_4, are most abundant. From these processes carbon is always obtained in amorphous condition, its properties depending somewhat on the material from which it is derived.

Amorphous carbon. *Charcoal* is one form of amorphous carbon. In the old way of preparing it, known as "charcoal burning," wood is piled in heaps, covered with turf, and set on fire. For two or three months it smolders, the slow burning of a part of the wood furnishing the heat necessary to char the remainder. Three fourths of the weight of the wood is lost as volatile products which pass off with the smoke. About two thirds of this amount is water and one third is combustible gas, chiefly marsh gas, CH_4. There is, however, about one per cent each of wood alcohol, acetic acid, and acetone. These products are more valuable than the charcoal, and their loss has caused this process to be abandoned to a large extent. In the newer process, known as "wood distillation," wood is piled on steel cars and run into huge masonry chambers heated to a high temperature. Here a few hours accomplish the work of the same number of weeks in the old process. The charcoal remains on the car; the volatile portions pass off. Acetic acid is removed by lime, the alcohol and acetone condense, and the gas is piped around under the furnace and used as fuel.

When wood burns in the air, a similar process takes place for a time. The heat from the burning of the outside distills the inner portions, driving out the gas that produces the flame and leaving the charcoal as the "glowing coals." The charcoal thus formed finally oxidizes completely, leaving only the mineral constituents of the wood as ashes.

Coal. A process somewhat similar to the distillation of wood has taken place on a large scale in nature. The dense forests of older geological ages (Fig. 41*a*) have been submerged, and, covered with silt, have undergone a peculiar kind of decomposition away from air. Wood consists largely of carbon, hydrogen, and oxygen. In this process hydrogen has united with oxygen to form water and has been for the most part removed, leaving a much larger percentage of carbon in the decomposition product called *coal* (Fig. 41*b*) than in the original material. Usually some hydrogen remains, however, united to the carbon in the form of compounds volatile at a high temperature.

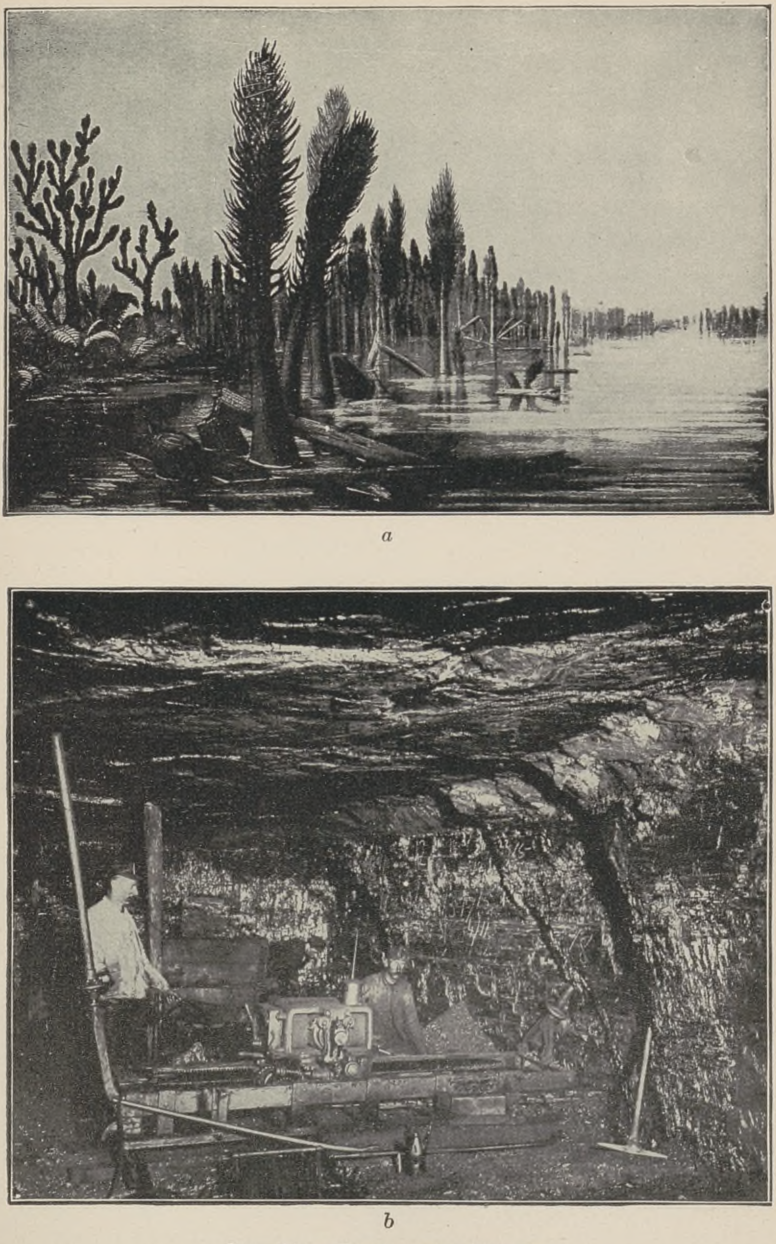


FIG. 41. — PREHISTORIC FORESTS

(*a*) As they were. (*b*) As they are — Interior of a coal mine.

Since various deposits have been subjected to varying degrees of pressure and heat, the decomposition has stopped at different stages, and the quality of coal varies widely. *Anthracite* is hard and dense, consisting of nearly pure carbon with but little volatile matter; *bituminous* coal, not having been subjected to so much heat and pressure, contains much volatile matter and is softer. In *lignite* the process is not far advanced and the woody nature is still evident. *Peat* is the product of the decay of organic matter under water in comparatively recent times, and hence is but little changed.

Much coal is dry distilled to form *coke*, a nearly pure form of amorphous carbon very important in the smelting industries, in which it is used as a reducing agent; also to form *illuminating gas*, which consists of the volatile matters of the coal.

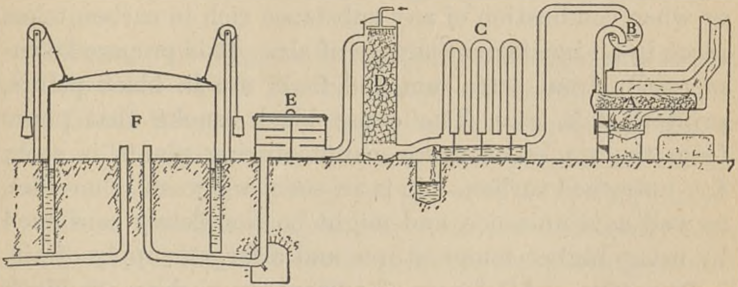


Fig. 42.

In order to remove injurious and foul-smelling impurities, the gas coming from coal heated in retorts (*A*, Fig. 42) is passed through a water trap, *B*, into the *condensers*, *C*, where many substances that will clog the pipes are condensed. It then passes into the *scrubbers*, *D*, where the ascending current of gas meets a descending stream of water trickling over brick. This removes ammonia (see p. 150). It is then led over trays, *E*, filled with slacked lime or iron oxid to remove sulfur compounds chiefly. Finally it reaches the gas tank, *F*, from which it is piped throughout the city.

The heaviest portion of the material obtained in purifying coal gas is *coal tar*, which itself may be dry distilled, leaving "retort carbon" or "gas carbon," an exceptionally dense form used in arc lamps. The greater the heat of the distillation, the more metallic do the properties of the carbon become, and the better does it conduct heat and electricity.

Animal charcoal, or *bone black*, is prepared by distilling bones, blood, and other animal refuse, the mineral matter often being dissolved out with acid. Just as coal and natural gas have been produced in nature largely by the distillation of vegetable matter, so from animal matter result *asphalt*, *petroleum*, and natural gas also.

Lampblack, or soot, results when a lamp or candle smokes or when combustion of any substance rich in carbon takes place in an insufficient supply of air. It is prepared commercially from petroleum and finds use in black paints, printer's ink, etc. The dense black smoke that pours from the stacks of many manufacturing plants is soot; *i.e.* unburned carbon. It is an economic waste, therefore, as well as a nuisance, and might be completely consumed by using higher temperatures and a larger supply of air.

Properties. All forms of amorphous carbon are black solids which do not melt at the highest temperatures attainable. They are without taste or odor and are insoluble in all ordinary solvents. Vegetable and animal charcoal are very porous and expose to the air or other fluid a very large surface for a small weight of material. They are both capable of absorbing many gaseous and liquid substances and are therefore used as purifiers and decolorizers in many industries, such as the filtration and purification of water and the refining of sugar and many commercial products.

Carbon is one of the most stable of substances. Charcoal left as the embers of fires lighted by peoples whose villages were destroyed thousands of years ago has been unearthed in many places. This is due to the fact that at ordinary temperatures carbon does not readily enter into combination with other elements. When heated it shows more activity, and at very high temperatures it unites with many metals to form compounds known as *carbids*. Calcium carbid and some others have become of importance.

When heated without access of air, carbon does not undergo any change ; but when air is admitted, it burns ordinarily to the dioxid. Its ready union with oxygen renders it indispensable in the reduction of metals from their ores, which in many cases are the oxids. When a mixture of a metallic oxid with carbon is heated, the oxygen leaves the metal and, uniting with the carbon, escapes as a gas.

Diamond, when pure, is a colorless, transparent, rather brittle solid. It is the hardest of all known substances, and hence is used in cutting glass and other hard materials. The property of diamond that gives it its beauty and value as a gem is its great power of refracting light.

When heated without access of air to a sufficiently high temperature, diamond swells up and becomes changed into a black substance resembling graphite, but there is no change in weight. Heated in air or oxygen, diamond burns to carbon dioxid.

It has been conjectured that diamonds are formed by the crystallization of carbon contained in certain rocks deep in the earth where conditions of great heat and pressure exist. This conjecture has been partly verified by the French chemist Moissan, who dissolved charcoal in molten iron and then plunged the crucible containing it in ice water. The iron, contracting as it cools, exerts a tremendous pressure on the interior of the mass. On dissolving the iron in acid, he obtained from the residue small particles of diamond.

Diamonds are found in nature rather widely distributed, but at present the most productive mines are in South Africa.

As gems diamonds were valued in ancient times, but as no means were known of cutting and polishing them the stones were used in their natural condition. About 250 years ago it was found that they might be polished by means of their own dust.

Graphite, or **plumbago**, is widely distributed in nature, occurring in grains in many rocks, but it is found in large quantities and in pure condition in only a few localities, chiefly in the Ural Mountains. It is a soft, black, crystalline solid. It is extensively used as a lining for crucibles, as a lubricating agent, and, when finely powdered and mixed with cement or other binding material, is used in lead pencils.

Graphite does not burn at temperatures where ordinary carbon takes fire; but if heated sufficiently, it burns slowly to carbon dioxid. Heated without access of air, it remains unchanged.

Graphite, like diamond, is formed by the crystallization of carbon dissolved in molten rocks, iron, or similar substances, but great pressure is not requisite as in the case of diamond. When cast iron solidifies, a part of the carbon separates out as dark scales of graphite. In the electric furnace, also, carbon is partly converted into graphite.

Allotropy. It has been proved that diamond, graphite, and charcoal consist of the element carbon only. This is done by burning equal weights of the three substances in oxygen and then weighing the products. In each case it is found that nothing but carbon dioxid is formed, and from equal weights of the three materials equal weights of carbon dioxid are produced.

A different amount of heat is liberated in each case, however, and it is evident that one form contains more energy than another. This difference in the amount of energy associated with a given amount of matter accounts for the difference in properties. The property possessed by some elements of existing in two or more distinct forms is called *allotropy*, and the forms are called *allotropic forms*.

SUMMARY

CARBON is found in carbon dioxid, in carbonates, and in living things and their remains. Several different forms of carbon are known.

Amorphous carbon results when carbonaceous materials are heated without access of air. *Charcoal* is made by heating wood without access of air. *Coal* is formed in nature by a somewhat similar process. *Coke* is obtained by the distillation of coal. *Animal charcoal*, or *bone black*, is made by charring bones, blood, and animal matter in general. *Lampblack*, or soot, is formed when material rich in carbon, such as petroleum, burns in an insufficient supply of air.

Properties. Amorphous carbon is black, odorless, tasteless, and insoluble. Being porous, some forms of it are used to absorb impurities in air, water, or other substances. It is not chemically active at ordinary temperatures, but when heated it burns to the oxids and may be made to unite with many elements to form *carbids*. It is a good reducing agent.

Diamond and **graphite** are crystallized forms of carbon.

Allotropy. Charcoal, diamond, and graphite consist of the element carbon only. The property possessed by some elements of existing in more than one modification is called *allotropy*, and the different modifications are said to be allotropic forms.

QUESTIONS

1. How could you prove that diamond, bone black, graphite, soot, and charcoal all consist of the same element?

2. What reducing agents have been mentioned thus far? What is a reducing agent?

3. Why are the ends of posts that are to be set in the ground sometimes charred?

4. May coal be truthfully called "black diamonds"?

5. Indelible inks frequently consist of finely divided carbon. What properties of carbon make it valuable in this way?

6. Why does soft coal burn with a flame when hard coal does not?

7. Explain chemically what happens when a lamp smokes, assuming that the oil has the composition C_8H_{18}. Suggest two ways of preventing a lamp from smoking. Can a hydrogen flame be made to smoke? What is smoke?

8. Suggest ways of avoiding the "smoke nuisance."

9. In 1 ton of marble, $CaCO_3$, how many pounds of carbon are held in chemical combination?

CHAPTER XVIII

THE COMPOUNDS OF CARBON

WHENEVER carbonaceous material burns freely in the air, its carbon is converted into carbon dioxid, CO_2. This may be obtained also by heating carbonates, as when calcium carbonate, limestone, is heated for the purpose of making lime.

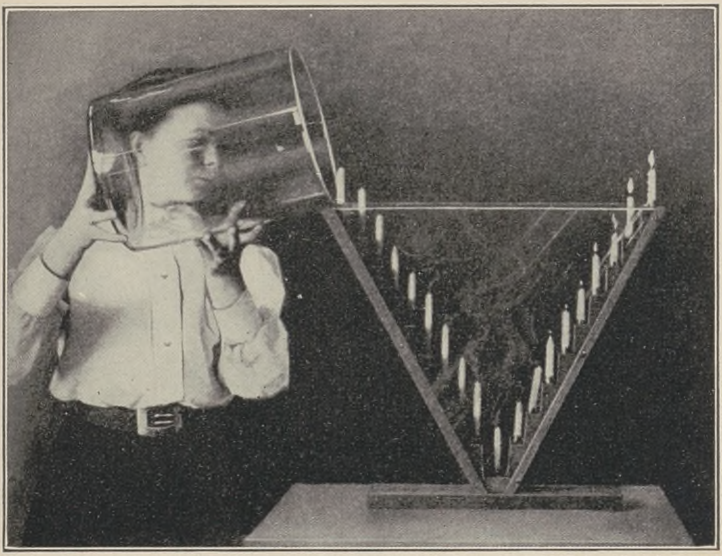
$$CaCO_3 \rightarrow CaO + CO_2$$

For laboratory and manufacturing purposes carbon dioxid is more conveniently prepared by the action of acids on carbonates, according to a reaction which may be written

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + CO_2 + H_2O.$$

Carbon dioxid is a colorless gas with a slightly acid taste and a pungent odor. It is half again as heavy as air, and hence it may be poured like water and has a tendency to collect at the bottom of old wells, in caves, and in mines. It is not in itself poisonous, but its presence in the air in any considerable quantity hinders the exchange of gases through the lungs, so that suffocation results from lack of oxygen in the blood. By pressure and cold it may be condensed to a colorless liquid, which, when exposed to the air, evaporates rapidly, absorbing so much heat in the process that a portion is frozen to a snowy solid.

Carbon dioxid does not burn, for it is the ash of carbon and is already oxidized as completely as possible. It does not support combustion (see Fig. 43*a*) and for this reason



From Brownlee's "First Principles of Chemistry." Copyright, 1907, by Allyn & Bacon

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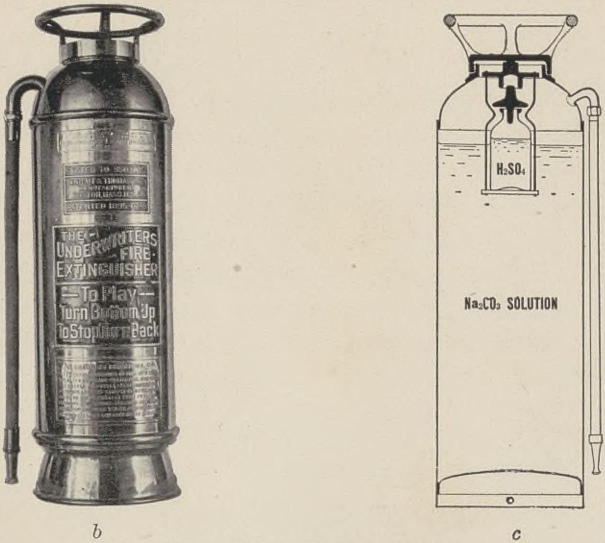


FIG. 43. — A FIRE EXTINGUISHER

(*a*) Extinguishing candles by pouring into the glass tank in which they are burnin the heavy gas, carbon dioxid.
(*b*) A commonly used fire extinguisher.
(*c*) Section of the same, showing construction.

it is the essential constituent of most fire extinguishers (Figs. 43*b* and *c*). They are charged with dilute solutions of carbonate of soda and sulfuric acid which interact and liberate a large quantity of carbon dioxid. This creates a high pressure within the cylinder, causing large quantities of the gas to dissolve in the water present. Thus a fire extinguisher is essentially a large siphon of "soda water."

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2$$

Carbon dioxid is somewhat soluble, 1 volume of water at ordinary temperatures absorbing a little more than 1 volume of the gas, and, as with other gases, the quantity is greatly increased by pressure. When the extra pressure is removed, the excess of carbon dioxid is given off by the water in small bubbles, causing foaming or effervescence. Mineral waters in which large quantities of carbon dioxid are dissolved usually contain bicarbonate of soda also. Hence they are known as "*soda waters.*" Artificially prepared "soda water" contains carbon dioxid only.

Carbonic acid. A solution of carbon dioxid in water has a slight acid taste and turns blue litmus red. Since neither dry carbon dioxid nor water affect litmus, some new body must have been formed by the interaction of these two substances. This is known as *carbonic acid.* Its probable formula is H_2CO_3, for, on neutralizing the solution of the acid with sodium hydroxid, sodium carbonate, Na_2CO_3, results. Of the reactions taking place, the first is distinctly reversible and runs to equilibrium.

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$
$$H_2CO_3 + 2\,NaOH \rightarrow Na_2CO_3 + 2\,H_2O$$

If, instead of sodium hydroxid, calcium hydroxid or limewater, $Ca(OH)_2$, is used to absorb the carbon dioxid, a white precipitate of calcium carbonate is formed. This reaction is used as a *test* for carbon dioxid. By allowing a dish of limewater to stand exposed to the air, the presence of carbon dioxid in the air may be demonstrated. Similarly by blowing the breath through limewater, its presence in the expired air may be proved.

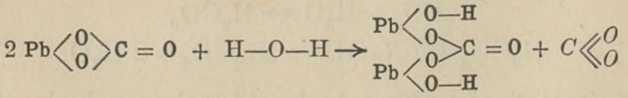
Carbonic acid is so unstable that it is unknown except in solution, for it decomposes readily into its anhydrid and water, as the first of the preceding equations indicates. It is so weak an acid that it is displaced from its salts by nearly all other acids. When acids are poured on **carbonates**, two equations express the change more correctly than the single one given on the preceding page.

$$\mathbf{CaCO_3} + 2\,\mathrm{HCl} \rightarrow \mathrm{CaCl_2} + \mathrm{H_2CO_3}$$
$$\mathrm{H_2CO_3} \leftrightarrow CO_2 + \mathrm{H_2O}$$

Analogously to this decomposition of the acid into oxids of carbon and hydrogen, most salts of carbonic acid when heated decompose readily into carbon dioxid and an oxid of the metal present in the salt. With the exception of the sodium, potassium, and ammonium salts, all the common carbonates are insoluble and may be prepared by mixing a solution of a soluble carbonate with a solution of a salt of the metal whose carbonate is desired, for the insolubility of the carbonate causes the reaction to run to completion.

$$\mathrm{FeCl_2} + \mathrm{Na_2CO_3} \rightarrow \mathbf{FeCO_3} + 2\,\mathrm{NaCl}$$

Many carbonates are so unstable that they lose a part of their carbon dioxid at ordinary temperatures and form basic carbonates, thus:



$$2\,\mathrm{Pb}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\rangle\mathrm{C}=\mathrm{O} + \mathrm{H{-}O{-}H} \rightarrow \begin{matrix}\mathrm{Pb}\left\langle\begin{matrix}\mathrm{O{-}H}\\ \mathrm{O}\end{matrix}\right.\\ \mathrm{Pb}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{O{-}H}\end{matrix}\right.\end{matrix}\!\!\!\rangle\mathrm{C}=\mathrm{O} + C\langle\!\langle\begin{matrix}O\\ O\end{matrix}$$

Carbon and life. Carbon in combination with other elements is the principal constituent of all living things.

Animals derive their food directly or indirectly from plants (p. 129), and the question arises whether plants get their carbon from the soil, or from the atmosphere as some plants do their nitrogen. Many species of air plants do not come in contact with the ground, hence they must derive all their food from the air. It has been proved by experiment that all plants derive their carbon from the atmosphere.

Plants absorb carbon dioxid from the air by means of their leaves. When sunlight falls on them, the carbon dioxid is decomposed by the chlorophyll, or green coloring matter. Oxygen is set free and returned to the atmosphere, and the carbon enters into complicated compounds which constitute the tissues of the plant. In the laboratory a considerable amount of energy is required to decompose carbon dioxid into its elements. In nature this energy is furnished by the sunlight.

When animals eat plants, the carbon compounds with their stored-up energy are transferred to the animal body. There in time these compounds unite with oxygen from the blood, and carbon dioxid is formed. By the process of respiration this is returned to the air, whence it originally came. The energy set free in this process is the residue of that derived at first from the sun and is transformed by the animal into heat, motion, etc. When plants and animals decay, their carbon is returned to the air in the course of time, though the completion of the process may be long delayed. There is not the slightest doubt that some of the particles of carbon which now constitute our own bodies have previously existed in animals and plants long since dead; or that at some future time they will again enter into the body of some other living thing. Of course, the same is true in regard to other elements.

o

This series of changes through which carbon passes is often called the *cycle of carbon in nature.*

Carbon monoxid. When carbon is burned in a good draft, the product is carbon dioxid; but when the supply of oxygen is deficient, carbon monoxid is formed according to the equation:

$$2\,C + O_2 \rightarrow 2\,CO$$

When hard coal burns, the portions at the bottom are in contact with fresh air and burn to carbon dioxid. This rises and comes in contact with heated carbon and is reduced to carbon monoxid.

$$CO_2 + C \rightarrow 2\,CO$$

The carbon monoxid then rises to the top of the mass, where it meets the air again and burns to carbon dioxid with a flickering, bluish flame.

$$2\,CO + O_2 \rightarrow 2\,CO_2$$

Producer gas is made by burning coal in a supply of air only sufficient to convert the carbon into carbon monoxid. It consists of about 30 % of carbon monoxid, 60 % of nitrogen, and 10 % of other gases, chiefly marsh gas, CH_4, hydrogen, and carbon dioxid. It is used for gas engines, but is a relatively poor fuel because it contains such a large percent of nitrogen.

Water gas, used for heating and lighting purposes, is made by passing steam through red-hot coal. Two reactions may take place, depending on the temperature and the proportions of the reagents.

$$C + H_2O \rightarrow CO + H_2 \text{ or}$$
$$C + 2\,H_2O \rightarrow CO_2 + 2\,H_2$$

As carbon monoxid is very poisonous, many deaths have been traced to its escape from stoves and gas-pipes.

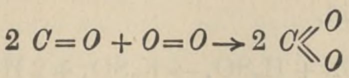
In the laboratory carbon monoxid is most conveniently made by heating oxalic acid, $H_2C_2O_4$, with sulfuric acid. From oxalic acid sulfuric acid abstracts water and combines with it, but since the sulfuric acid is not changed otherwise, it need not appear in the equation.

$$H_2C_2O_4 \rightarrow H_2O + CO_2 + CO$$

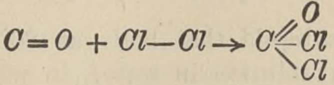
Equal volumes of carbon monoxid and dioxid are formed, but the latter may be removed when necessary by bubbling the mixed gases through sodium hydroxid, which does not react with carbon monoxid under these conditions.

Properties. Carbon monoxid is a colorless, transparent, odorless gas slightly heavier than air. It is very poisonous, uniting with the blood and preventing the absorption of oxygen. When ignited, it burns with a pale blue flame to carbon dioxid.

Since carbon acts ordinarily with a valence of 4, in carbon monoxid it does not seem to be showing its full valence. This idea is supported by the fact that the monoxid is very active chemically, the carbon combining with many substances directly and becoming tetravalent. Compounds in which certain of the elements are not showing their ordinary full valence are said to be *unsaturated*. Such bodies are usually very reactive, uniting with other substances by direct addition, as the following equations indicate:



$$2\ C=O + O=O \rightarrow 2\ C\!\begin{array}{l} \diagup\!\!\!\diagup O \\ \diagdown\!\!\!\diagdown O \end{array}$$



$$C=O + Cl{-}Cl \rightarrow C\!\begin{array}{l} \diagup\!\!\!\diagup O \\ -Cl \\ \diagdown Cl \end{array}$$

Carbon monoxid acts as a powerful reducing agent on this account, and is very valuable in obtaining metals from their ores. It is probable that when carbon is used in smelting, carbon monoxid is formed and plays the principal part in the reduction. It has the advantage over carbon of being a gas, and therefore comes in contact with all parts of the ore. The following reactions may be considered typical:

$$CuO + C \rightarrow Cu + CO$$
$$CuO + CO \rightarrow Cu + CO_2$$

Cyanogen compounds. The elements carbon and nitrogen do not readily combine except under the influence of the electric arc, when cyanogen, $(CN)_2$, is formed. When material containing carbon and nitrogen is heated with a base, compounds known as the *cyanids* are formed, consisting of a metal in combination with carbon and nitrogen. The process is usually carried on by heating potassium carbonate, scrap iron, and charcoal together with refuse animal matter, such as hoofs, horns, hair, etc. Under these circumstances when the cooled mass is treated with water *potassium ferrocyanid*, $K_4FeC_6N_6$, is dissolved out. This substance serves as the starting point in the preparation of other cyanogen compounds; for by heating with metallic potassium or sodium, simple cyanids are formed, as the equation shows:

$$K_4FeC_6N_6 + 2\,K \rightarrow 6\,KCN + Fe$$

Hydrocyanic acid, HCN, is obtained by treating a cyanid with sulfuric acid.

$$2\,KCN + H_2SO_4 \rightarrow K_2SO_4 + 2\,HCN$$

It is a colorless liquid that boils at 26°. Hence it is usually kept in solution in water, in which it is very soluble. The solution is known as *prussic acid;* it is a weak acid and a very powerful poison.

The salts of hydrocyanic acid are the *cyanids.* They resemble in many respects the corresponding salts of hydrochloric acid. The sodium and potassium salts are extensively used in the plating industry and in the extraction of gold and silver from their ores.

Hydrolysis. When potassium cyanid is dissolved in water, the solution turns red litmus blue, yet potassium cyanid is a normal salt, not a base or basic salt. At the same time the solution smells strongly of hydrocyanic acid, yet potassium cyanid contains no free acid and is not an acid salt. To explain the presence of free acid and free base in the solution, it is necessary to assume that a reaction takes place between the salt and water as given in the following equation. That this reaction actually takes place is proven by experiments.

$$\mathrm{KCN} + \mathrm{HOH} \rightarrow \mathrm{KOH} + \mathrm{HCN}$$

The interaction between a salt and water to produce an acid and a base is known as hydrolysis, a term meaning "decomposition by means of water." To litmus the solution gives the reaction of the stronger component. That is, if the base is stronger than the acid, the salt formed will react alkaline. If the acid is stronger than the base, the salt formed will react acid. Potassium and sodium carbonate solutions turn litmus blue because potassium and sodium hydroxids are stronger as bases than carbonic acid is as an acid. Copper sulfate and ferric chlorid turn litmus red because sulfuric and hydrochloric acids are stronger as acids than copper and ferric hydroxids are as bases.

Complete hydrolysis of a salt does not usually take place, because the acid and base formed in the reaction begin to neutralize each other and reverse the reaction, for obviously *hydrolysis is the reverse of neutralization.* Analogously, when the attempt is made to neutralize weak acids or weak bases, the reaction does not run to completion, but some free base and free acid are left in solution because of hydrolysis of the salt which is formed. Why the neutralization of weak acids and weak bases runs to equilibrium and not to completion will be explained later (p. 266).

Burning and supporting combustion. Whenever chemical combination takes place between two substances, it is customary to say that one acts on the other, the inference being that the other is more or less passive and permits the first to act. We have no reason for believing that the action is not mutual, however. When two substances unite, each reacts on the other, and neither acts more strongly than the other. Thus illuminating gas is said to burn in air because the oxygen of the air supports the combustion. Experiment shows, however, that the action is mutual, for either may be made to support the combustion of the other.

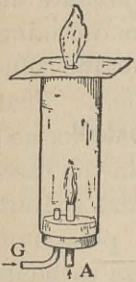


Fig. 44.

The apparatus shown in Fig. 44 consists of a lamp chimney, the upper end of which is covered with a sheet of asbestos or moistened cardboard having a hole in the center of it. The lower end is closed by a stopper pierced with two holes, through which pass two tubes, one of which is shorter and broader than the other. The longer tube, *G*, is connected with a gas jet, and illuminating gas is allowed to flow at full pressure for a moment into the apparatus. It is then turned down and the gas is lighted above the cardboard. If a lighted match is thrust up into the broader tube, *A*, something catches fire. Air passes up this tube and burns in an atmosphere of illuminating gas at the same time that illuminating gas is burning in air above the cardboard.

From this experiment it appears that the distinction between burning and supporting combustion depends not on any peculiar chemical properties, but rather on the relative amounts of the substances concerned. Ordinarily, when a thing burns, it is wasted away, while the air, which also takes part in the burning, is present in such great quantity that it seems not at all affected by the burning. So it has become the custom to say that the substance which is present in smaller quantity, and therefore disappears first, is the one that burns; and that the gas abundantly present even after the reaction has ceased is the one that supports combustion.

Luminous flames. The reason why some flames are luminous while others are not is not entirely understood. Any flame may be made luminous by sifting into it minute particles of any solid substance. Flames that give considerable light usually contain carbon compounds, and it is believed that in such cases the light usually comes from the hot carbon particles separated in certain parts of the flame. That carbon is present in such flames may be shown by the fact that when any cold object is held in the flame, it becomes "smoked," *i.e.* covered with particles of carbon.

To prevent the deposition of soot on an object held in a gas flame, the Bunsen burner was invented. The openings at the bottom of the tube are so arranged that as the gas issues from the fine jet, air is drawn in and mixes with the gas. In this way more complete combustion is obtained, the flame is hotter, and all carbon is burned to the dioxid. "*Blue flame*" *gas or oil stoves* depend on this same principle.

The structure of a flame. We have noted previously that a flame is simply a body of burning gas. Inspection of a Bunsen burner flame shows that it consists of three zones or parts (Fig. 45):

1. The inner zone, *G*, inside the greenish cone consists of unburned gas, as may be demonstrated by drawing off some of the gas through a tube held inside this cone.

The gas may be ignited at the end of the tube as shown in Fig. 46.

2. There is a bluish or greenish zone surrounding the inner cone, in which combustion is proceeding vigorously. The amount of oxygen is deficient, however, and the combustion is incomplete. Since carbon monoxid is present, this zone is known as the *reducing flame* (*R*, Fig. 45). Many metallic oxids held in this part of the flame are reduced, sometimes to the metallic condition.

Fig. 45.

3. In the outer, almost invisible, envelope, combustion is completed in the presence of an excess of air. Since this outer flame is very hot, oxidation caused by the presence of air takes place rapidly. Hence this zone is called the *oxidizing flame* (*O*, Fig. 45).

In a candle flame the same parts exist, with these differences: The inner cone is around the wick and is hard to see because it is surrounded by the second zone, which in this case is a bright yellow instead of bluish. It deposits soot on cold objects. The outer envelope is nearly invisible and is not as hot as in the Bunsen flame. By lessening the supply of air, the Bunsen flame is made like a candle flame.

A burning candle is a miniature gas manufactory. The heat from the flame melts the paraffine or tallow which then rises in the wick by capillary action, and is decomposed by the heat into gases which burn and form the flame.

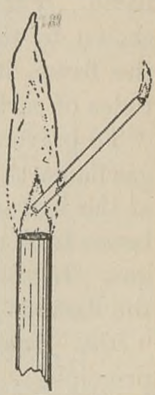


Fig. 46.

The **blowpipe** is an instrument for consuming gas by means of a forced draft of air, so that the gas burns more quickly and gives an intenser heat. The mouth blowpipe (Fig. 47) consists of a tube bent at right angles near one extremity and ending in a fine opening. This end is placed in a flame, the other end in the mouth, and the breath is blown forcibly through the tube. By blowing properly one may make the blowpipe flame show the same three parts as a Bunsen flame. The outer envelope is very efficient as an oxidizing agent, and most metals or metallic compounds heated in it are converted into oxids.

In blowpipe work the substance to be heated is usually supported on a piece of charcoal. Oxids often differ in appearance and have characteristic colors. In such cases it is easy to detect what metal is in a compound by heating it in the oxidizing flame. On the other hand, characteristic results may be obtained by the reducing flame. The determination of substances in this way is known as *blowpipe analysis.*


Fig. 47.

Industrial applications. The value of carbon and its compounds to the industrial world depends in considerable degree on the energy liberated when carbon oxidizes. It is the energy of burning carbon which generates the animal heat of our bodies, warms our buildings, and turns most of the wheels of industry. The amount of heat liberated by burning a mole of carbon is only about one eighth as great as that produced when a mole of hydrogen burns. The hydrogen is much more than eight times as expensive, however. On this account, carbon is generally used as fuel instead of hydrogen, for it liberates a larger amount of heat at smaller cost than any common substance.

The temperature (1200–1400°) produced by burning carbon or its compounds, such as coal, wood, gas, or oil, is not high enough for many industrial purposes, hence it is increased to 1800–2000° by the use of forced draughts of heated air, or by an oxygen blast when necessary. For the highest temperatures the electric furnace is used.

An **electric furnace** is a furnace heated by electricity. Usually there is no electrolysis or other action of the current except the heating effect. The latter is caused by forcing the current through substances which do not readily allow the electricity to flow. The greater the resistance to the flow of the current, the higher is the temperature produced. By leaving breaks in the conductor, the current is forced to jump across the air spaces and form *arcs* (Fig. 48). In this way the greatest effect is produced. Temperatures as high as 3000–3500° may be produced in this way.

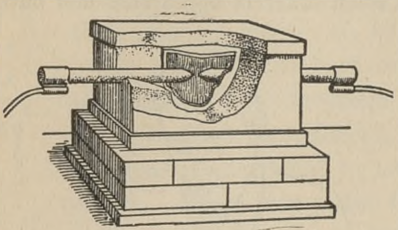


Fig. 48.

Fuels. Wood, coal, and oil are the substances burned most generally when it is desired to transform chemical energy into heat and other forms of energy. Since wood contains about 42 % of oxygen, it is obvious that, weight for weight, it is not as valuable as coal or oil, which contain no oxygen; for oxygen may be obtained without cost from the atmosphere. For this and other reasons wood is not as good a fuel as coal or oil.

Oil and gas leave no solid ash, hence are often preferable to wood or coal.

For use in gas engines, gaseous fuel is necessary; hence coal is often converted into producer gas or water gas, as has been stated (p. 194). Since gas engines are coming into greater use every year, these fuels are becoming increasingly important.

SUMMARY

CARBON COMPOUNDS

Carbon dioxid, CO_2, is formed when

1. carbon or any of its compounds burns in a good supply of air;
2. a carbonate is sufficiently heated;
3. a carbonate is treated with an acid.

Properties. Carbon dioxid is a colorless, pungent gas heavier than air. It causes suffocation by preventing the absorption of oxygen by the blood. It does not burn or support combustion and is an ingredient of fire extinguishers.

Carbonic acid. When carbon dioxid dissolves in water, the solution contains carbonic acid, an unstable substance, the salts of which are carbonates. Soda water is a solution of carbon dioxid under pressure.

Carbon monoxid, CO, is formed when

1. carbonaceous material is burned in an insufficient supply of air, as in making *producer gas;*
2. water is passed over hot carbon, as in making *water gas;*
3. oxalic acid is heated with sulfuric acid.

Properties. It is a colorless, odorless, poisonous gas that burns with a blue flame to carbon dioxid. Being an *unsaturated* compound, it is a good reducing agent and is employed in extracting metals from their ores.

Cyanogen compounds contain carbon and nitrogen and usually some metal. They are generally very poisonous. The cyanids, salts of hydrocyanic acid, HCN, are most important.

Cycle of carbon. Carbon dioxid is taken out of the air by plants. The energy of the sunlight, absorbed by the green coloring matter of the leaves, decomposes carbon dioxid into its elements. Oxygen is returned to the atmosphere and carbon with its energy enters into compounds which are the tissues of the plants. Animals eat plants and so obtain the carbon and its associated energy. When food is oxidized in the body, carbon dioxid is returned to the air, and the energy thus liberated is converted by the animal into heat, motion, etc. When an animal or plant dies, the carbon in its body is converted into the dioxid, and so the cycle is completed.

Burning and supporting combustion are relative terms. The chemical action is mutual, but the substance that is used up first is said to burn, and the other substance is said to support the burning.

A flame consists of three parts:

1. An inner portion consisting of unburned gas;
2. A middle, *reducing flame* where there is incomplete combustion due to an insufficient supply of air;
3. An outer, *oxidizing flame* containing an excess of air.

The *Bunsen burner* prevents soot depositing on objects held in the flame by mixing the gas with air, thus insuring complete combustion of all carbon. *Blue flame gas and oil stoves* depend on this same principle.

The *blowpipe* is useful for oxidizing or reducing substances and so affording information as to their composition.

Luminosity of ordinary flames is probably caused by the heated particles of carbon in the burning gas.

The **temperature** produced by combustion of carbonaceous substances (1200–1400°) may be increased to 1800–2000° by air or oxygen blasts. For higher temperatures the electric furnace is used.

Fuels. Wood is not so good as coal or oil because it contains oxygen. Gas fuels are needed for gas engines, hence coal is often converted into *producer gas* or *water gas.*

QUESTIONS

1. Why will carbon dioxid not burn? Are fire-proof substances similar to or different from carbon dioxid in chemical character?

2. Why is it sometimes dangerous to remain in the vicinity of a lime kiln? In the making of 1 ton of lime, how much carbon dioxid is produced?

3. Show how the carbon in your body was derived originally from the atmosphere and will finally return to the atmosphere.

4. From what is the energy of a steam engine derived? What is the original source of this energy?

5. How could the presence of large quantities of carbon dioxid in a well be ascertained? How may the carbon dioxid in air be removed?

6. Write equations for the action of two common acids on marble. How many standard liters of carbon dioxid should be obtained from 100 grams of marble in each case?

7. How is a fire extinguisher made, and how does it put out a fire?

8. More than 300 years ago Van Helmont made the following experiment: A young willow tree weighing 5 pounds was planted in a box of earth weighing 200 pounds. For 5 years nothing was added except distilled water. The tree grew until it weighed 170 pounds. The earth in which it was planted lost only 2 ounces during the same time. Explain. Whence does a growing tree derive the material by which it grows?

9. Suppose that the earth had an atmosphere of illuminating gas. If air were distributed through pipes, which gas would then burn?

10. Why is a Bunsen flame non-luminous?

11. Why does blowing a fire cause it to burn more vigorously? Why does blowing against a candle flame extinguish it?

12. It has been calculated that the average man breathes out 465 grams of carbon dioxid each day. How many grams of starch ($C_6H_{10}O_5$) must be oxidized to produce this amount of carbon dioxid?

13. Silver carbonate is insoluble. How would you prepare it from silver nitrate, $AgNO_3$? Write the chemical equation.

14. How may hydrogen be distinguished from carbon monoxid?

15. Compare the action of carbon monoxid and of hydrogen on cupric oxid, CuO. Write the two equations.

16. Why is "water gas" more likely to cause death if inhaled than illuminating gas?

CHAPTER XIX

ORGANIC CHEMISTRY

ANIMAL and vegetable material consists of compounds of carbon united with hydrogen and oxygen, and sometimes also with nitrogen, phosphorus, sulfur, and other elements. These compounds are very numerous, and by their interaction many others may be produced. At one time chemists did not know how to prepare any of these substances in the laboratory, and it was supposed that they could be made only by the action of "vital force" acting through some living organism. Hence the study of their composition and properties was known as *organic chemistry*, as distinguished from mineral or *inorganic chemistry*.

Since that time, however, so many products usually of organic origin have been made in the laboratory without the aid of living things, that the distinction between organic chemistry and inorganic chemistry is now largely lost. To-day organic chemistry means only the study of the compounds of carbon. The chemistry of carbon differs from the chemistry of the other elements mainly in the number and complexity of the substances formed by this element, for all chemical changes and the formation of all compounds follow the same laws.

Compounds of carbon with hydrogen. While most elements form with hydrogen one, two, three, or at most a few more compounds, carbon unites with hydrogen in more than a hundred different proportions. The compounds thus formed are called *hydrocarbons*. The hydrogen of the hydrocarbons may be wholly or in part replaced by other elements or groups of elements, and the number of derivatives thus obtained is practically limitless.

Although the number of known hydrocarbons now amounts to more than a hundred, it has been shown by investigation that the relations existing among them are not so complicated as might at first be supposed. They may be grouped in a few classes, and a general formula may be written for each class, which expresses the composition of every member of that class. The following table illustrates some of the most important series or classes:

COMPOUNDS OF CARBON AND HYDROGEN

Series	MARSH GAS	ETHYLENE	ACETYLENE	——	BENZENE
Formula	C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}	C_nH_{2n-4}	C_nH_{2n-6}
$n=1$	CH_4	——	——	——	——
$n=2$	C_2H_6	C_2H_4	C_2H_2	——	——
$n=3$	C_3H_8	C_3H_6	C_3H_4	——	——
$n=4$	C_4H_{10}	C_4H_8	C_4H_6	——	——
$n=5$	C_5H_{12}	C_5H_{10}	C_5H_8	C_5H_6	——
$n=6$	C_6H_{14}	C_6H_{12}	C_6H_{10}	C_6H_8	C_6H_6
$n=7$	C_7H_{16}	C_7H_{14}	C_7H_{12}	C_7H_{10}	C_7H_8
$n=8$	C_8H_{18}	C_8H_{16}	C_8H_{14}	C_8H_{12}	C_8H_{10}

Properties and sources of hydrocarbons. Hydrocarbons are in general colorless, inflammable substances, burning readily to carbon dioxid and water. The luminosity of their flames increases with the percentage of carbon. When their molecular weights are small, the hydrocarbons are gaseous, but with increasing molecular weights, their boiling points rise until they become liquid, and finally solid.

The *marsh gas series* contains a large number of compounds, the number of carbon atoms rising from 1 to 24 without a break in the series. After this many members are wanting, and after the compound $C_{60}H_{122}$ none are known except $C_{120}H_{242}$. Practically all of this series is found in petroleum, which is a mixture of these and many other carbon compounds. The members of this series containing less than six carbon atoms are gaseous at ordinary temperature, and are the substances constituting *natural gas.* The rest of the series, liquids and solids, are *petroleum* (Fig. 49*a*). When the crude oil is distilled and otherwise purified, the various products are *naphtha*, *gasoline*, *benzine*, *kerosene*, *machine oil*, *vaseline*, *paraffine*, etc. In these liquid fractions the members of the methane series, containing from 6 to about 16 carbon atoms, are found. The higher members of the series are solid and constitute the substance which we call paraffine. For this reason the whole series is often called the *paraffine series.*

The bubbles of gas that are seen rising through pools of stagnant water are, on examination, found to contain a large proportion of methane or marsh gas. This hydrocarbon is usually the chief constituent of natural gas, and is found in mines, being called "*fire-damp*" by miners. Like all combustible gases, it forms an explosive mixture with air (Fig. 49*b*). After an explosion, carbon dioxid, "*choke damp*," is left and sometimes carbon monoxid. Rescue workers in mines after an explosion wear helmets supplied with oxygen from cylinders carried on the back. The carbon dioxid breathed out is absorbed by potassium hydroxid inside the helmet. Thus the oxygen is breathed over and over again until it is converted entirely into carbon dioxid.

When a candle or lamp is burning, the oil rises into the wick because of capillarity, and is decomposed by the heat of the flame into various gases, some of which belong to the *ethylene series.* Members of this series burn with a brightly luminous flame and are therefore valuable for lighting purposes.

Courtesy of the "Scientific American"

FIG. 49. — HYDROCARBONS IN NATURE

(*a*) A California oil gusher.

(*b*) A coal-mine explosion.

The only important member of the *acetylene series* is acetylene itself. For a long time it was difficult to prepare, but it is now made in large quantities from calcium carbid, an electric furnace product. This treated with water liberates acetylene, which is in use as an illuminant. The reactions are:

$$\mathrm{CaO} + 3\,\mathrm{C} \rightarrow CO + \mathrm{CaC_2}$$
$$\mathrm{CaC_2} + 2\,\mathrm{HOH} \rightarrow \mathrm{Ca(OH)_2} + C_2H_2$$

Coal tar is a product formed when coal is dry distilled in coke ovens or in gas works. It is a complex mixture containing many valuable constituents, one of which is *benzol*, often called *benzene*. From benzene, C_6H_6, is made *aniline*, $C_6H_5NH_2$, indispensable in the dye industry.

Naphthalene, $C_{10}H_8$, commonly used as "moth balls," belongs to another different series of hydrocarbons.

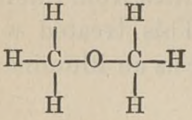
Isomerism. There are a number of organic substances that have the same formulas, such as

$$\left.\begin{matrix}\text{Methyl ether}\\ \text{Alcohol}\end{matrix}\right\} C_2H_6O$$

$$\left.\begin{matrix}\text{Cane sugar}\\ \text{Milk sugar}\\ \text{Malt sugar}\end{matrix}\right\} C_{12}H_{22}O_{11}$$

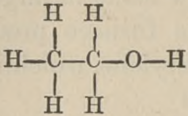
Substances such as these, possessing the same composition but exhibiting different properties, are said to be *isomeric*, and such a condition is called *isomerism*. There are many instances of it in organic chemistry and a few in inorganic chemistry. The molecules of isomeric substances contain the same elements and the same number of atoms of each element. Isomerism is explained on the basis of a different arrangement inside the molecules.

The way in which methyl ether and alcohol react with other substances has led to the belief that their molecules have the structure given below:



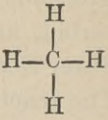
$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & -O- & C & -H \\ & | & & | & \\ & H & & H & \end{array}$$

Methyl ether



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

Ethyl alcohol

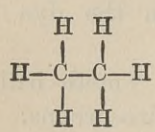


$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

Methane

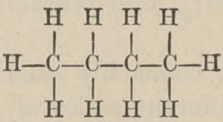
Isomeric carbon compounds are so frequently encountered that structural formulas have been the subjects of much attention in organic chemistry. The structural formula for methane is given above.

For other members of the series similar structural formulas are written, thus:



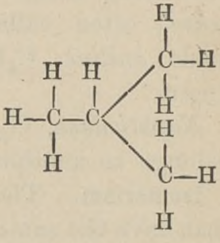
$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & H & \end{array}$$

Ethane



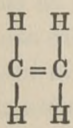
$$\begin{array}{ccccccccc} & H & & H & & H & & H & \\ & | & & | & & | & & | & \\ H- & C & - & C & - & C & - & C & -H \\ & | & & | & & | & & | & \\ & H & & H & & H & & H & \end{array}$$

Normal butane



An isomeric butane

Members of the ethylene series seem to have one pair of carbon atoms joined together by a double linking, and in the acetylene series there seems to be a triple linking, as the formulas below indicate. In benzene six carbon atoms seem to be united into a ring or nucleus something like that shown in the formula. As these formulas indicate, members of the ethylene, acetylene, and benzene series all act as typical unsaturated compounds.

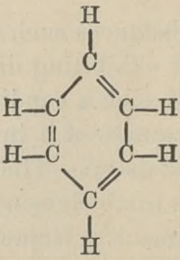


$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

Ethylene

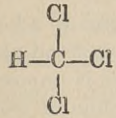
$H{-}C{\equiv}C{-}H$

Acetylene



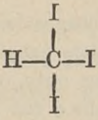
Benzene

By proper means chlorin, oxygen, sulfur, and many other elements may be substituted for the whole or a part of the hydrogen of hydrocarbons. As a result there is an almost infinite series of substitution products. The structural formulas for some important substances are given below:



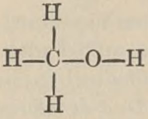
$\mathrm{H{-}\overset{Cl}{\underset{Cl}{C}}{-}Cl}$

Chloroform



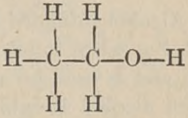
$\mathrm{H{-}\overset{I}{\underset{I}{C}}{-}I}$

Iodoform



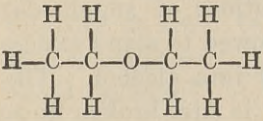
$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}O{-}H}$

Wood alcohol



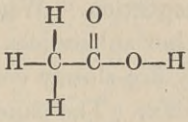
$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}H}$

Grain alcohol



$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$

Ether



$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H}$

Acetic acid

From the preceding formulas it is seen that hydroxyl radicals may be substituted for some of the hydrogen in hydrocarbons. Organic hydroxids such as these are called *alcohols*, and organic oxids are called *ethers*. Some organic groups or radicals are found in a series of compounds similarly to NH_4 or other radicals in inorganic chemistry. The more important organic radicals are methyl, CH_3; ethyl, C_2H_5, etc.

Alcohols. The first member of the series of alcohols is *methyl alcohol*, CH_3OH, or *wood alcohol*. It is obtained in the distillation of wood and is used as a solvent in making paints, varnishes, and the like. It is very poisonous. It burns with a blue flame which is very hot and deposits no soot on cold objects held in the flame.

Ethyl alcohol, C_2H_5OH, common alcohol, is obtained by the fermentation of starch, sugar, and similar substances, hence its name of *grain alcohol*. It is a liquid boiling at 78°, but not freezing until – 130°. It is of importance industrially in all the ways mentioned for wood alcohol.

Since it can be manufactured at less cost than wood alcohol, it is preferable commercially. Like wood alcohol, it is poisonous in large quantities; when diluted it produces intoxication. It is an essential constituent of whisky, brandy, and other liquors.

Alcohol intended for use in making beverages is subject to a high tax, but when it has been mixed with a little gasoline or wood alcohol and is used for manufacturing purposes only, no tax is imposed. Such alcohol is said to be "*denatured*," since the gasoline or wood alcohol renders it unfit for drinking purposes.

Fermentation. When solutions of sugar, starch, and some other substances are allowed to stand exposed to the air, they are slowly converted into alcohol. The change is complex. The cane sugar is first broken up according to the equation:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2\ C_6H_{12}O_6$$

Several isomeric substances of the formula $C_6H_{12}O_6$ are known, one of which is grape sugar or glucose. This decomposes into alcohol and carbon dioxid according to the equation:

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$$

It has been found that this and many other cases of fermentation and decay are caused by the presence of certain organisms, known as *ferments*. Each ferment causes a definite change and forms substances not usually produced by other ferments. Milk becomes sour because of the production of lactic acid from milk sugar through the action of the lactic acid ferment (Fig. 50). The conversion of cider into vinegar is due to the change of fruit sugar into acetic acid by another ferment, known as "the mother of vinegar" (Fig. 51). Yeast contains several ferments commonly used in changing starch into sugar and finally into alcohol, the carbon dioxid produced causing the bread to rise. Another instance is the formation of nitric acid from decaying animal matter, and still others will occur to the reader.

As germs are always present in the air, most organic substances are liable to ferment and decay. Decomposition may be retarded or prevented by low temperature — "cold storage" —or by drying, both of which hinder the growth of germs. By the addition of a "preservative" or by heating, germs may be killed and decomposition prevented. A preservative is any substance which will kill germs. When added to foods it must, of course, be harmless to man. "Canned goods" are heated or treated with a preservative before being sealed up.

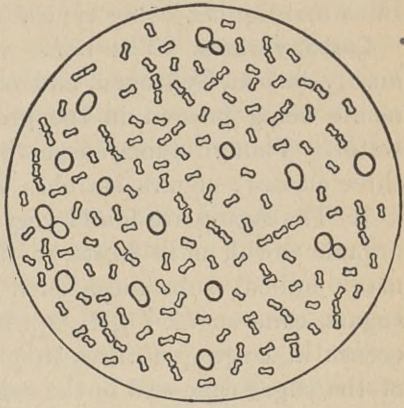


FIG. 50. — Lactic acid bacteria highly magnified.

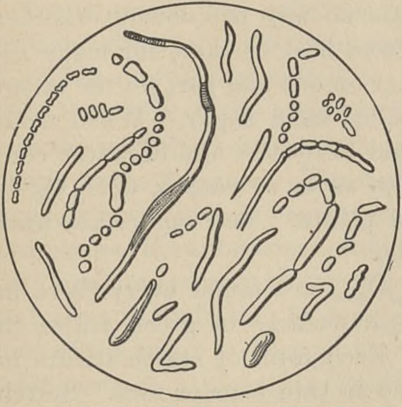


FIG. 51. — Mother of vinegar highly magnified.

Fermentation is believed to be due to substances secreted by the germs, and not due to any decomposition carried on by the germ itself. These substances act as ordinary catalytic agents. The digestive processes which take place in our bodies are of this nature, ptyalin in the saliva, pepsin in the gastric juice, and pancreatin in the intestinal liquids, being typical catalytic agents.

Carbohydrates. The name *carbohydrate* signifies primarily carbon, hydrogen, and oxygen, the two latter elements being present in the proper proportions to form water. Though numerous, carbohydrates fall readily into three classes: sugars, starches, and celluloses.

1. The *sugars* are found very widely distributed in the organic world, as in fruits, in the juices of plants, and in many animal substances such as milk. Of the many sugars, cane sugar, $C_{12}H_{22}O_{11}$, is the most important. It occurs in large quantities in plants, especially in the sap of the sugar cane and in the sugar beet. After the sirup from the juice of these plants is purified by animal charcoal, the sugar crystallizes in colorless prisms. The common belief that beet sugar is inferior to cane sugar in any way is entirely wrong, for they are absolutely the same substance. The grocer has no way of knowing whether the sugar he sells came from beet or cane, for many refineries run part of the year on one and part on the other, and both products are called cane sugar. When moderately heated, it melts and is by the loss of water converted into *caramel*. *Grape sugar* or *glucose*, $C_6H_{12}O_6$, is found in many fruits and plants. The sugars are used almost exclusively as foods.

2. The *starches*, $(C_6H_{10}O_5)_x$, are found everywhere in the vegetable kingdom, particularly in green fruits, in potatoes, and in cereals. Each form of starch occurs in microscopic grains, inclosed in thin bags or sacs. Starch is nearly insoluble in cold water. In hot water the thin membranes covering the grains are ruptured and the contents escape, forming a partial solution that on cooling

gives a jelly called *starch paste.* When boiled with dilute acids, starch is converted into sugars. The same transformation is brought about by the digestive ferments present in the fluids of the mouth and intestines, and also by certain other ferments. During the process of digestion starch is converted into glucose before metabolism takes place. The predominant use of starch is as a food; an insignificant proportion is used in the laundry and for other purposes.

3. *Cellulose*, $(C_6H_{10}O_5)_y$, forms the fibrous parts of plants. It varies somewhat in composition and properties according to the source from which it is derived; but in general it does not crystallize, is insoluble in water and ordinary liquids, and is changed to sugar by boiling with dilute acids. Cotton fiber and filter paper are almost pure cellulose. The important uses of cellulose in the form of wood, cotton, linen, etc., are for the clothing and shelter of man and for the manufacture of paper.

Sugar, starch, and cellulose in plants. It has already been mentioned (p. 193) that though the carbon in carbon dioxid is very firmly united to the oxygen, yet the sunlight that falls on the green parts of plants is able to separate the two elements, so that oxygen is given out by the plants in the daytime. The carbon of the carbon dioxid remains in the leaf and enters into new combinations. In this process the substances produced are simple sugars, and they are transported in the sap to all parts of the plant and serve as its food. In some manner not understood a part of the sugar is changed to cellulose and builds up the solid parts of a plant; another part is used up in the life processes of the plant; and the remainder is stored up, mostly in the form of starch, to serve as nourishment for future growth.

When the alcohols are oxidized, many of them are converted into bodies called *aldehydes*. Thus wood alcohol is oxidized to formaldehyde according to the equation:

$$CH_3OH + O \rightarrow CH_2O + H_2O$$

Common alcohol is in like manner changed to acetaldehyde.

$$C_2H_5OH + O \rightarrow C_2H_4O + H_2O$$

Formaldehyde is a powerful antiseptic and preservative. A 40% solution in water is known as *formalin*. Acetaldehyde finds use in medicine. Among other useful aldehydes may be mentioned *benzaldehyde* or *oil of bitter almonds*, C_7H_6O, and *vanillin*, $C_8H_8O_3$, the chief constituent of "vanilla extract" which is still obtained to some extent from vanilla pods, though principally manufactured in the laboratory.

Organic acids. All organic acids contain the COOH radical; *carboxyl* it is called. If this group be introduced into any compound, acid properties make their appearance and the substance becomes an organic acid. Organic acids do not possess acid properties in so great a degree as do the common mineral, or inorganic, acids. Their reactions are similar, however.

Among organic acids may be mentioned the following:

Formic acid, $H(COOH)$, so named from the Latin word meaning an ant, because it is found in ants and other insects. It is often the poisonous substance injected when one is bitten or stung by an insect. It may be neutralized by ammonia or baking soda and the pain lessened. Wet mud, applied to the wound, accomplishes the same purpose.

Acetic acid, $CH_3(COOH)$, the acid in vinegar.

Butyric acid, $C_3H_7(COOH)$, may be obtained from butter.

Oxalic acid, $(COOH)_2$, found in *oxalis* or sorrel.

Tartaric acid, $C_2H_4O_2(COOH)_2$, and *malic acid*, $C_2H_4O(COOH)_2$, found in most fruits, especially when not ripe.

Citric acid, $C_3H_5O(COOH)_3$, in lemons, oranges, and other citrus fruits.

Lactic acid, $C_2H_5O(COOH)$, formed in sour milk.

Salicylic acid, $C_6H_5O(COOH)$, obtained from willow bark, used in medicine and as a preservative.

Palmitic acid, $C_{15}H_{31}(COOH)$, *stearic acid*, $C_{17}H_{35}(COOH)$, and *oleic acid*, $C_{17}H_{33}(COOH)$, made from fats and oils.

Acetic acid is formed in large quantities in the distillation of wood for the purpose of making charcoal, the crude product obtained from this source being called *pyroligneous acid.* It is also made by a double fermentation of fruit juices, the alcohol from the first fermentation being oxidized through the instrumentality of a minute organism found in "mother of vinegar."

$$C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$$

Acetic acid is a colorless liquid, boiling at 118° and possessing a peculiar, characteristic odor. Vinegar contains about 5 per cent of it. In its chemical conduct it resembles other acids, affecting the color of organic dyes and neutralizing bases, but it is much weaker than the common mineral acids. When it is treated with a base, only that one of the hydrogen atoms which is in the carboxyl group is replaced by metal. Its salts, the *acetates*, when treated with any less volatile acid, yield acetic acid.

Organic salts or **esters.** A comparison of the structural formulas of the metallic bases and of the alcohols shows that there is a resemblance:

$K—O—H$	potassium hydroxid
$Na—O—H$	sodium hydroxid
$NH_4—O—H$	ammonium hydroxid
$CH_3—O—H$	methyl alcohol, or methyl hydroxid
$C_2H_5—O—H$	ethyl alcohol, or ethyl hydroxid

Though alcohols do not affect the color of litmus, yet they possess to a considerable degree the power of neutralizing acids. Thus, when ethyl alcohol is treated with nitric acid, the ethyl group, C_2H_5, displaces the hydrogen of the acid, forming ethyl nitrate, $C_2H_5NO_3$, a salt in which not a metal, but the radical C_2H_5, is united with the residue of the acid.

$$C_2H_5OH + HNO_3 \rightarrow C_2H_5NO_3 + H_2O$$

Similar reactions are possible with organic acids.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Acetic acid}}{HOOCCH_3} \rightarrow \underset{\text{Ethyl acetate}}{C_2H_5OOCCH_3} + H_2O$$

Organic salts usually have pleasant odors, and it has been found that the delicate perfume and flavor of many flowers and fruits is due to the presence of such organic salts. Thus, bananas owe their perfume to amyl acetate, a salt formed from amyl alcohol and acetic acid. The flavor of wintergreen is methyl salicylate, a salt of methyl (wood) alcohol and salicylic acid. Since many of these flavors and perfumes can be made in the laboratory more cheaply than they can be extracted from fruits and flowers, they are largely produced in this way.

Natural fats and oils are for the most part mixtures of organic salts, the most common ones being compounds of the alcohol *glycerine*, $C_3H_5(OH)_3$, with various organic acids. Butter contains the salt of glycerine and butyric acid. The glycerine salt of oleic acid constitutes a large part of olive oil and lard. The same salt of palmitic acid is found in palm oil and human fat, and the stearic acid salt in lard and tallow.

Soap. When a soluble hydroxid is added to a solution of a salt of a metal whose hydroxid is insoluble, the insoluble hydroxid is formed. A similar action takes place when a soluble hydroxid is heated with an organic salt, the latter being decomposed. Thus, ethyl nitrate with sodium hydroxid gives ethyl alcohol and sodium nitrate.

$$C_2H_5NO_3 + NaOH \rightarrow NaNO_3 + C_2H_5OH$$

This process is called *saponification.*

When fats and oils are saponified, their base, glycerine, is set free, and the metal from the hydroxid combines with the organic acid to form a salt. Thus the action of sodium hydroxid on hard fat is represented by the equation:

$$\underset{\text{Glycerine stearate}}{C_3H_5(OOCC_{17}H_{35})_3} + 3\,NaOH \rightarrow \underset{\text{Glycerine}}{C_3H_5(OH)_3} + \underset{\text{Sodium stearate}}{3\,NaOOCC_{17}H_{35}}$$

Sodium stearate is a *soap.* Other common soaps are sodium palmitate and sodium oleate. When potassium hydroxid is used, potassium soaps are formed. Ordinary *hard soap* is a mixture of sodium stearate, palmitate, and oleate. *Soft soap* contains the corresponding potassium salts.

Soaps owe their cleansing power to their ability to remove oily matter by forming an emulsion with it.

When ordinary soap solution is mixed with "hard" water, *i.e.* water containing salts of calcium or magnesium (p. 318), an insoluble lime or magnesia soap is formed which floats on the surface of the water as a curdy mass or scum. Since these salts do not dissolve, they cannot emulsify fats; hence they have no cleansing power. Hard water causes an annual loss to the civilized world of many million dollars.

Foods. The food of mankind consists of compounds of carbon united with hydrogen and oxygen, and sometimes with nitrogen and other elements. In analyzing a foodstuff the following substances are generally determined: (*a*) fats; (*b*) carbohydrates; (*c*) proteid; (*d*) water; and (*e*) mineral matter or ash.

While large quantities of *water* — about 5 pints or 5 pounds a day — are needed by the average individual, it is not properly a food in that it does not help to build up the body or furnish it energy. *Mineral matter* is needed for bone, etc. *Fat* and *carbohydrate* are oxidized in the body to furnish heat and energy just as oil, coal, and wood are burned to furnish heat and other forms of energy in an industrial plant. *Proteid* is the name given to foodstuffs which contain nitrogen. It is used to build up the tissues of the body; to make muscle and sinew. When these are worn out, they are burned in the body, also. Animal and vegetable oils, such as butter, lard, olive oil, etc., are an important factor in human food. Sugar and starch are the chief carbohydrates. Lean meat and eggs, peas, beans, lentils, etc., are the main sources of proteid. The following table gives the composition of some typical foods. Fig. 52 brings out the same points by diagrams.

COMPOSITION OF SOME TYPICAL FOODS

	FATS	CARBOHYDRATES	PROTEID	WATER	MINERAL
Oats	6.04	66.26	11.73	12.92	3.05
Wheat	1.77	73.55	12.23	10.63	1.82
Flour (wheat)	1.18	76.80	11.12	10.52	.40
Bread (home-made)	1.95	56.00	7.94	32.50	1.61
Potatoes	.30	21.00	2.70	75.00	1.00
Peas (green)	.50	16.50	4.00	78.10	.90
Peas (dry)	1.80	61.60	21.00	13.00	2.60
Milk	3.64	4.88	3.55	87.22	.71
Eggs	10.50	.00	14.80	73.70	1.00
Meats (medium lean)	5.50	.00	21.00	72.50	1.00
Cheese	30.25	2.03	25.35	38.60	4.07

Butter, lard, and the oils ordinarily used as food, whatever be their source, have about the same food value. Turnips, carrots, cabbage, cauliflower, celery, and "greens" contain 89 % of water, or over. They do not furnish as much food value as milk, which is 87 % water. The chief food value of fruits lies in the sugar which they contain, which varies from 3 % in the watermelon to 19 % in some plums. The proportion of proteid in dry peas and beans and in meat is practically the same, yet peas or beans cost much less per pound than meat. It is obvious, therefore, that some foods are much more expensive than others when the cost of a pound of fat, or carbohydrate, or proteid, derived from different food stuffs is taken as the basis of reckoning.

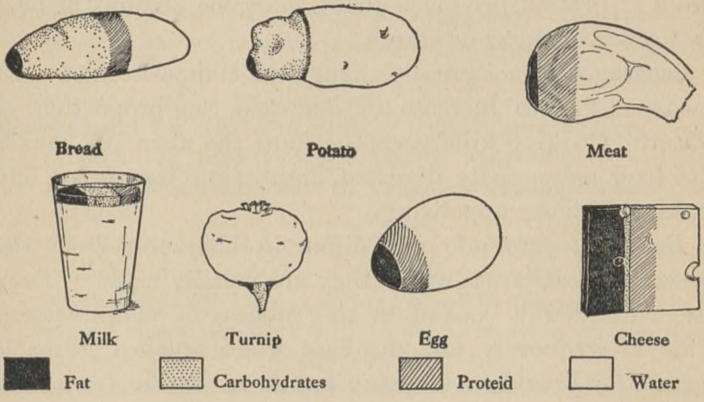


Fig. 52.

The amounts of the different constituents needed by an average individual in a day are given in the following table. The weights are given in grams of dry material; *i. e.* food dried at 105° until no more water is lost.

Amount of Food needed per Day

	Fats	Carbohydrates	Proteid	Total
Man at hard work	150	500	150	800
Man at moderate work	125	450	125	700
Woman at light work	44	400	92	536
Children (5–15 years)	43	325	75	443

Since sugar and starch are both carbohydrates, as a food one is equal to the other, weight for weight. Since fat contains less oxygen than carbohydrates, fat is a better fuel, 1 gram of fat being about equal to 2¼ grams of sugar or starch. Hence more fat is eaten by people living in cold countries than in warm regions. When oxidized, 1 gram of proteid produces about the same amount of heat as 1 gram of sugar or starch.

Cooking does not greatly change the composition of most foods except to increase or decrease the proportion of water. Cooking kills germs, softens the fiber and makes the food more easily digested, improving the flavor and making it more appetizing.

Breakfast foods do not differ in character from the wheat and oats from which they are usually made. They are usually well cooked in the process of manufacture. This is frequently not the case when crushed grain is served for breakfast in many families. Aside from this, they have no advantage over oatmeal or crushed wheat, though they cost several times more per pound. There is no reason why breakfast foods should be eaten rather than the cheaper cereals if both are well cooked; "for no process of manipulation can give a greater food value than was contained in the original grain."

SUMMARY

ORGANIC CHEMISTRY is the chemistry of the compounds of carbon. It differs from inorganic or mineral chemistry mainly in the number of compounds formed and in their complexity.

Hydrocarbons are compounds of hydrogen and carbon. Though numerous, they may readily be classified in a few series, of which the principal are the marsh gas, the ethylene, the acetylene, and the benzene series.

Properties and Sources. Hydrocarbons are inflammable, and are gases, liquids, or solids, according as their molecular weights are low or high. They are found in various sources, such as mines, swamps, natural gas, petroleum, and coal tar. Petroleum is a complex mixture of very many hydrocarbons.

Isomerism. Many organic compounds are *isomeric*, *i.e.* they have the same percentage composition and molecular weight, but have different properties. These differences are a result of different arrangements of the atoms in their molecules.

Alcohols are organic hydroxids. They may be formed by the introduction of one atom of oxygen into a hydrocarbon. The best known are wood alcohol, from the dry distillation of wood; and common alcohol, from the fermentation of the sugar in fruit juices, or of starch in grain or potatoes, by the action of certain ferments.

Carbohydrates are related to alcohols. They are: 1. Sugars, found principally in fruits and vegetables. 2. Starches, found in plants, as in potatoes and cereals. 3. Celluloses, forming the solid parts of plants.

Organic acids contain the group COOH. They may be formed by oxidizing alcohols. One of the most important is *acetic acid*, which is found in vinegar and is formed by the oxidation of the alcohol of wine or hard cider through the action of a ferment. It does not differ essentially from other acids.

Organic salts or **esters** are formed when an alcohol neutralizes an acid. Fats, oils, and many perfumes and flavoring extracts are organic salts. When an organic salt, such as fat, is boiled with a solution of an alkali, it is *saponified* and a *soap* is one of the products. Ordinary soap is a mixture of the alkali salts of the organic acids found in common fats and oils.

Foods consist of mixtures of (*a*) *fats*; (*b*) *carbohydrates*; (*c*) *proteid*; (*d*) *water*; and (*e*) *mineral matter*. Proteid makes muscle, sinew, and nerves. Fats and carbohydrates are burned in the body to furnish heat and energy much as oil and wood are burned under a boiler.

Cooking does not greatly change the chemical composition of foods. It kills germs, softens the fiber and makes it more digestible and appetizing.

QUESTIONS

1. What is the gas density of marsh gas; of acetylene?

2. What are the products formed when acetylene burns, and what are the volume relations?

3. Compare alcohol and sodium hydroxid in their deportment toward acids.

4. What salts of glycerine do you know of? (One was mentioned in a previous chapter.)

5. What is the difference between a carbohydrate and a hydrocarbon?

6. Compare soap and sodium chlorid in chemical constitution.

7. What part does fermentation play in making bread?

8. Through what changes does the sugar in sweet cider pass, if allowed to ferment?

9. How does cold storage preserve fruits or eggs? Why do dried fruits not spoil?

10. Why must canned goods be put in air-tight receptacles?

11. Compare isomerism and allotropy.

12. With what volume of oxygen should marsh gas be mixed if we wish to explode it most satisfactorily? With what volume of air?

13. Farmers generally use rain water for washing instead of water from springs or wells. Why?

14. If a soap solution is treated with hydrochloric acid, what are the products formed?

15. Ascertain the cost per pound of round steak, green peas, dried beans, cheese, and eggs, and calculate what a pound of proteid from each source will cost. Arrange these foods in the order of relative cheapness. (Dried beans have about the same composition as dried peas.)

16. Grape Nuts, Malta-Vita, Ralston's Health Breakfast Food, Vitos, Pettijohn's, and Shredded Wheat have practically the same composition as wheat or wheat-flour. Ascertain the cost per pound of carbohydrate in each, and arrange in order of relative cost.

17. Illuminating gas consists largely of methane, CH_4, and hydrogen. Water gas is a mixture of carbon monoxid and hydrogen. Both are used as fuel. Comment on the statement: "This gas is poor because so much water collects on the cold windowpanes when the gas is burning."

CHAPTER XX

THE HALOGENS

We have thus far considered a few typical elements, gaining from them besides facts an understanding of chemical methods and principles. Nearly a hundred elements are now known. We might consider these in any order that we choose: alphabetically, or according to their reacting weights, or in any other sequence. Experience has taught us that although no two elements are alike, certain ones very closely resemble others. We may minimize the burden on the memory if we consider at one time all those which are chemically similar, and then proceed from these to that type which is most closely related. From now on we shall consider the elements according to their natural groups, beginning with the chlorin group.

Halogens is a name given to a group of elements all of which show very close similarity to one another. Named in the order of their reacting weights they are *fluorin*, *chlorin*, *bromin*, and *iodin*. The term *halogens* signifies "salt-formers," and is applied to these elements because several of the compounds formed by them with the metals resemble common salt. A review of the properties of chlorin will serve to fix the type in mind. Bromin most closely resembles chlorin and will be considered first; after this, iodin, and finally fluorin, for the last differs more from the others than they do among themselves.

BROMIN (Br — 80), like chlorin, is too active an element to be found free in nature. Combined with potassium, sodium, and magnesium as bromids of these elements, it occurs in small amounts in sea water, mineral springs, and salt beds. In the United States the chief source of bromin is the salt deposits of West Virginia, Ohio, and Michigan.

Bromin is readily obtained in the free state by heating manganese dioxid and a bromid with sulfuric acid. When sodium bromid is used, the reaction is analogous to that for the liberation of chlorin from salt. Hydrobromic acid is doubtless set free at first and then oxidized by manganese dioxid as the equations indicate.

$$\mathbf{NaBr} + H_2SO_4 \rightarrow \mathbf{NaHSO_4} + \mathit{HBr}$$
$$4\,\mathit{HBr} + \mathbf{MnO_2} \rightarrow MnBr_2 + 2\,H_2O + \mathit{Br_2}$$

Bromin is a heavy, dark red substance, the only element except mercury that is liquid at ordinary temperatures. It fumes abundantly, producing vapors which have a strong, unpleasant odor and produce an irritation of the mucous membranes of the eyes, nose, and throat, as is the case with chlorin. Liquid bromin in contact with the skin causes painful wounds. The solution of bromin in water is called *bromin water*.

Like chlorin, bromin is a bleaching agent, but its action is less rapid. The other chemical properties of bromin also suggest those of chlorin. It combines directly with many elements, the union being sometimes accompanied by the evolution of light. Under the influence of bright sunlight it slowly unites with hydrogen to form hydrogen bromid or hydrobromic acid, HBr.

Being less active chemically than chlorin, bromin is displaced from many of its compounds by the former element. Advantage is sometimes taken of this fact in the commercial preparation of bromin from salt residues. For the purpose of purification, rock salt is recrystallized. As the solution concentrates, sodium chlorid separates continually, since it is relatively little soluble. In the mother liquors, called *bittern*, the more soluble of the impurities are left, among others being magnesium bromid, $MgBr_2$. This solution is sprayed into the top of towers (Fig. 53) filled with brick or other material so that a large surface of the liquid may be exposed. Chlorin gas enters at the bottom of the towers and the following reaction takes place:

$$MgBr_2 + Cl_2 \rightarrow MgCl_2 + Br_2$$

While trickling down through the mass of brick, the solution reacts with the gas and becomes continually poorer in bromids. At the bottom of the towers the weakest solution meets the most concentrated chlorin. The bromin is liberated in gaseous form and rises with the chlorin to the top of the towers where the strongest solution meets the mixed gases containing the smallest percentage of chlorin. This *principle of counter currents* is found to be most advantageous in industrial operations. (Note the use of this principle in purifying illuminating gas, p. 185.) On passing from the towers, the bromin is condensed in receivers.

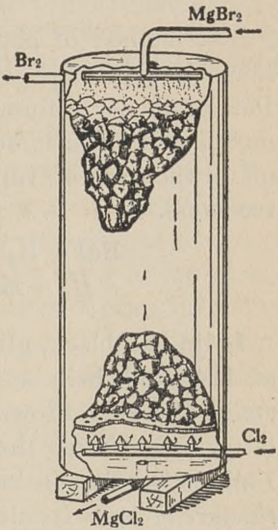


FIG. 53.

IODIN (I — 127) occurs in nature much as bromin does. Sodium, potassium, and magnesium salts are found in sea water and mineral springs, and also in the saltpeter beds of Chili. It is from this latter source that most of the iodin of commerce is now obtained.

There are several species of seaweeds which have the power of withdrawing sodium iodid from sea water and storing it up in their tissues. When these seaweeds are cast ashore, they are dried and burned. The ash, which contains a considerable quantity of sodium iodid, is known as *kelp* and is used to obtain the element. As the burning involves a considerable waste, a more modern process consists in charring the seaweeds in retorts or soaking them in fresh water and evaporating the solution.

The method of obtaining iodin in the free state is the same as that employed in making chlorin and bromin. Potassium or sodium iodid is treated with manganese dioxid and sulfuric acid; on heating, the iodin is given off in the form of vapor and is condensed in appropriate receivers.

$$\mathbf{NaI} + H_2SO_4 \rightarrow \mathbf{NaHSO_4} + \mathit{HI}$$
$$4\,\mathit{HI} + \mathbf{MnO_2} \rightarrow MnI_2 + 2\,H_2O + \mathit{I_2}$$

Iodin is a black, glistening, crystalline solid. It melts at 114° and boils at 184°, forming a violet vapor. It stains the skin brown, and turns starch dark blue, the latter action being the most delicate test for the element. Iodin is but little soluble in water, but under the name of *tincture of iodin* its alcoholic solution is used for reducing swellings. Iodin as well as bromin is used in photography.

Chemically iodin resembles chlorin and bromin, but in general it is weaker in its action. It combines readily with many elements. With hydrogen it forms hydrogen iodid or hydriodic acid, HI. Both chlorin and bromin displace iodin from iodids, as the following equations indicate. The first of these reactions is utilized in the commercial preparation of iodin.

$$2\,NaI + Cl_2 \rightarrow 2\,NaCl + I_2$$
$$2\,NaI + Br_2 \rightarrow 2\,NaBr + I_2$$

FLUORIN (F — 19) is found in nature chiefly in combination with the metal calcium in the mineral *fluor spar* or *fluorite*, CaF_2, and in *cryolite*, Na_3AlF_6. It is of interest to know that it occurs in the enamel of the teeth.

Because of its chemical activity the element was not isolated from its compounds and known in the free state until 1886, when the French chemist, Moissan, prepared it by electrolyzing liquefied hydrogen fluorid containing potassium fluorid in a platinum vessel at low temperatures. Its properties were studied through windows of fluor spar.

Fluorin is a greenish yellow gas, having an odor somewhat resembling that of bleaching powder. Chemically it is the most active substance known. It decomposes water, with the formation of hydrofluoric acid and oxygen. When mixed with hydrogen it explodes, even in the dark. Most elements take fire spontaneously and burn brightly in fluorin, forming fluorids. However, it has not been made to unite with oxygen as yet. From chlorids, bromids, and iodids, fluorin displaces all three halogens.

Halogen acids. *Hydrogen fluorid*, *hydrogen chlorid*, *hydrogen bromid*, and *hydrogen iodid* are colorless gases that fume strongly in the air and are very soluble in water, forming solutions of *hydrofluoric acid*, *hydrochloric acid*, *hydrobromic acid*, and *hydriodic acid* respectively. These act on bases and form fluorids, chlorids, bromids, and iodids. There is considerable difference in the stability of the hydrogen compounds. Hydrogen fluorid is exceedingly stable. Hydrogen chlorid is stable under ordinary circumstances but begins to dissociate into its elements at high temperatures. Hydrogen bromid decomposes somewhat at ordinary temperatures and to a considerable extent when heated. When a bromid is treated with concentrated sulfuric acid, the hydrogen bromid formed is always colored brown owing to partial decomposition into hydrogen and bromin. When an attempt is made to prepare hydrogen iodid by treating an iodid with concentrated sulfuric acid, the hydrogen iodid is almost entirely decomposed into hydrogen and iodin.

To prepare *pure hydrobromic acid*, bromin is added to red phosphorus, forming phosphorus tribromid. When this compound is treated with water, phosphorous acid and hydrobromic acid are formed, as the equation shows.

$$PBr_3 + 3\,HOH \rightarrow PO_3H_3 + 3\,\mathit{HBr}$$

Pure hydriodic acid may be prepared by a similar reaction with phosphorus and iodin, or by passing hydrogen sulfid into a solution of iodin in water.

$$H_2S + I_2 \rightarrow 2\,HI + S$$

In the solubility of some of its salts, fluorin differs markedly from the other halogens. Calcium fluorid is highly insoluble; the chlorid, bromid, and iodid of the same metal are extremely soluble. Silver, lead, and mercury fluorids are soluble; the other halogen compounds of these elements are usually insoluble.

Hydrogen fluorid is usually prepared by the action of sulfuric acid on fluorids. From fluor spar it is made according to the equation

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\,\mathit{HF}$$

As hydrogen fluorid is much more stable than the other corresponding halogen compounds, fluorin cannot be prepared by the methods that serve for the other elements of the family, *i.e.* heating with manganese dioxid or some other oxidizing agent.

Hydrofluoric acid is valuable chiefly as a reagent for etching and dissolving glass. This property it owes to its action on the silica, SiO_2, in the glass, with which it unites to form water and gaseous silicon fluorid, SiF_4.

$$SiO_2 + 4\,HF \rightarrow \mathit{SiF_4} + 2\,H_2O$$

On account of this action, hydrofluoric acid must be preserved in bottles made of rubber or paraffine. The other halogen acids have no action on glass. Lead, platinum and gold are not attacked by hydrofluoric acid.

Fig. 54 shows a piece of glass coated with paraffine, in which some letters have been drawn. Calcium fluorid and sulfuric acid are placed in the lead dish. These react to liberate hydrofluoric acid, which etches the glass where the paraffine has been removed.

Fig. 54.

Some of the more important properties of the halogen group of elements are presented in tabular form.

Halogen Group

	Fluorin	Chlorin	Bromin	Iodin
React. wt.	19	35.5	80	127
Valences	1	1 (7, 5, 3)*	1(5)*	1(7, 5)*
Melt. pt. State Boil. pt.	−223° gas −187°	−102° gas −34°	−7° liquid 59°	114° solid 184°
Activity	greatest	less	less	least
Hyd. comp.	HF	HCl	HBr	HI
Its stability	most	less	less	least
Oxygen acids	None	HClO $HClO_2$ $HClO_3$ $HClO_4$	HBrO —— $HBrO_3$ ——	HIO —— HIO_3 HIO_4

As the table indicates, fluorin does not form any compounds containing oxygen. Bromin and iodin form some compounds with

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* The less typical valences are inclosed in parentheses.

oxygen analogous to those of chlorin. *Hypobromites* and *hypoiodites* are formed somewhat as hypochlorites are, and their reactions are similar. Hypoiodites are so unstable that they have never been obtained out of solution. *Bromates* and *iodates* are known; also *periodates;* but no perbromates, or any compounds of bromin or iodin corresponding to chlorites.

SUMMARY

THE HALOGENS, or "salt-formers," are so called because many of their compounds resemble salt. They are fluorin, chlorin, bromin, and iodin. These elements are very similar and their compounds show marked resemblances.

BROMIN occurs in combination associated with chlorin compounds, and is obtained by reactions similar to those used in preparing chlorin. Since it is displaced from bromids by chlorin, it may be obtained, also, by treating the former with the latter. Its usual source is the mother liquor from salt works. It is a heavy, dark red liquid which readily passes into vapor. Chemically it is like chlorin, but its action is generally weaker.

IODIN is found in small quantities in salt beds, in the ashes of certain sea plants, and in Chili saltpeter deposits. Its compounds are similar to those of bromin and it is prepared by similar processes. It is a black, crystalline solid that gives a violet vapor, stains the skin brown, and is used in medicine and photography. Chemically it resembles chlorin and bromin, but in general is weaker.

FLUORIN is difficult to prepare. It occurs in fluor spar and cryolite. It is the most active of the elements.

HALOGEN ACIDS. Hydrogen fluorid, chlorid, bromid, and iodid are colorless, strongly fuming gases that dissolve readily in water and form solutions of hydrofluoric, hydrochloric, hydrobromic, and hydriodic acids. In general the others resemble hydrochloric acid. Hydrofluoric acid has the power to dissolve glass and is used in etching.

QUESTIONS

1. Compare the occurrence and manner of preparation of fluorin, chlorin, bromin, and iodin.

2. Compare the ease with which fluorin, chlorin, bromin, and iodin unite with hydrogen and the stability of the products formed.

3. How would you test for the presence of a fluorid, a chlorid, a bromid, and an iodid?

4. Write the equations for preparing hydrogen fluorid, hydrogen chlorid, hydrogen bromid, and hydrogen iodid. In which cases would you obtain pure products?

5. State how you would go to work to etch your autograph on glass. Explain the reaction taking place. Why would you use a lead dish to hold the reagent rather than a porcelain dish? (See p. 231.)

6. Write the equation for the union of hydrogen with bromin vapor, Br_2. If 100 ccm. of hydrogen are used, how many cubic centimeters of hydrogen bromid will result?

7. Write the equations for the action of bromin on potassium hydroxid (*a*) in the cold; (*b*) when heated.

8. Why does hydriodic acid turn dark on standing?

9. What is the essential feature in the principle of counter currents so much used in the industries? Show (by diagram, if you choose) how you could apply this principle to absorb in sodium hydroxid the tetroxid of nitrogen produced when an electric arc burns in air.

CHAPTER XXI

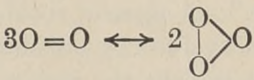
THE OXYGEN-SULFUR GROUP

The group. The members of this group — *oxygen*, *sulfur*, *selenium*, and *tellurium* — occur in nature both free and in combination with other elements. This fact indicates at once that they are not as active chemically as the halogens, which are found only in combination. Oxygen differs somewhat from the other members of the family, just as in the halogen group the element with the lowest reacting weight, fluorin, differs more from the type than chlorin, bromin, and iodin do from one another. Sulfur, selenium, and tellurium are very much alike, and as the chemical character of these elements is studied and compared with that of oxygen, — the properties of which should be reviewed, — it will be found that oxygen is not so different from sulfur as its physical properties might seem to indicate at first sight.

OZONE. The peculiar odor which arises in air where dynamos or other electrical machines are in operation has long been known. It is found that when oxygen is submitted to an electrical discharge it takes on entirely different properties. In fact, it becomes a new substance, *ozone*. At ordinary temperatures this is a colorless gas with a pungent odor, much more active chemically than oxygen. It will bleach dyes and tarnish silver readily. On the application of cold and pressure it condenses to a deep blue liquid (b. p. – 119°), which is liable to explode spontaneously. In the gaseous, liquid, and solid states it is very different from oxygen, yet when heated to 300° it is converted entirely into oxygen without any change in weight. When ozone changes to oxygen, energy is liberated, and we may write the equation

$$\text{ozone} = \text{oxygen} + \text{energy}.$$

This fact sufficiently accounts for the difference in properties, and it seems undoubtedly true that all instances of allotropism are to be explained in this way. It is known also that when oxygen changes to ozone a contraction in volume occurs equal to one third; *i.e.* three volumes contract to two. The following equation expresses this change and shows that the molecule of ozone is different from the molecule of oxygen. The reaction is reversible and runs to equilibrium, under ordinary conditions only a part of any volume of oxygen being converted into ozone.



$$3O{=}O \longleftrightarrow 2\begin{matrix}O\\ |\\ O\end{matrix}\!\!>\!O$$

Ozone is formed in small quantities whenever oxygen is liberated. It is a powerful oxidizing agent and is used industrially for bleaching, as in the manufacture of flour, and for sterilizing purposes, as in the purification of water supplies.

SULFUR (S — 32). Sulfur or *brimstone* is deposited by the gases which issue from volcanoes, and to this fact is probably due an old belief of uneducated people that beneath the earth's crust there is a "lake burning with fire and brimstone." From the volcanic region of Italy a large part of the world's supply is derived. Other deposits, undoubtedly of different origin, are found in connection with gypsum in Louisiana, and from this source most of the domestic supply comes. Sulfur in combination occurs as the salts of sulfuric acid, the insoluble sulfates being of course the most common, such as *gypsum*, $CaSO_4.2\ H_2O$; and *barite* or *heavy spar*, $BaSO_4$. Large deposits of insoluble sulfids occur also, such as *iron pyrites*, FeS_2; *copper pyrites*, $CuFeS_2$; *galenite*, PbS; and *blende*, ZnS. Volcanic gases almost always contain sulfur compounds. *Hydrogen sulfid* is found in many mineral waters. Sulfur enters as a constituent also into many compounds associated with life, such as egg albumen, of which it constitutes about 1 %.

Preparation. Some sulfur is obtained by heating iron pyrites without access of air, the decomposition being according to the equation

$$3\,FeS_2 \rightarrow Fe_3S_4 + 2\,S.$$

However, most of the sulfur of commerce comes from native or free sulfur. In Sicily the process suggests "charcoal burning." A mass of rock containing sulfur is set on fire, the heat evolved by burning a part of the sulfur being sufficient to melt the rest, which runs off and is collected. When thus obtained it contains various foreign substances. It may be further purified by distillation, the vapors being condensed in brick chambers. The first vapors entering these cold condensing chambers are cooled suddenly, and the sulfur is deposited in a fine powder known as *flowers of sulfur;* but as the process continues the chambers become heated and the sulfur collects as a liquid. This is drawn off into wooden molds and allowed to solidify, and is then frequently called *roll sulfur*.

Physical properties. Sulfur is capable of existing in a number of allotropic modifications. The ordinary lemon-yellow form, whose specific density is 2.06, is obtained from solution in the form of *rhombic* crystals as shown in Fig. 55. If the temperature is raised somewhat above 96°, its specific density changes to 1.96. Crystals formed above this temperature are called *monoclinic* and have the needle-like form shown in Fig. 56. If cooled below 96°, they change slowly into the rhombic form. The temperature 96° is called a *transition point.* Above this temperature the needle form is stable; below it the rhombic is the stable modification. This temperature is the transition point between two solids. The transition point between the solid and liquid states is the melting point, and the boiling point is the transition temperature from the liquid to the gaseous state.

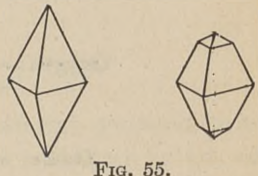


Fig. 55.

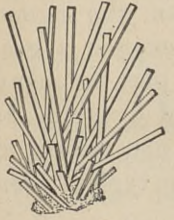


Fig. 56.

When rhombic sulfur is heated rapidly to 114° it liquefies, but afterwards solidifies, for it changes into monoclinic sulfur, the melting point of which is 119°. Sulfur just above its melting point is a clear, light-yellow liquid, which solidifies in the needle form. As it is heated, it grows dark and more viscous until 160° is reached, when the test tube containing it may be inverted without any of its contents being lost. This is the second allotropic form of liquid sulfur. If heated higher, this form becomes sufficiently liquid to be poured into water. The cooling action transforms it into a yellowish, elastic mass known as *plastic* sulfur, which slowly changes into the rhombic form.

Heated to 448°, sulfur boils, forming an almost black vapor. Its gas density is 128, indicating a molecular weight of 256 and the molecular formula S_8. At about 1000° the gas density is 32, indicating a molecular weight of 64 and the molecular formula S_2.

There are six different forms of sulfur just as there are six modifications of oxygen, but the relationship between these forms differs in the two cases as the diagram shows.

Oxygen

$$\begin{tikzcd}
\textbf{Oxygen}:\text{ — solid} \arrow[r, leftrightarrow, "-227^\circ"] & \text{liquid} \arrow[r, leftrightarrow, "-188"] & \text{gas} \arrow[d, leftrightarrow] \\
\textbf{Ozone}:\text{ — solid} \arrow[r, leftrightarrow] & \text{liquid} \arrow[r, leftrightarrow, "-119^\circ"] & \text{gas}
\end{tikzcd}$$

Sulfur

$$\text{rhombic} \xleftrightarrow{96^\circ} \text{needles} \xleftrightarrow{119^\circ} \text{liquid} \xleftrightarrow{160} \text{plastic} \xleftrightarrow{448^\circ} \text{gas } S_8 \xleftrightarrow{1000^\circ} \text{gas } S_2$$

Chemical properties. At ordinary temperatures sulfur is a much less active element than oxygen, the reason being largely that sulfur is a solid and oxygen a gas. But at higher temperatures sulfur takes part in many reactions which are very similar to those of oxygen. It combines with all metals and with most non-metals to form sulfids, the reactions frequently being typical combustions.

Uses. By far the largest proportion of the sulfur of commerce is consumed in making sulfuric acid, but in bleaching and disinfecting and in making iron sulfid and carbon disulfid large quantities are also used. In *vulcanizing rubber*, *i.e.* treating it so as to preserve its elastic properties, a small percentage of sulfur is added.

Hydrogen sulfid, H_2S. If hydrogen is bubbled through melted sulfur, hydrogen sulfid may be formed, but the reaction is reversible, and equilibrium is soon reached with but a small proportion of the elements in combination. Since the action of sulfur on most metals is reversible only at very high temperatures, metallic sulfids may be made in quantity by heating the elements together

When such sulfids are treated with acids, a reaction liberating hydrogen sulfid takes place in many instances. Hydrogen sulfid is usually prepared by the action of dilute acid on iron sulfid, as the equations show.

$$\mathrm{Fe} + \mathrm{S} \rightarrow \mathrm{FeS}$$
$$\mathrm{FeS} + 2\,\mathrm{HCl} \rightarrow \mathrm{FeCl_2} + H_2S$$

The decomposition of organic material converts much of the sulfur which it contains into hydrogen sulfid, and to this compound decaying eggs and similar substances owe much of their odor.

Physical properties. Hydrogen sulfid is a colorless gas with a disagreeable odor. It acts as a poison, causing dizziness, nausea, and finally death if its action is long continued. The best antidote is the inhalation of dilute chlorin, which may be obtained from chlorin water, or by adding hydrochloric acid to a solution of potassium chlorate or of "chloride of lime" (bleaching salt).

Hydrogen sulfid is readily soluble in water, 1 volume of the latter dissolving about 4 volumes of the gas. The solution has a weak acid reaction and is sometimes called *hydrosulfuric acid.* It is often used in the laboratory in place of the gaseous reagent.

Chemical properties. In air hydrogen sulfid burns with a pale blue flame to water and sulfur dioxid. If the supply of air is diminished, or if a cold object is held in the flame, some of the sulfur escapes oxidation and may be deposited as a yellow film. Chemically the deposition of sulfur by a hydrogen sulfid flame resembles the formation of soot in a candle flame.

When exposed to air, solutions of hydrogen sulfid are oxidized to water and free sulfur. A mineral water containing hydrogen sulfid is known as "**sulfur water.**" The opalescent character of these waters is caused by finely divided sulfur formed by the oxidation of the hydrogen sulfid, and the yellowish deposit of leathery texture along the banks of such springs is sulfur.

In chemical composition hydrogen sulfid resembles water, the corresponding oxygen compound; but it is less stable, being easily decomposed into its elements at about 500°. On account of its greater instability it is capable of effecting many chemical changes that water cannot bring about. Thus it acts on metals and some other elements more readily than does water.

All of the halogens quickly decompose hydrogen sulfid in a way analogous to the similar but slower action of these elements on water, as the typical equation indicates:

$$Cl_2 + H_2S \rightarrow 2\,HCl + \mathrm{S}$$

The action of hydrogen sulfid on the salts of the metals, converting them into sulfids, is especially important. To consider a typical illustration: When hydrogen sulfid is added to a solution of copper sulfate, copper sulfid and sulfuric acid are formed, according to the equation:

$$\mathrm{CuSO_4} + H_2S \rightarrow \mathrm{CuS} + \mathrm{H_2SO_4}$$

Chemical Analysis. — Although hydrogen sulfid is both disagreeable and poisonous, nothing has ever been found that can supersede it in chemical analysis. It owes its value to the reaction noted above; *i.e.* its ability to transform the salts of metals into their sulfids.

Metals may be separated into groups according to the solubility of their sulfids. Some sulfids are soluble in water, some are insoluble in water but soluble in dilute acids, and some are insoluble in both water and dilute acids. Metals thus fall into three groups, as the following table shows:

Metals whose sulfids are insoluble in water and in dilute acids.	Metals whose sulfids are insoluble in water but soluble in dilute acids.	Metals whose sulfids are soluble in water and in dilute acids.
Silver	Iron	Calcium
Lead	Aluminum *	Strontium
Mercury	Chromium *	Barium
Bismuth	Cobalt	Magnesium
Copper	Nickel	Potassium
Cadmium	Manganese	Sodium
Arsenic	Zinc	Ammonium
Antimony		
Tin		
Gold		
Platinum		

If a chemist is to analyze a solution and determine what metals are contained in it in the form of salts, he adds some acid to the solution, hydrochloric acid being the one generally used. This reagent causes the formation of insoluble chlorids of silver and, under proper conditions, of mercury and lead; hence any precipitate indicates that a salt of one or more of these metals is present. Into the filtrate from the treatment with hydrochloric acid, hydrogen sulfid is introduced. If a precipitate forms, a salt of one or more of the metals given in the first column is present. After filtration, the substances in the precipitate are separated by further treatment. The filtrate is then made alkaline and hydrogen sulfid again passed in, or ammonium sulfid may be added. A precipitate then means the presence of one or more of the metals in the second column.* After filtering, the metals of the third column are left in the filtrate.

Oxids of sulfur. When sulfur burns in the air, it is converted into sulfur dioxid, a colorless gas with a sour taste and a sharp, suffocating odor, the "odor of burning sulfur." Although the gas does not support combustion or burn in the ordinary sense, it may be oxidized to sulfur trioxid, a white, asbestos-like solid of chief interest as the anhydrid of sulfuric acid.

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* In the treatment indicated aluminum and chromium would be precipitated as insoluble hydroxids, owing to the decomposition of their sulfids.

Sulfurous acid, H_2SO_3. When sulfur dioxid is passed into water, more than 40 volumes are absorbed and the solution becomes acid, owing to a reaction forming sulfurous acid. Only a small proportion of the gas is actually united chemically with the water, for the reaction soon runs to equilibrium. Whenever the attempt is made to get sulfurous acid from the solution, the reaction is reversed and the result is only sulfur dioxid and water.

$$SO_2 + H_2O \longleftrightarrow H_2SO_3$$

Sulfurous acid acts as a weak acid, uniting with bases to form acid and normal salts called *sulfites.*

$$H_2SO_3 + NaOH \rightarrow NaHSO_3 + H_2O$$
$$H_2SO_3 + 2\,NaOH \rightarrow Na_2SO_3 + 2\,H_2O$$

When **sulfites** are treated with acids, sulfurous acid is set free and decomposes into the anhydrid and water.

All sulfites readily take up oxygen and are converted into sulfates, hence sulfurous acid, its salts, and its anhydrid, are all strong reducing agents.

Sulfur dioxid may sometimes act as an oxidizing agent, however. Both sulfur dioxid and hydrogen sulfid occur generally in volcanic gases. Their interaction accounts for the occurrence of sulfur in volcanic regions, as the equation indicates:

$$2\,H_2S + SO_2 \rightarrow 3\,S + 2\,H_2O$$

Sulfur dioxid is not the most or the least oxidized compound of sulfur, as the table below shows. It may give up or take on oxygen. Substances of this character may usually act both as oxidizing and as reducing agents according to circumstances.

$H_2S + 4\,O$ gives SO_3 $(+ H_2O)$
$S + 3\,O$ gives SO_3
$SO_2 + 1\,O$ gives SO_3
$SO_3 + 0\,O$ gives SO_3

Uses. The predominating use of sulfur dioxid and sulfurous acid is in the manufacture of sulfuric acid, yet they find extensive industrial application in preserving foods, especially fruits, and as disinfecting and bleaching agents. In the latter case the chemical action is of an opposite character to that of chlorin. The result of the action of chlorin is an oxidation of the dye, but sulfur dioxid owes its bleaching effect to its reducing action, which converts the coloring matter into colorless substances. This bleaching effect is likely not to be permanent, for the action of the atmosphere is that of an oxidizing agent, which sooner or later re-forms some of the colored material. For this reason straw hats, etc., bleached by sulfur dioxid, frequently turn yellow or brown on exposure. Silk and wool must be bleached with sulfur dioxid, for chlorin or hypochlorites injure and discolor these materials.

Sulfuric acid — Its manufacture. Between sulfur dioxid and air or oxygen but little action takes place at any temperature. If the mixed gases are passed over finely divided platinum, ferric oxid, or certain other substances which act as catalyzers, sulfur dioxid is converted into the trioxid. This unites vigorously with water to form sulfuric acid. These reactions are carried out on a large scale in the so-called *contact process* for manufacturing sulfuric acid.

In the older process for making sulfuric acid, sulfur or iron pyrites is burned to sulfur dioxid. This gas, coming in contact with steam, forms sulfurous acid. The oxidation of sulfurous acid by air is brought about by the catalytic action of oxids of nitrogen. Reactions take place, the results of which may be expressed by the equations:

$$\mathrm{H_2SO_3} + NO_2 \rightarrow \mathrm{H_2SO_4} + NO$$
$$2\,NO + O_2 \rightarrow 2\,NO_2$$

The oxygen of the atmosphere really accomplishes the change, for the oxid of nitrogen is alternately reduced by the sulfurous acid and oxidized by the air. The reactions take place in huge chambers made of sheet lead, the cheapest metal not attacked by the acid; hence, this method of manufacture is known as the *chamber process.*

Fig. 57 shows a diagram of the chamber process for manufacturing sulfuric acid. *A*, *A*, are pyrite burners; *C*, the Glover tower.

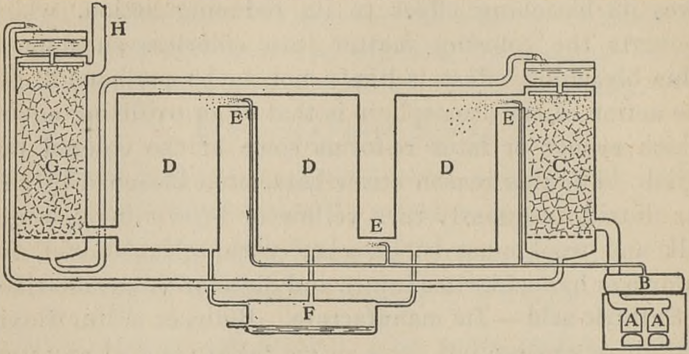


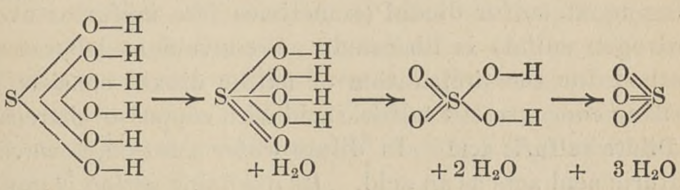
Fig. 57.

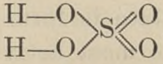
This is a masonry tower filled with earthenware or other material over which concentrated sulfuric acid containing oxids of nitrogen (obtained from the Gay-Lussac tower — see later) is trickling. The hot gases, — sulfur dioxid and air, — coming in contact with the acid, liberate the nitrogen oxids, which pass into the chambers, *D*, *D*, *D*, where the main reaction takes place. *E*, *E*, *E*, are steam jets. The sulfuric acid collects on the bottom of the chambers and flows into the reservoir, *F*. The gases — nitrogen from the air and oxids of nitrogen — pass to the chimney, *H*, through the Gay-Lussac tower, *G*. This is similar in construction to the Glover tower. Concentrated sulfuric acid flows over the earthenware, absorbing the oxids of nitrogen. This acid is then forced by compressed air to the top of the Glover tower as previously stated. In a large plant this saving of the oxids of nitrogen amounts to many thousands of dollars each year. A small amount fails to be absorbed, however, and is lost; hence it must be added continually. This is done by heating jars containing niter and sulfuric acid in the pyrite burner. *B* is a boiler, heated by the pyrite burners, furnishing steam for the plant.

As a result of the process a rain of dilute (60%) sulfuric acid falls to the bottom of the chambers. This is concentrated in lead pans up to about 80 %, at which point it attacks lead; hence it always contains some lead sulfate. To obtain pure sulfuric acid, it is concentrated or distilled in platinum or porcelain vessels. What is called **concentrated sulfuric acid** contains 96–98 % of H_2SO_4 and 4–2 % of water. The cost of concentrating is quite as great as the cost of the dilute acid, thus making the chamber process more expensive than the contact process. Hence the latter is displacing the former process.

Properties. Pure sulfuric acid is a colorless, oily liquid nearly twice as heavy as water. Because of these properties it is frequently called "*oil of vitriol.*" It boils at 330° with partial decomposition into the anhydrid and water, and at $-10°$ it freezes to colorless crystals. The commercial acid is colored by iron salts and other impurities.

Sulfuric acid is very active chemically. When mixed with water, it evolves a large amount of heat, and, if the resulting liquid is cooled, crystals are deposited having the composition represented by the formula SO_6H_6. This is evidently the hexa-hydroxid of sulfur. When warmed it loses one molecule of water; but on higher heating a second molecule is driven off, and finally the last of the water departs, leaving the anhydrid. These reactions may be expressed by the structural formulas:



For these and other reasons the structural formula for sulfuric acid is written  $\begin{matrix}H-O\\H-O\end{matrix}>S<\begin{matrix}O\\O\end{matrix}$. The compounds with water are sometimes written $H_2SO_4.2\ H_2O$ and $H_2SO_4.H_2O$.

On account of the energetic way in which it combines with water, **concentrated sulfuric acid** is used for drying gases and for hastening chemical action when one of the products is water. Because of this property it exerts a charring action on wood, paper, and other organic substances, decomposing them largely into charcoal and water.

With metallic oxids and hydroxids, also with most metals, sulfuric acid reacts, forming sulfates. In proportion as sulfuric acid is free from water it loses its acid properties and acts as an oxidizing agent. For this reason hot, concentrated sulfuric acid is reduced by charcoal according to the equations:

$$\mathrm{C} + \mathrm{H_2SO_4} \rightarrow CO + \mathrm{H_2SO_3} \rightarrow \mathrm{H_2O} + SO_2$$
$$CO + \mathrm{H_2SO_4} \rightarrow CO_2 + \mathrm{H_2SO_3} \rightarrow \mathrm{H_2O} + SO_2$$

Under these conditions metals are oxidized similarly:

$$2\,\mathrm{Ag} + \mathrm{H_2SO_4} \rightarrow \mathrm{Ag_2O} + \mathrm{H_2SO_3}$$
$$\mathrm{Cu} + \mathrm{H_2SO_4} \rightarrow \mathrm{CuO} + \mathrm{H_2SO_3}$$
$$\mathrm{Hg} + \mathrm{H_2SO_4} \rightarrow \mathrm{HgO} + \mathrm{H_2SO_3}$$

The metallic oxids formed unite with additional sulfuric acid to form sulfates. When sulfuric acid acts as an oxidizing agent, sulfur dioxid (sometimes free sulfur or even hydrogen sulfid) is liberated. A convenient laboratory method for the preparation of sulfur dioxid consists in heating concentrated sulfuric acid with copper or charcoal.

Dilute sulfuric acid. In dilute water solution, however, sulfuric acid acts as an acid. Its oxidizing action is gone. When zinc is placed in dilute sulfuric acid, hydrogen is liberated and zinc sulfate is formed. Although nascent hydrogen is one of the most active reducing agents, the sulfuric acid is not reduced.

A similar lessening of oxidizing power when in dilute solution is noted with nitric acid and all other acids that can act as oxidizing agents. In proportion as they are concentrated, they lose their acid properties and act as oxidizing agents, while in dilute aqueous solutions their oxidizing action is at a minimum and their acid properties at a maximum. These substances in water solution must be in some different condition from that in which they exist when they are free from water. We shall take up the consideration of this subject in the next chapter.

Sulfuric acid acts on the salts of other acids, forming sulfates and liberating the acids, provided that these acids are more volatile than sulfuric acid. It forms both acid and normal salts of the types $NaHSO_4$ and Na_2SO_4. Most normal sulfates are stable and are decomposed only by intense heat. All are soluble in water except the sulfates of barium, strontium, lead, and calcium, the last one mentioned being slightly soluble.

Soluble sulfates, including hydrogen sulfate, may be detected by dissolving the substance to be tested in water, making the solution acid with hydrochloric acid, and adding a little of a solution of barium chlorid, $BaCl_2$. If a precipitate forms, it is barium sulfate, and a sulfate was present in the substance tested.

The sulfates of a number of common metals separate from solution in the same crystal form, each crystal containing seven molecules of water. These substances are known as "*vitriols.*" Some of them find important uses in the industries, as "*white vitriol,*" $ZnSO_4.7\,H_2O$ and "*green vitriol,*" $FeSO_4.7\,H_2O$.*

Substances which have the same crystal form and contain the same amount of "water of crystallization" are

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* Copper sulfate, $CuSO_4.5\,H_2O$, is commonly called "blue vitriol," but it is not a true "vitriol," as its formula shows.

said to be *isomorphous.* This term is derived from Greek words which mean "having the same shape."

All sulfates are reduced to sulfids by heating with charcoal. In making this test, the substance to be investigated is mixed with sodium carbonate and powdered charcoal and heated before the blowpipe on a piece of charcoal. The fused mass is placed on a silver coin and moistened with a little water. If a sulfate is present, a black stain of silver sulfid appears on the coin. The same test of course applies to sulfites also. The following equations indicate the reactions taking place:

$$BaSO_4 + 4\,C \rightarrow BaS + 4\,CO$$
$$BaS + Na_2CO_3 \rightarrow BaCO_3 + Na_2S$$
$$Na_2S + 2\,Ag + H_2O + O \rightarrow Ag_2S + 2\,NaOH$$

Uses. Beyond question sulfuric acid is the most important chemical substance manufactured, for upon it, directly or indirectly, we depend for many of the things which are characteristic of civilized man. Most other acids require sulfuric acid in their manufacture, and industries which use hydrochloric, nitric, and acetic acids or their salts are directly dependent on sulfuric acid. Fertilizers to increase crops, dynamite for our mines, washing soda and soap for our laundries, baking powder for our cooking, bleaching powder for our fabrics and clothing, glass, and petroleum products,—for all these things and many others sulfuric acid is needed. Hundreds of thousands of tons are manufactured every year in the United States alone, the cost of the ordinary commercial article being less than one cent a pound.

Other acids of sulfur also exist in considerable numbers. *Fuming sulfuric acid*, $H_2S_2O_7$, is made by dissolving sulfur trioxid in concentrated sulfuric acid. When warmed, this substance decomposes and the anhydrid may be obtained again. The following equation indicates the formation and decomposition of fuming sulfuric acid:

$$H_2SO_4 + SO_3 \longleftrightarrow H_2S_2O_7$$

Fuming sulfuric acid is so called because it decomposes in this way to some extent at ordinary temperatures, and the sulfur trioxid, coming in contact with moisture in the air, unites with it and condenses as fumes of sulfuric acid.

Thiosulfuric acid, $H_2S_2O_3$, is another rather important acid. It is best known as the sodium salt, $Na_2S_2O_3$, sodium thiosulfate, known to the trade as "*hypo*" and sometimes incorrectly called "*hyposulfite of soda.*" The salt is prepared by boiling a solution of sodium sulfite with sulfur. The sulfite is oxidized by the sulfur exactly as it may be by oxygen, as the equations show:

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$
$$Na_2SO_3 + O \rightarrow Na_2SO_4$$

It has been shown that thiosulfuric acid, $H_2S_2O_3$, is sulfuric acid in which one oxygen atom is replaced by a sulfur atom. The chemical analogy between oxygen and sulfur is thus well illustrated in these reactions.

Thiosulfuric acid is very unstable, and when a solution of a thiosulfate is acidified, only the decomposition products of the acid are obtained.

$$Na_2S_2O_3 + 2\ HCl \rightarrow 2\ NaCl + H_2S_2O_3 \rightarrow H_2O + SO_2 + S$$

This reaction suggests the similar decomposition of sulfurous acid, the only difference in this case being the separation of sulfur. Thiosulfates are similar to sulfites in many ways, and like them are good reducing agents. For this reason sodium thiosulfate is used in bleaching establishments to remove excess chlorin from fabrics, and is known as "*antichlor.*" As a "*fixer*" in photography it is more generally known, but the reactions which take place in this process must be deferred until later. (See p. 360.)

Carbon disulfid, CS_2, is made by passing sulfur vapor over hot carbon, and is thus analogous to carbon dioxid, CO_2, in both formula and manner of preparation. When pure, it is a colorless, sparkling liquid. The ordinary product contains sulfur and other impurities, is yellow in color, and has a disagreeable odor. It is poisonous and very volatile, giving an inflammable vapor that burns to carbon dioxid and sulfur dioxid. It is an excellent solvent for many substances that do not dissolve in water, such as sulfur, phosphorus, and rubber. It is much used to kill ground squirrels and other rodents.

SELENIUM (Se — 79) received its name from the Greek noun *selene*, meaning the "moon," in analogy with the related element tellurium, which was so called from *tellus*, the Latin name for earth. In nature it is almost always associated with sulfur, but occurs only in small quantities. Like sulfur, it has several allotropic forms, one modification resembling black sealing wax, another being a brick-red powder. Like all non-metals it is a poor conductor of electricity, but possesses the unusual property of conducting the current better when it is exposed to light. It unites with metals to form *selenids*, and with hydrogen it gives *hydrogen selenid*, H_2Se, which possesses properties like those of hydrogen sulfid, and is made in a similar way. Selenium burns with a blue flame to *selenium dioxid*, SeO_2, a gas which is the anhydrid of *selenious acid*, H_2SeO_3, resembling sulfurous acid. This by oxidation gives *selenic acid*, H_2SeO_4, analogous to sulfuric acid.

TELLURIUM (Te — 124) occurs both native and combined, its compound with gold being the so-called "tellurid gold ore." The commonest of its allotropic forms is a crystalline substance possessing a metallic luster. Its compounds show close analogy to selenium and sulfur, as the table on page 251 shows.

While the similarity between sulfur, selenium, and tellurium is obvious, it should be stated that each acid of selenium is weaker than the corresponding acid of sulfur, and the acids of tellurium are weaker still. As the reacting weights of these three elements increase, there is a decrease in non-metallic or acid-forming properties, and this means, of course, an increase in metallic or base-forming properties. In fact, tellurium dioxid will dissolve in acids under proper conditions to form rather unstable salts, in which tellurium acts as a metal.

Some of the most important properties of the elements belonging to the sulfur group are set down in tabular form.

OXYGEN-SULFUR GROUP

	OXYGEN	SULFUR	SELENIUM	TELLURIUM
React. wt.	16	32	79	124
Valences	2	2, 4, 6	2, 4, 6	2, 4, 6
Melt. pt. State Boil. pt.	−227° gas −183°	119° solid 448°	217° solid 680°	452° solid 1390°
Hyd. comp.	H_2O *	H_2S *	H_2Se	H_2Te
Its stability	most	less	less	least
Oxids	OO_2 (ozone)	SO_2 * SO_3	SeO_2 SeO_3	TeO_2 TeO_3
Acids		H_2SO_3 * H_2SO_4	H_2SeO_3 H_2SeO_4	H_2TeO_3 H_2TeO_4
Strength of acids		greatest	less	least
Chlorids	OCl_2 *	SCl_2 *	$SeCl_2$ *	$TeCl_2$ *

* Other similar compounds are known.

SUMMARY

OZONE is an allotropic form of oxygen, formed by an electric discharge. Its chemical formula is O_3, and, as it readily gives up oxygen, it is an excellent oxidizing agent.

SULFUR is found in the free state, in sulfids and sulfates, and in living things.

Preparation. It is obtained

1. To some extent by roasting iron pyrites.
2. By setting fire to the mixture of free sulfur and rock, as found in Sicily and elsewhere. A small part of the sulfur burns, the rest melts and runs out. The crude sulfur is purified by distillation, and forms *flowers* of sulfur and *roll* sulfur.

Allotropic forms. Sulfur may be obtained in several forms, among which are

A. Two solid forms.

1. *Rhombic* sulfur, obtained by crystallizing the element from a solution in carbon disulfid.
2. *Monoclinic* sulfur, obtained when the element crystallizes from the molten condition.

B. Two liquid forms.

1. Formed by melting sulfur; on cooling it changes into monoclinic sulfur.
2. Formed by heating sulfur to 160°. When poured into water, it forms *plastic* sulfur, which slowly changes into rhombic sulfur.

C. Two gaseous forms, S_8 and S_2.

Rhombic sulfur is the form stable under ordinary conditions. Chemically, sulfur resembles oxygen and forms corresponding compounds. With most elements it combines to form sulfids.

Hydrogen sulfid, H_2S, is prepared by treating ferrous sulfid with hydrochloric acid. It is a colorless, ill-smelling gas. Being rather unstable, it is able to cause many chemical changes, and is used in chemical analysis to precipitate the sulfids of certain metals from solutions of their salts.

Sulfur dioxid, SO_2, is formed when sulfur burns. It is a colorless, stifling gas, used in the manufacture of sulfuric acid and also in bleaching, in disinfecting, and in preserving foods. Its solution in water contains *sulfurous acid*, H_2SO_3, an unstable substance which acts on bases to form sulfites. In bleaching the action of sulfur dioxid is the opposite of that of chlorin; it *reduces* the dye.

Sulfuric acid, H_2SO_4.

Preparation. Sulfuric acid is made by burning sulfur to the dioxid, oxidizing this to the trioxid, and combining the latter with water. Two processes are in use.

1. In the *contact process* a mixture of sulfur dioxid and air is passed over finely divided platinum or ferric oxid. By catalytic action sulfur trioxid is formed, and this unites with water to form sulfuric acid.
2. In the *chamber process* sulfur dioxid, steam, and air are brought together in the presence of oxids of nitrogen as catalyzers. This process gives dilute sulfuric acid.

Properties. The chemical character of sulfuric acid is twofold, according to whether it is concentrated or is in water solution.

1. When concentrated, it unites readily with water, chars organic matter, and acts on charcoal, sulfur, and on metals in general as an oxidizing agent, being itself reduced at the same time to sulfurous acid. The oxids of the metals are then changed by excess sulfuric acid to sulfates. For laboratory purposes sulfur dioxid may be prepared by heating together copper and concentrated sulfuric acid.
2. In dilute water solution it displays the properties of a strong acid and cannot be reduced by nascent hydrogen. Other acids that may act as oxidizing agents exhibit a similar deportment. Solution in water brings out acid properties but lessens their oxidizing action.

Uses. Sulfuric acid is the most important chemical made. It is necessary at some stage in the making of such important substances as other acids, fertilizers, soda, soap, bleaching powder, glass, and petroleum products.

Sulfates may be either acid or normal salts. They may be tested for by dissolving the substance in water, acidifying the solution with hydrochloric acid, and then adding a solution of barium chlorid. A white precipitate indicates a sulfate.

Other acids of sulfur are known. Among them are

1. *Fuming sulfuric acid*, $H_2S_2O_7$, obtained by dissolving sulfur trioxid in concentrated sulfuric acid.
2. *Thiosulfuric acid*, $H_2S_2O_3$, best known in its sodium salt, commonly called "*hypo*" or "*hyposulfite of soda*" and used in bleaching works and in photography.

Carbon disulfid, CS_2, corresponds to carbon dioxid, and like it is made by union of its elements. It is used as a solvent.

SELENIUM and **TELLURIUM** resemble sulfur and form analogous compounds.

QUESTIONS

1. Compare the manufacture of sulfur with that of charcoal.

2. The gas density of sulfur vapor at 450° is 128. At 1000° it is 32. Calculate the formula of the molecule of sulfur vapor at each temperature.

3. If you had nothing but water, air, sulfur, and iron to work with, how would you prepare hydrogen sulfid in quantities?

4. Write the equation for the oxidation of hydrogen sulfid by air. Write the equation for the burning of hydrogen sulfid in oxygen. If 100 ccm. of hydrogen sulfid are burned, how much oxygen is required? What is the volume of the products?

5. If 10 grams of hydrogen sulfid are required for an operation, how many grams of ferrous sulfid must be taken to produce it?

6. It is desired to precipitate as sulfid the copper in a solution containing 20 grams of copper sulfate, $CuSO_4.5\,H_2O$. How much ferrous sulfid must be taken to furnish the necessary hydrogen sulfid?

7. Explain why sulfuric acid is able to act on ferrous sulfid with the evolution of hydrogen sulfid, without a reversal of the reaction.

8. Why cannot nitric acid be used in the preparation of hydrogen sulfid?

9. Write the equations for the action of hydrogen sulfid on (*a*) lead chlorid, $PbCl_2$; (*b*) silver nitrate, $AgNO_3$; (*c*) stannic chlorid, $SnCl_4$; (*d*) arsenic trichlorid, $AsCl_3$.

10. What is the valence of sulfur in hydrogen sulfid; in sulfur dioxid; in sulfur trioxid; in carbon disulfid; in sulfuric acid?

11. Have you ever smelled sulfur dioxid outside of a chemical laboratory? How was it formed?

12. Compare the respective chemical actions taking place in the preparation of nitrogen dioxid (nitric oxid) and sulfur dioxid.

13. In what respects is sulfurous acid like carbonic acid?

14. If you were given a mixture of nitric and sulfuric acids, how might you separate the two?

15. Dishes containing concentrated sulfuric acid are often placed inside cases of instruments used for exact work, such as delicate balances or clocks. Why? These dishes are likely to overflow on long standing. Why?

16. Bottles of concentrated sulfuric acid leave dark rings on wooden tables or shelves. Why?

17. Coal often contains iron pyrites, FeS_2. What sulfur compounds do you think would be found in illuminating gas made from such coal?

18. Write the chemical equation for the burning of carbon disulfid vapor in oxygen. If 100 ccm. of oxygen are used, what are the volumes of the products of combustion?

19. How would you distinguish between a sulfid, a sulfite, and a sulfate?

20. A certain smelter treats each day 100 tons of ore, averaging 33% of sulfur. In the process the sulfur is burned and passes out of the chimneys, being finally converted into sulfuric acid by the atmosphere. How much acid is deposited on the neighboring fields each year?

CHAPTER XXII

REACTIONS IN SOLUTION

Electrolytes in solution. We have learned from our study so far that solids do not as a rule interact when brought together, but that, if dissolved in water, they react readily. This statement refers to acids, bases, and salts, all of which are electrolytes. It does not apply to the sugars, alcohols, starches, and other substances which are non-electrolytes. In the case of electrolytes, solution in water increases their chemical activity. How great this effect is will be evident if the fact is recalled that dry hydrogen chlorid, whether gaseous or liquefied, shows no acid properties whatever. When it is dissolved in water, even in very dilute solutions, the characteristics of a strong acid are evident.

From these facts it is seen that there is reason to believe that acids, bases, and salts in aqueous solution are in an essentially different condition from that of the dry state. This idea is supported by the different character of the reactions taking place when the reagents are in solution or are free from water.

Reactions in solution are uniform. Chlorids, when dry, do not all act alike; yet in solution they give certain reactions so generally that these reactions are known as "tests for chlorids."

When free from water, sulfates of different metals react usually in different ways. In solution, however, all sulfates give definite reactions or "tests for sulfates." The same is true for metallic components. All copper salts when in solution turn dark blue when ammonia is added. Each metal responds to tests regardless of the acid radical with which it may have been united before the salt was dissolved in water. In solution these substances act as though the metals and the acid radicals were independent of each other.

Dry reactions are often complex. When copper nitrate and ammonium carbonate are heated together, they react violently. Gases are liberated in abundance, the mixture consisting of oxids of nitrogen, carbon, and hydrogen; and in the crucible only copper oxid is left. Yet in solution these same substances react smoothly and simply to form copper carbonate and ammonium nitrate. When in solution, electrolytes tend to break up into relatively simple parts, which then change places with each other by simple metathesis. Whether a reagent actually breaks up into these parts on going into aqueous solution, or only tends to do so, is a question for which we can obtain an answer without difficulty.

Abnormal freezing points and boiling points. We have learned the general rule that when a mole of a substance is contained in a liter of solution, the solution boils 0.52° higher and freezes 1.89° lower than pure water. Since moles of all substances contain the same number of molecules (p. 161), it is evident that this effect is caused by the *number of particles* in solution, for the *character* of the substance does not influence the result.

Let us consider concrete illustrations. By comparing the weights of equal volumes of hydrogen and hydrogen chlorid, we find that the latter is 18.1 times as heavy as hydrogen; *i.e.* the gas density of hydrogen chlorid is 18.1. Its molecular weight is 36.5, therefore, and its mole consists of 36.5 grams. The molecular weight of alcohol, C_2H_6O, is 46; therefore 46 grams of alcohol contains just as many molecules as 36.5 grams of hydrogen chlorid. We should expect a liter of solution containing 46 grams of alcohol to boil and freeze at the same temperature as a liter of solution containing 36.5 grams of hydrogen chlorid. Yet the mole of hydrogen chlorid causes a rise of the boiling point and a lowering of the freezing point about twice as great as that caused by the mole of alcohol. The inference is obvious. There must be about twice as many particles in the solution of hydrogen chlorid as in the solution of alcohol. But the same number of molecules of each substance was put into solution. Each molecule of hydrogen chlorid must have decomposed into two smaller particles, therefore.

Abnormal results of this kind are obtained with all electrolytes. The rise in boiling point and fall in freezing point is not always twice as great, but sometimes approximately three or more times the normal result, indicating that a solution containing a mole of such substance may contain two, three, or more times as many particles as would be expected.

Electrolytes decompose in solution. What happens in typical cases may be shown by the following graphic equations, Fig. 58.

The evidence indicating a decomposition of this kind seems to be beyond question, yet it is well known that upon evaporation of the liquid the original substance may be obtained. This fact gives us the further information that the decomposition is reversible and is a typical dissociation. When the substance goes into solution or the solution is diluted, dissociation takes place. When the water is evaporated, the parts come together again to form the original substance.

Ionization. Dissociation of this kind is known as *ioni-*

zation, and the parts into which the molecules decompose are called *ions*.

Arrhenius, a Swedish chemist, first (1888) suggested this explanation of the behavior of substances in solution, and since that time so much evidence has been discovered pointing to the truth of his idea that the ionization theory has been generally accepted. A photograph of Arrhenius is shown in Fig. 59.

$$\boxed{C_2H_6O} \longrightarrow \boxed{C_2H_6O}$$

$$\boxed{HCl} \longrightarrow \boxed{H} + \boxed{Cl}$$

$$\boxed{NaCl} \longrightarrow \boxed{Na} + \boxed{Cl}$$

$$\boxed{CaCl_2} \longrightarrow \boxed{Ca} + \boxed{Cl} + \boxed{Cl}$$

$$\boxed{FeCl_3} \longrightarrow \boxed{Fe} + \boxed{Cl} + \boxed{Cl} + \boxed{Cl}$$

FIG. 58.

Every solution which has an abnormally high boiling point and an abnormally low freezing point will conduct an electric current. No substance acts as an electrolyte if the solution does not give evidence that dissociation has taken place. It seems beyond question, therefore, that the conduction of electricity through solutions is brought about by the ions.

Ions. Since in electrolysis the metals and hydrogen travel to one electrode, while the non-metallic elements and radicals go to the other electrode, it seems fairly certain that the ions carry the electricity through the solution. The ions of the metals and of hydrogen carry positive electricity and go to the cathode. They are called *cations*. The ions of non-metallic elements and radicals carry negative electricity and go to the anode. They are called *anions*. Since ions are always charged with electricity, it is customary to indicate that an element is in the ionic condition by placing plus (+) or minus (−) signs over its symbol.

Salt in water. In order that we may understand this principle the more clearly, let us consider some concrete case. Dry salt consists of sodium combined with chlorin. When salt is put into water, the molecules of sodium chlorid dissociate into particles (ions) of sodium which are charged with positive electricity and particles (ions) of chlorin which are charged with negative electricity. The salt itself is uncharged, the meaning of this term being not that the salt contains no electricity whatever, but that whatever positive electricity it may contain is neutralized by an equal amount of negative electricity. It is customary to consider that an uncharged body contains an indefinite amount of both plus and minus electricity. When the molecule decomposes into ions, equal amounts of positive and negative electricity separate, the former going on to the metallic ion, charging it positively. The latter goes on to the non-metallic ion, giving it a negative charge. In writing equations, the ions formed by a dissociating substance are often separated by a dot, as the equation shows:

$$\mathrm{NaCl} \longleftrightarrow \overset{+}{\mathrm{Na}} \, . \, \overset{-}{\mathrm{Cl}}$$

Considering the well-known reactions of these elements, to some it may seem improbable that particles of sodium

Fig. 59. — Svante Arrhenius (1859-   )

A Swedish chemist who first set forth the theory of the dissociation of electrolytes in solution and who has contributed as much as any one to the advancement of modern chemistry.

and of chlorin could exist in water without decomposing it. It must be remembered, however, that these particles are charged with electricity, and that the amount of energy they carry is different from that of the elements in their ordinary form. The ions are to be regarded as allotropic modifications of the more familiar forms of the elements. It is but natural, therefore, to expect that they would exhibit different properties.

Electrolysis. If the electrodes connected with an electric battery are immersed in a solution of salt, the negative electricity on the negative pole repels the negative electricity on the chlorin ions. It attracts the positive electricity of the sodium ions, however, and draws them to the negative pole. On reaching the cathode, the sodium ions give up their charges, pass out of the ionic condition, and then show all the properties of metallic sodium. Water is decomposed with the formation of sodium hydroxid and the liberation of hydrogen.

The positive electricity on the anode attracts the negative electricity on the chlorin ions and draws them to the positive pole. On touching the electrode, they give up their charges of electricity, pass out of the ionic condition, and show all the properties of gaseous chlorin. They attack water, forming hydrogen chlorid and oxygen. It is thus seen that as soon as an element gives up its ionic charge and passes out of the ionic condition, it assumes all the properties of the element in its ordinary form.

An explanation of the action of salt in the electrolysis of water thus becomes possible. It is the sodium and the chlorin which first separate at the electrodes, but these substances react with the water to form hydrogen and sodium hydroxid, and oxygen and hydrochloric acid. The acid and base neutralize each other, reforming salt which acts as a catalytic agent. Here again we see that the catalytic agent only appears to be inactive. In reality it is the most active substance present.

The **degree of dissociation,** *i.e.* the ratio of the number of molecules that have dissociated to the total number of molecules placed in the solution, is proportional to the dilution. In very dilute solutions we have reason to believe that electrolytes are completely dissociated. In ordinary solutions, however, ionization is not complete. In some cases there may be a relatively small proportion of ions to molecules. In other instances most of the molecules may be dissociated into ions.

Water is the only common solvent causing ionization to any great extent. Many less familiar solvents, such as liquefied ammonia, hydrogen chlorid, and sulfur dioxid, may cause considerable dissociation, however.

Not all substances dissociate in aqueous solution. Strong acids, strong bases, and salts ionize to a high degree; weak acids and bases ionize but little, while most organic substances do not appreciably dissociate. Inorganic substances are generally either acids, bases, or salts; and since these are the substances with which the student of elementary chemistry is most concerned, the ionization theory is of great importance.

That **acids separate hydrogen ions,** $\overset{+}{\mathbf{H}}$, has been shown by investigation. Whenever there are no hydrogen ions, there are no acid properties. This indicates that *what we call acid properties are in reality the properties of hydrogen in the ionic condition. Those acids which in aqueous solution dissociate most completely, produce most hydrogen ions and possess acid properties in greatest degree. They are the strong acids.* The common strong acids are hydrochloric and nitric. Sulfuric acid dissociates about two thirds as much and is about two thirds as strong. All other common acids are much weaker.

Basic properties are due to the hydroxyl ion, $\overset{-}{\mathrm{O}}\mathrm{H}$. *Those bases which dissociate most completely are the strongest.* Sodium and potassium hydroxids are the strongest of bases; barium and calcium hydroxids dissociate about two thirds as much. Ammonium hydroxid is about four hundred times weaker than sodium or potassium hydroxid. It forms the ions $\mathrm{N}\overset{+}{\mathrm{H}}_4$ and $\overset{-}{\mathrm{O}}\mathrm{H}$.

The more important acids which we have studied thus far ionize as shown in the following equations. The last two in the list are very weak, however, and dissociate only to a slight extent.

$$\mathrm{HCl} \longleftrightarrow \overset{+}{\mathrm{H}} \,.\, \overset{-}{\mathrm{C}}\mathrm{l}$$

$$\mathrm{HNO_3} \longleftrightarrow \overset{+}{\mathrm{H}} \,.\, \overset{-}{\mathrm{N}}\mathrm{O}_3$$

$$\mathrm{H_2SO_4} \longleftrightarrow \overset{+}{\mathrm{H}} \,.\, \overset{+}{\mathrm{H}} \,.\, \overset{=}{\mathrm{S}}\mathrm{O}_4$$

$$\mathrm{H_2S} \longleftrightarrow \overset{+}{\mathrm{H}} \,.\, \overset{+}{\mathrm{H}} \,.\, \overset{=}{\mathrm{S}}$$

$$\mathrm{H_2CO_3} \longleftrightarrow \overset{+}{\mathrm{H}} \,.\, \overset{+}{\mathrm{H}} \,.\, \overset{=}{\mathrm{C}}\mathrm{O}_3$$

From these equations we see that ions need not always be elementary, consisting of single atoms. A group of atoms — a radical — often acts as an ion. Most metals are capable of forming simple ions. Many non-metals, however, do not readily form simple ions, but enter the ionic condition usually combined with oxygen or other elements.

All univalent elements or radicals carry one unit charge of electricity; *i.e.* the same charge that the hydrogen ion carries. Bivalent elements form ions which have twice this charge. The ions of trivalent and tetravalent elements carry three or four times the unit charge, as the symbols for the following ions indicate:

$$\overset{+}{\mathrm{H}} \quad \overset{+}{\mathrm{K}} \quad \mathrm{N}\overset{+}{\mathrm{H}}_4 \quad \overset{-}{\mathrm{C}}\mathrm{l} \quad \overset{-}{\mathrm{O}}\mathrm{H} \quad \overset{++}{\mathrm{C}}\mathrm{a} \quad \overset{++}{\mathrm{Z}}\mathrm{n} \quad \overset{=}{\mathrm{S}} \quad \mathrm{S}\overset{=}{\mathrm{O}}_4 \quad \mathrm{C}\overset{=}{\mathrm{O}}_3$$

$$\overset{+++}{\mathrm{Fe}} \qquad \overset{+++}{\mathrm{Al}} \qquad \mathrm{P}\overset{\equiv}{\mathrm{O}}_4 \qquad \overset{++++}{\mathrm{Sn}}$$

The amount of positive electricity on the cations is always equal to the amount of negative electricity which goes on the anions formed at the same time. Substances not in solution, of course, are not ionized.

Most **reactions in solution are reactions between ions** and not between molecules. This single fact brings about a great simplification of the study of chemistry, for it is not necessary to study the reactions of each reagent on every other chemical substance. It is sufficient to learn the reactions of the common metallic ions, for any soluble salt of a metal will furnish the same cation. Similarly, we become familiar with the reactions of the commoner ions of the acids, knowing that every nitrate, for instance, will give the same nitrate ion, every sulfate the same sulfate ion, and every chlorid the same chlorid ion.

Ionic equations. Reactions in aqueous solutions being usually reactions between ions, the equations expressing them should indicate this fact. In expressing the interaction of a base with an acid in a typical case we have written

$$\mathrm{NaOH + HCl \rightarrow NaCl + HOH.}$$

We know now that sodium hydroxid is a very strong base and hydrochloric acid a very strong acid, hence in dilute solutions they will be almost completely ionized. Sodium chlorid dissociates readily also. Water is the only substance entering into this equation that does not ionize appreciably; hence an ionic equation may be written

$$\overset{+}{\mathrm{Na}}\,.\,\overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{H}}\,.\,\overset{-}{\mathrm{Cl}} \rightarrow \overset{+}{\mathrm{Na}}\,.\,\overset{-}{\mathrm{Cl}} + \mathrm{HOH}.$$

We note that sodium and chlorin ions appear on both sides of this equation. By subtracting equal quantities from both sides of an equation we do not change its value. The present equation may be simplified by striking from both sides the common terms, and it then appears

$$\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}} \rightarrow \mathrm{HOH}.$$

Neutralization. The molecular equation tells us that when an acid acts on a base, a salt is formed, and water also. The ionic equation indicates that during the interaction of an acid and a base in dilute solution, acid and basic properties disappear, for $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{O}}\mathrm{H}$ ions disappear by combining to form water. *The formation of water from its ions is the essential point in the neutralization of dilute solutions of acids with bases*, as is shown by the following equations:

$\overset{+}{\mathrm{K}}.\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{C}}\mathrm{l} \rightarrow \overset{+}{\mathrm{K}}.\overset{-}{\mathrm{C}}\mathrm{l} + \mathrm{HOH}$, simplified, $\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}} \rightarrow \mathrm{HOH}$

$\overset{+}{\mathrm{K}}.\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{N}}\mathrm{O}_3 \rightarrow \overset{+}{\mathrm{K}}.\overset{-}{\mathrm{N}}\mathrm{O}_3 + \mathrm{HOH}$, simplified, $\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}} \rightarrow \mathrm{HOH}$

$\overset{+}{\mathrm{K}}.\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{B}}\mathrm{r} \rightarrow \overset{+}{\mathrm{K}}.\overset{-}{\mathrm{B}}\mathrm{r} + \mathrm{HOH}$, simplified, $\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}} \rightarrow \mathrm{HOH}$

$\overset{+}{\mathrm{N}}\mathrm{a}.\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{N}}\mathrm{O}_3 \rightarrow \overset{+}{\mathrm{N}}\mathrm{a}.\overset{-}{\mathrm{N}}\mathrm{O}_3 + \mathrm{HOH}$, simplified, $\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}} \rightarrow \mathrm{HOH}$

$\overset{+}{\mathrm{N}}\mathrm{a}.\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}}.\overset{-}{\mathrm{B}}\mathrm{r} \rightarrow \overset{+}{\mathrm{N}}\mathrm{a}.\overset{-}{\mathrm{B}}\mathrm{r} + \mathrm{HOH}$, simplified, $\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}} \rightarrow \mathrm{HOH}$

According to these equations, when the two solutions are mixed, a salt is not formed; water only is formed. On evaporating the solutions, the metallic ions unite with the non-metallic ions and then a salt is formed.

In neutralizing acids with bases in many instances it will be found that none of the reagents or products of the reaction are gaseous or insoluble, yet the reactions generally run to completion. Such instances introduce to us a **third reason why reactions do not run to equilibrium.** Neutralization is a reaction between ions. If certain of the ions of the acid and the base are removed, there will be no possibility of a reversal of the reaction. By the formation of water, hydrogen and hydroxyl ions are removed. Hence the reaction is not reversed and does not run to equilibrium. *In all reactions between ions, whenever a substance is formed that does not ionize, the reaction runs to completion, and the substance that does not ionize will be formed as long as there is material present to form it.*

Weak acids and bases ionize so little that reactions tend to run to completion whenever a weak acid or a weak base is formed. If the substances indicated in the following equations are mixed with an abundance of water so that no gas will escape from solution, the reactions will take place as indicated because hydrogen sulfid and carbonic acid do not ionize sufficiently to cause any great reversal of the reactions.

$\overset{+}{Na}_2.\overset{=}{S}+2\overset{+}{H}.\overset{-}{Cl}\rightarrow 2\overset{+}{Na}.\overset{-}{Cl}+H_2S$, simplified, $\overset{=}{S}+2\overset{+}{H}\rightarrow H_2S$

$\overset{+}{Na}_2.\overset{=}{CO}_3+2\overset{+}{H}.\overset{-}{Cl}\rightarrow 2\overset{+}{Na}.\overset{-}{Cl}+H_2CO_3$, simplified, $\overset{=}{CO}_3+2\overset{+}{H}\rightarrow H_2CO_3$

Hydrolysis. When the attempt is made to neutralize weak acids and weak bases, the reaction runs to equilibrium and not to completion, for hydrolysis of the salt formed reverses the reaction. The reason for this result will be apparent if typical cases are considered. The reaction

$$KOH + HCN \longleftrightarrow KCN + HOH$$

is reversible because there is present on each side of the reaction a substance that does not ionize appreciably. The fact that water is practically undissociated tends to force the neutralization reaction to completion, but this tendency is opposed by the fact that hydrocyanic acid is very weak and does not ionize appreciably. This tends to reverse the reaction, hence equilibrium ensues. The solution turns litmus blue because potassium hydroxid ionizes to a much greater degree than hydrocyanic acid does. Hence there are more $\overset{-}{OH}$ ions in the solution than $\overset{+}{H}$ ions.

The reaction

$$Fe(OH)_3 + 3\ HNO_3 \longleftrightarrow Fe(NO_3)_3 + 3\ HOH$$

is reversible also because a substance that does not ionize is present on each side of the equation. Because water does not dissociate, the reaction between the acid and the base tends to run to completion. This action is overcome partially, because ferric hydroxid ionizes very little, hence equilibrium results. The solution reacts acid, for more $\overset{+}{H}$ ions are put into the solution by nitric acid than $\overset{-}{OH}$ ions by ferric hydroxid.

SUMMARY

ELECTROLYTES IN SOLUTION. Solids as a rule do not react when brought together in the dry state, but when in solution acids, bases, and salts — electrolytes — react with the greatest readiness. Such reactions are generally simple metatheses, and they usually take place with such ease as to indicate that the reagents in solution are already broken up into the parts which exchange places. This idea is confirmed by a study of the boiling and freezing points of aqueous solutions of electrolytes.

Ionization. When an electrolyte goes into solution, its molecules decompose into smaller parts called *ions*. The process is known as *ionization*. It is a distinctly reversible reaction, and, on evaporation of the water, the ions come together to form the original substance.

Ions carry electric charges, hydrogen and metallic ions carrying positive charges, and non-metallic elements and radicals carrying negative charges. As a result of these charges, the amount of energy on an ion is different from that on an atom of the same substance. Ions may be regarded as allotropic modifications of the elements. When a solution is electrolyzed, the ions give up their charges and then show the ordinary properties of the elements.

Degree of ionization. Water is the only common solvent causing ionization to any great extent. The degree of dissociation is proportional to the dilution, and in ordinary solutions ionization is not complete. Strong acids, strong bases, and salts are much more dissociated than weak acids and bases.

Solutions of acids owe their properties to hydrogen ions. Those acids are strongest which dissociate most completely. Similarly, bases owe their properties to hydroxyl ions. The amount of electricity on the hydrogen ion is called the unit charge. Univalent metals or radicals form ions which have 1 unit charge. Bivalent elements carry 2 charges, while trivalent and tetravalent ions carry 3 and 4 times the charge of the hydrogen ion.

Reactions in solution, as a general rule, are reactions between ions. To understand these reactions it is only necessary to learn the reactions of the commoner metallic and non-metallic ions, for all the salts of a given metal will form the same cation, and all the salts of a given acid will liberate the same anion.

Neutralization. When an acid and a base neutralize each other, the hydrogen ions of the acid unite with the hydroxyl ions of the base to form water, leaving in solution ions which on evaporation produce a salt.

Third reason why reactions do not run to equilibrium. *In all reactions between ions whenever a substance is formed that does not ionize, the reaction runs to completion.* A reversal of the reaction is prevented because one substance does not ionize, hence equilibrium is impossible.

Hydrolysis. The neutralization of weak acids and weak bases is never complete, but the reaction always runs to equilibrium. The reason for this is that a weak acid or a weak base dissociates but little, and this tends to reverse the neutralization reaction. *The reverse of neutralization is hydrolysis.*

QUESTIONS

1. Write equations showing how the following substances ionize: HCl; HNO_3; H_2SO_4; $NaOH$; NH_4OH; $Ca(OH)_2$; $ZnCl_2$; $ZnSO_4$; $FeCl_3$; $Fe(NO_3)_3$.

2. Write ionic equations for the interactions of the following substances. Do the reactions run to equilibrium or to completion? Why in each case?

$NaOH + HCl$ —

$Ca(OH)_2 + HCl$ —

$NaOH + H_2SO_4$ —

$Ca(OH)_2 + H_2SO_4$ —

$Na_2CO_3 + HNO_3$ —

$K_2S + H_2SO_4$ —

$BaCl_2 + Na_2SO_4$ —

$AgNO_3 + HCl$ —

3. Why do less volatile acids decompose the salts of more volatile acids and liberate the latter?

4. Dilute sulfuric acid decomposes all phosphates and liberates phosphoric acid, even though the latter is less volatile than the former. Why? (Consult p. 275.)

5. Boric acid is a very weak acid, readily soluble, and not volatile. What will be the action of nitric acid on a solution of sodium borate, $NaBO_2$? Why?

6. How will solutions of the following substances affect litmus? Explain. (*a*) K_2S. (*b*) $FeCl_3$. (*c*) $CuSO_4$. (*d*) Na_2CO_3. (If necessary in order to answer these questions, drop a crystal of the substance into a little water and test the resulting solution in each case.)

7. Why does liquefied hydrogen chlorid possess no acid properties? Would you expect it to conduct an electric current?

8. Pure sulfuric acid (100% H_2SO_4) may be kept in a tin can without any difficulty. Explain why. If it is allowed to stand in moist air, it soon attacks the can and dissolves it. Explain why.

9. A solution of hydrogen chlorid gas in petroleum does not conduct an electric current. Explain why. Will it attack zinc or turn blue litmus red?

10. What is it that affects the sense of taste (*a*) when sugar is put into coffee; (*b*) when salt is added to soup?

11. To what is the sour taste of lemon juice, vinegar, and unripe apples due? So far as the sour taste is concerned, mention some other substances which would produce it. (Cheap lemonade and vinegar are sometimes made from dilute solutions of sulfuric acid.)

CHAPTER XXIII

THE NITROGEN GROUP

The group. The members of this group — *nitrogen*, *phosphorus*, *arsenic*, *antimony*, and *bismuth* — form compounds of the same general character as the compounds of nitrogen, the properties of which should be reviewed at this time. As we have noted in other groups, the element with the lowest reacting weight, in this case nitrogen, differs more from the other members of the group than they do among themselves. Each element of the present group shows valences of three or five. With nitrogen and phosphorus the pentavalent condition is the more stable, and trivalent compounds oxidize readily to the higher form. With arsenic one state of oxidation is about as stable as the other, but with antimony and bismuth, pentavalent compounds tend to decompose and give the lower form.

Phosphorus occurs in nature chiefly as salts of phosphoric acid. Arsenic is found in combination with metals, thus acting as a non-metallic element; and also combined with sulfur and with oxygen, in these instances acting as a metal. Antimony and bismuth either occur free or else united with non-metals. These simple facts show that within this group the properties of the elements change gradually from the strong acid-former, nitrogen, to the characteristic metal, bismuth.

PHOSPHORUS (P — 31) occurs in nature as *phosphates*, *i.e.* salts of *phosphoric acid*, H_3PO_4. The most important salt, calcium phosphate, $Ca_3(PO_4)_2$, is found in the minerals, *phosphorite* and *apatite*; it constitutes most of the mineral matter of the bones of vertebrates, and occurs everywhere in the soil in small amounts.

From the natural phosphate or from bone-ash, the element may be prepared by liberating phosphoric acid and reducing this with carbon in an atmosphere that is free from oxygen. A mixture of phosphate, sand (SiO_2), and charcoal is fed into an electric furnace (Fig. 60); by the screw, A; the reaction given below takes place, and phosphorus distills out through B and is collected under water. The slag, $CaSiO_3$, is drawn off through D. C and C are working openings which are ordinarily closed when the furnace is running.

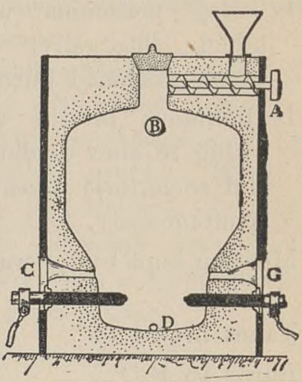


Fig. 60.

$$Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C \rightarrow 3\,CaSiO_3 + 5\,CO + 2\,P$$

Allotropic forms. Phosphorus exists in two allotropic modifications, yellow and red.

Yellow Phosphorus	Red Phosphorus
Is a light yellow, waxy substance, separating from carbon disulfid as colorless crystals.	Is a dark red, apparently amorphous substance, insoluble in carbon disulfid.
Has the specific gravity 1.82.	Has the specific gravity 2.16.
Melts at 44° and boils at 269°.	Does not melt; sublimes at about 300°.

Yellow Phosphorus	Red Phosphorus
Has a slight odor.	Has no odor.
Is very poisonous when taken internally, and causes poisoned burns.	Is not poisonous.
Is luminous in the dark owing to slow oxidation, and sometimes takes fire spontaneously.	Is not luminous in the dark, and does not oxidize in the air.
Must be kept under water.	May be kept in uncorked bottles.
Takes fire at 50°.	Takes fire above 250°.
Burns to P_2O_5.	Burns to P_2O_5.
When exposed to sunlight, or when heated to 250° without access of air, changes to red phosphorus.	When heated to about 300° without access of air, is converted into vapor which condenses as yellow phosphorus.

Matches. The use of phosphorus in matches began in 1827. The tips of the sticks are dipped into melted sulfur or paraffine, and then into a mixture of phosphorus, glue, and some oxidizing agent, often potassium chlorate and lead dioxid. When the match is struck, the heat from friction ignites the phosphorus, its combustion being aided by the oxidizing agent. The sulfur or paraffine is thus raised to its kindling temperature and in turn ignites the wood. Because of the odor when burning, sulfur is practically out of use now. Because of the poisonous properties of phosphorus, the sulfid, P_4S_3, has been substituted in matches.

Safety matches are tipped with antimony sulfid and an oxidizing agent. This mixture can not be ignited by friction except when drawn across a surface coated with a mixture containing red phosphorus. The friction converts a bit of red phosphorus into the yellow form, ignites it and this sets fire to the match head.

Phosphids. Phosphorus is an active element, combining at high temperatures directly with many metals to form *phosphids*, and also with many non-metals, such as the members of the halogen and sulfur groups. Hydrogen phosphid is commonly known as *phosphin.* It may be formed by treating a metallic phosphid with acid, exactly as hydrogen sulfid is formed when a sulfid reacts with an acid, as the following equations show:

$$Ca_3P_2 + 6\,HCl \rightarrow 3\,CaCl_2 + 2\,H_3P$$
$$FeS + 2\,HCl \rightarrow FeCl_2 + H_2S$$

It is formed, also, whenever organic material containing phosphorus, such as fish, decays without free access of air. In this respect its formation resembles the formation of ammonia in the decay of nitrogenous substances, or hydrogen sulfid in the decomposition of eggs. For laboratory purposes it may be made by heating yellow phosphorus in a strong solution of potassium or sodium hydroxid. Hydrogen or some other gas is passed into the apparatus (Fig. 61) to remove all oxygen. A complex reaction takes place as the equation shows.

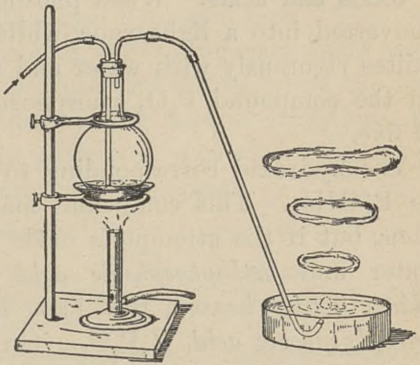


FIG. 61.

$$3\,NaOH + 4\,P + 3\,H_2O \rightarrow PH_3 + 3\,NaH_2PO_2$$

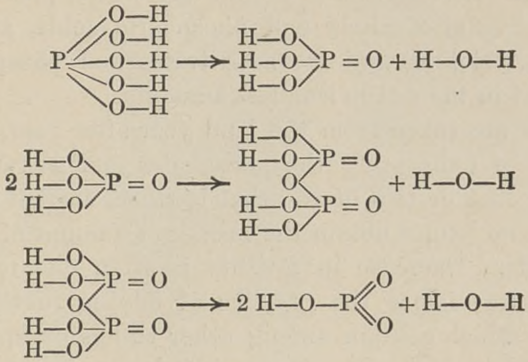
Phosphin, when thus prepared, takes fire as soon as it comes in contact with air, each bubble of gas, as it burns, producing a beautiful "smoke ring" consisting of phosphorus pentoxid (see fig. 61). The spontaneous combustion is due to the presence of a small quantity of another hydrid of phosphorus, P_2H_4, for the kindling temperature of pure phosphin is about 100°. Phosphin is a colorless, poisonous gas, smelling somewhat like decaying fish and resembling in many ways ammonia, the corresponding nitrogen compound. Like ammonia, phosphin unites with acids to form *phosphonium* salts. These are more unstable than ammonium salts, however, being decomposed by water into phosphin and the acid.

$$NH_3 + HCl \rightarrow \mathrm{NH_4Cl}$$
$$PH_3 + HCl \rightarrow \mathrm{PH_4Cl}$$

Oxids and acids. When phosphorus burns in air, it is converted into a light, snow-white powder, P_2O_5, which unites vigorously with water and forms phosphoric acid. In the compound P_2O_5 phosphorus acts with a valence of five.

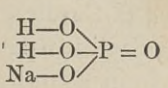
The hydroxid corresponding to the oxid, P_2O_5, would be $P(OH)_5$. This compound may exist in water solutions, but if the attempt is made to separate it, it loses water and *orthophosphoric acid*, H_3PO_4, is obtained. When gently heated, this loses more water and forms *pyrophosphoric acid*, $H_4P_2O_7$. On further heating more water disappears and *metaphosphoric acid*, HPO_3, results. The last step in this process would be the formation of the anhydrid, P_2O_5, but this reaction does not take place, for metaphosphoric acid is very stable and boils without decomposition at 550°. This fact makes phosphorus pentoxid an excellent drying agent, for, when once it has united with a small amount of water, it does not part with it again.

The structural equations representing these changes are as follows:

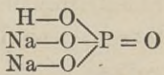


In composition these compounds of phosphorus differ only in the amount of water which is combined with the anhydrid in each case. Each substance acts as a weak acid, dissociating but little into hydrogen ions. The formula for metaphosphoric acid, HPO_3, suggests nitric acid, HNO_3, but the former is weak and stable, while the latter is strong and unstable. Under natural conditions, all acids of phosphorus are converted into the ortho form and salts of this acid are most important.

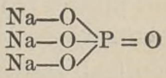
Three types of salts are known:



Diacid sodium phosphate



Acid disodium phosphate



Trisodium phosphate

Salts of the first type are soluble generally; of the third type all salts except those of the alkali metals are insoluble; the solubility of the second type is intermediate.

Fertilizers. Compounds of phosphorus in small amounts are necessary for the development of living things, both animal and vegetable. Animals receive their phosphorus from the vegetable world, and this obtains its supply from the soil. A proper food supply is necessary if a plant is to flourish. Besides carbon dioxid and water, plant food consists of salts of nitric and phosphoric acids, and of potassium, calcium, and iron. Nitrates and phosphates are present in the soil in smallest amounts.

If crops are taken from the land year after year, there is danger of exhausting the phosphates and nitrates in the upper foot or two of soil that is tilled, so that vegetation can no longer obtain the necessary amount of these plant foods. Decrease in fertility is often due to lack of phosphate; hence the practice of adding to the soil fertilizers which contain among other things phosphates, nitrates, and often potassium salts, known as potash. Fig. 62 shows the striking difference in the growth of plants in the same soil with and without fertilizers. Note that the peas (the upper row) do as well without nitrogen as when it is added; for peas obtain their nitrogen from the air (p. 130). Oats cannot get nitrogen in this way, and it must be added as fertilizer if they are to do well on land that is exhausted.

In the manufacture of artificial fertilizer hundreds of thousands of tons of phosphate rock, $Ca_3(PO_4)_2$, are treated with sulfuric acid and converted into calcium sulfate (land plaster) and diacid calcium phosphate, $H_4Ca(PO_4)_2$, known as *soluble phosphate*. (See p. 275.) Chili saltpeter or animal matter, *i.e.* refuse of all kinds from slaughter houses, known as "tankage," furnishes the nitrogen. Wood ashes contain potassium carbonate and are valuable as a fertilizer.

Phosphorous acid. If phosphorus is burned in a limited supply of air, P_2O_3 is formed, which is the anhydrid of phosphorous acid, H_3PO_3, an unstable substance which oxidizes readily to phosphoric acid.

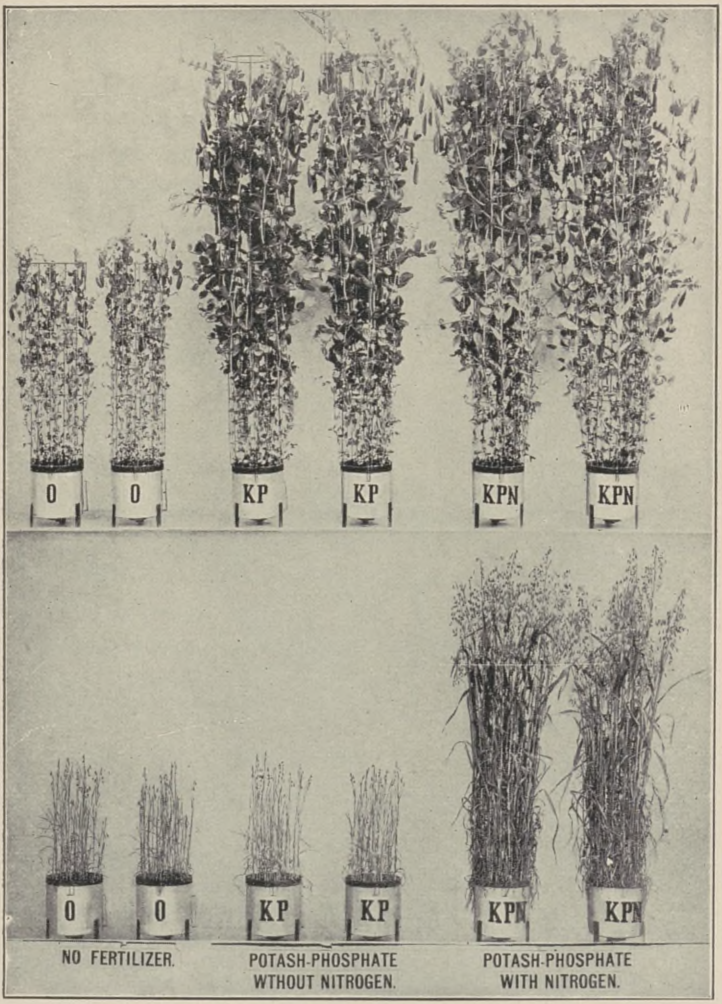


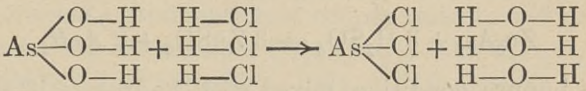
Fig. 62. — The Effect of Fertilizers

Upper row — Peas.
Lower row — Oats.

ARSENIC (As — 75) is a widely distributed element, occuring in nature in connection with metallic sulfids. Since the ores of many metals consist largely of sulfids, they are *roasted*, *i.e.* heated in air. During this process arsenic is burned to the trioxid, As_2O_3, a heavy white solid which is known as "*white arsenic.*" A large part of this settles in the smelter flues, from which it may be removed. The oxid on being heated with charcoal yields the element. But part of the oxid passes out of the "stacks" of the smelters and is deposited upon the fields in the neighborhood, often causing loss of cattle, for arsenic compounds are very poisonous

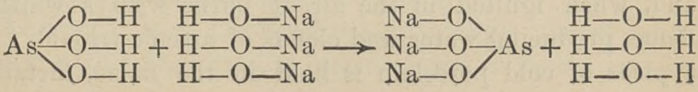
When heated with charcoal, arsenic oxid yields the element. Several allotropic modifications of arsenic are known, but the ordinary form is a steel-gray, crystalline substance with a metallic luster. When heated it passes into gas without melting, for its melting point is higher than the temperature at which it vaporizes. Its vapor has a garlic-like smell. It readily oxidizes in the air; and when raised to its kindling temperature, it burns with a white flame, forming the trioxid.

The hydroxid corresponding to the trioxid is $As(OH)_3$. This acts either as an acid or as a base. It dissolves in acids, forming compounds such as arsenic chlorid, $AsCl_3$, in which the arsenic is playing the part of a metal.



$$\mathrm{As}\begin{array}{l}\diagup\mathrm{O{-}H}\\ {-}\mathrm{O{-}H}\\ \diagdown\mathrm{O{-}H}\end{array} + \begin{array}{l}\mathrm{H{-}Cl}\\ \mathrm{H{-}Cl}\\ \mathrm{H{-}Cl}\end{array} \longrightarrow \mathrm{As}\begin{array}{l}\diagup\mathrm{Cl}\\ {-}\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{array} + \begin{array}{l}\mathrm{H{-}O{-}H}\\ \mathrm{H{-}O{-}H}\\ \mathrm{H{-}O{-}H}\end{array}$$

It dissolves in bases also, forming compounds in which arsenic is acting as an acid-forming element. If sodium hydroxid is used, sodium arsenite, Na_3AsO_3, is formed. Under these circumstances arsenious hydroxid acts as an acid and is called *arsenious acid.*



$$\mathrm{As}\begin{array}{l}\diagup\mathrm{O{-}H}\\ {-}\mathrm{O{-}H}\\ \diagdown\mathrm{O{-}H}\end{array} + \begin{array}{l}\mathrm{H{-}O{-}Na}\\ \mathrm{H{-}O{-}Na}\\ \mathrm{H{-}O{-}Na}\end{array} \longrightarrow \begin{array}{r}\mathrm{Na{-}O}\diagdown\\ \mathrm{Na{-}O}{-}\\ \mathrm{Na{-}O}\diagup\end{array}\mathrm{As} + \begin{array}{l}\mathrm{H{-}O{-}H}\\ \mathrm{H{-}O{-}H}\\ \mathrm{H{-}O{-}H}\end{array}$$

It is thus seen that arsenic has no decided character of its own. Several other *elements whose properties are not decidedly metallic or non-metallic may act either as base-formers or as acid-formers, depending on the nature of the substances with which they are placed. In the presence of a strong acid they act as base-formers, while in the presence of a strong base they act as acid-formers.* As would be expected from elements of such qualities, if they act as acid-formers, the acids are very weak; and if they act as base-formers, the bases are very weak.

Subjected to the action of oxidizing agents, compounds of trivalent arsenic are changed into compounds of pentavalent arsenic. The pentavalent hydroxid, $As(OH)_5$, is unknown, for it loses water just as the corresponding compound of phosphorus does. We know that it may act as a base, for compounds like $AsBr_5$ are known. It acts more readily as an acid, and salts of ortho-, meta-, and pyro-*arsenic acids* are well known. They closely resemble the corresponding salts of the phosphoric acids.

Arsin. The hydrid of arsenic, *arsin*, AsH_3, is analogous in composition to phosphin and ammonia. It may be made by the decomposition of arsenids by acids. If zinc arsenid is used, the equation is

$$\mathbf{Zn_3As_2} + 3\,H_2SO_4 \rightarrow 3\,ZnSO_4 + 2\,\mathit{AsH_3}$$

In an impure condition, mixed with hydrogen, it may be made by the action of nascent hydrogen on soluble arsenic compounds.

It is a colorless, extremely poisonous gas. Unlike ammonia and phosphin, it does not combine with acids. When heated, it is easily decomposed into its elements, and, when ignited in the air, it burns with a whitish flame, producing water and clouds of arsenic trioxid. If a piece of cold porcelain is held in the flame, metallic arsenic is deposited as a black coloration, just as soot is deposited in a candle flame. The *Marsh test*, a most delicate means of detecting traces of arsenic in large amounts of other matter, depends upon the formation of arsin.

To illustrate the method of applying this test, let us take the case of a suspected death from arsenic poisoning. The stomach and other viscera are removed from the body and oxidized with nitric acid or potassium chlorate. The organic matter is converted chiefly into carbon dioxid and water, and any arsenic present is converted into arsenic acid. The concentrated solution containing the arsenic is introduced into a hydrogen generator, and the nascent hydrogen reduces the arsenic acid to arsin, according to the equation:

$$H_3AsO_4 + 8\,\mathit{H} \rightarrow \mathit{AsH}_3 + 4\,H_2O$$

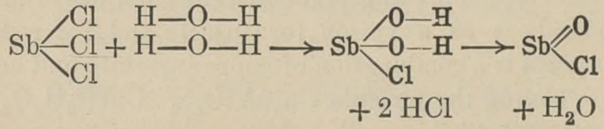
The exit tube from the generator is heated and as the arsin passes through, it is decomposed and a deposit of elementary arsenic is formed.

Uses of arsenic. Though used to a slight extent in medicines and in making pigments, the chief use of arsenic compounds is as a poison for insects and for rodents. *Paris green* is a combination of copper arsenite and copper acetate having the formula $Cu_3(AsO_3)_2 \cdot Cu(C_2H_3O_2)_2$.

ANTIMONY (Stibium, Sb — 120). This element and its compounds so closely resemble arsenic and its compounds that lengthy description seems unnecessary. Antimony is found in nature chiefly as *stibnite*, Sb_2S_3, a crystalline, black substance. The artificial sulfid has the same composition but is orange-colored. When heated, it becomes black and retains this color on cooling.

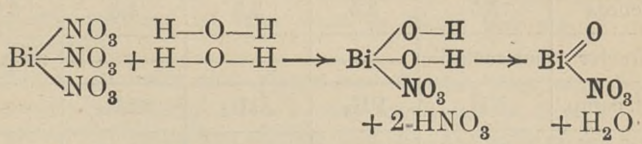
Antimony is a light-colored, crystalline, heavy substance with a fine metallic luster, so brittle that it may be powdered in a mortar. It melts at 625° and on solidifying expands, thus filling every portion of the mold into which it may be poured. Many alloys of antimony with other metals are used industrially, such as *type metal*, and *Babbitt metal* for bearings in machinery. Its compounds are less poisonous than those of arsenic and are used in medicine. *Tartar emetic* is an antimony potassium compound of tartaric acid.

Properties. Antimony may act both as a trivalent and as a pentavalent element, and in either state of oxidation the hydroxid may act either as an acid or as a base. The acids are weaker than those of arsenic, however, and the bases stronger, indicating that antimony is more of a metal than arsenic and less of a non-metal. The hydrid, *stibin*, SbH_3, closely resembles arsin in properties and methods of preparation, and like arsin it responds to Marsh's test. Almost all salts in which antimony plays the part of a base are decomposed by water to a considerable extent. Thus antimony chlorid, $SbCl_3$, dropped into water precipitates white antimony oxychlorid, SbOCl, the reaction being hydrolysis and dehydration.

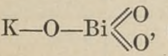


BISMUTH (Bi — 208) resembles antimony almost as closely as antimony does arsenic. It is hard, crystalline, and brittle, has a reddish hue, melts at 264° and expands on solidifying. The most productive mines are in Saxony. Though a comparatively rare metal, bismuth finds many uses, for it forms several alloys that melt at low temperatures. *Wood's metal*, consisting of bismuth 4 parts, lead 2 parts, tin 1 part, cadmium 1 part, melts at 60°. By choosing proper proportions of the metals an alloy melting at almost any desired temperature above 60° may be obtained. When used as *safety plugs* in boilers, such alloys melt out and relieve the pressure when the temperature gets sufficiently high so that there is danger of bursting the boilers. *Stereotype plates* used in printing are made from a low-melting alloy.

Bismuth ordinarily acts as a trivalent metal. The hydroxid, $Bi(OH)_3$, will not dissolve in bases, *i.e.* will not act as an acid, thus showing that bismuth is considerably more metallic than antimony. Bismuth salts are quite unstable, however, thus indicating that bismuth does not possess metallic properties to any great degree. It acts as a weak base-former usually, and its salts tend to hydrolyze greatly. Its chlorid, $BiCl_3$, forms an oxychlorid, BiOCl, similar to that of antimony, and the nitrate, sulfate, and other salts act similarly. A typical reaction is given below:



This salt, $BiONO_3$, is known as bismuth *subnitrate* and finds use in medicine.

In the pentavalent condition bismuth forms compounds of the type  $K{-}O{-}Bi\begin{matrix}=O\\=O\end{matrix}$, a salt of bismuthic acid similar to KNO_3, KPO_3, $KAsO_3$ and $KSbO_3$.

Three very rare elements, *vanadium* (V — 51), *niobium* (Nb — 94), and *tantalum* (Ta — 183), belong to this group and resemble the other elements closely. Vanadium forms the oxids V_2O, V_2O_2, V_2O_3, V_2O_4 and V_2O_5, like nitrogen, and a corresponding series of chlorids is known: VCl, VCl_2, VCl_3, VCl_4, and $VOCl_3$. Tantalum is used as a filament in the tantalum light.

Comparison. The following chart presents in tabular form the compounds of the common elements of the nitrogen group, and shows the change from the strong acid-forming non-metal, nitrogen, to the base-forming, metallic element bismuth. It might be expected that bismuth, acting as a metal, would form pentavalent compounds, but all these bodies seem to be too unstable to exist.

NITROGEN GROUP

	N	P	As	Sb	Bi
React. wt.	14	31	75	120	208
Melt. pt.	−214°	44°	above 450°	625°	264°
State	gas	solid	solid	solid	solid
Boil. pt.	−194°	269°	450°	1450°	1600°
Spec. grav.	0.885	1.82	5.7	6.7	9.8
Valences	3,5	3,5	3,5	3,5	3,5
Character	non-metallic	———	———	———→	metallic
Hyd. comp.	NH_3	PH_3	AsH_3	SbH_3	——
Oxids	N_2O	——	——	——	——
	N_2O_2	——	——	——	Bi_2O_2
	N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3
	N_2O_4	——	——	Sb_2O_4	Bi_2O_4
	N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5
Hydroxids					
Trivalent	——	$(HO)_3P$	$(HO)_3As$	$(HO)_3Sb$	$(HO)_3Bi$
	HONO	——	HOAsO	HOSbO	HOBiO
	weak acid	weak acid	acid or base	acid or base	base
Pentavalent	——	$(HO)_3PO$	$(HO)_3AsO$	$(HO)_3SbO$	——
	$HONO_2$	$HOPO_2$	$HOAsO_2$	$HOSbO_2$	$HOBiO_2$
	strong acid	weak acid	weak acid	acid or base	very weak acid

SUMMARY

PHOSPHORUS occurs in nature chiefly as salts of phosphoric acid. It is prepared from calcium phosphate. It occurs in two allotropic forms.

Yellow phosphorus is crystalline, poisonous, takes fire at 50°, and changes to the red at 250° or on exposure to sunlight. Its chief use is in making matches.

Red phosphorus is amorphous, not poisonous, takes fire about 250° and changes to yellow when heated to about 300°.

Hydrid. Phosphorus unites at high temperatures with other elements to form *phosphids*. Hydrogen phosphid or *phosphin*, PH_3, may be prepared by treating a metallic phosphid with dilute acid, and is a gas resembling ammonia in some respects.

Oxids. There are two oxids, P_2O_3 and P_2O_5. The latter is formed in ordinary combustion and is the more important. It unites with water to form the phosphoric acids.

Acids. Phosphoric acids are formed from the normal hydroxid, $P(OH)_5$, which possibly exists in water solutions, by the loss of water. They are *orthophosphoric acid*, H_3PO_4, *pyrophosphoric acid*, $H_4P_2O_7$, and *metaphosphoric acid*, HPO_3. Of these, orthophosphoric acid and its salts occur in nature and are the most important.

Fertilizers. In order that plants may flourish, they must have a proper food supply. The mineral foods, derived from the soil, are salts of potassium, calcium, and iron, and salts of nitric and phosphoric acids. Removal of crops results in the removal of these food substances, and to restore fertility to the soil it is necessary to add to it the above substances, especially phosphates and nitrates, as these occur in smallest amount.

ARSENIC occurs in connection with metallic sulfids, and when these are roasted, the arsenic is oxidized to the trioxid and may be collected. The usual form is a steel-gray crystalline substance. Its soluble compounds are very poisonous. Chemically, arsenic has no decided character of its own, acting as a base when in the presence of acids and as an acid when in the presence of bases.

Hydrid. Hydrogen arsenid, or *arsin*, AsH_3, may be made like phosphin. It is an exceedingly poisonous gas, easily decomposed by heat. In Marsh's test for arsenic it is formed by the action of nascent hydrogen on arsenic compounds.

Oxygen compounds. The oxid, As_2O_3, is formed by ordinary combustion of the element and is known as *white arsenic*. The hydroxid corresponding to it, $As(OH)_3$, may be either an acid or a base. Pentavalent arsenic forms compounds corresponding to those of pentavalent phosphorus.

ANTIMONY is found as Sb_2S_3, *stibnite*. The element is a crystalline, brittle, metallic substance that expands on solidification and so finds use in many valuable alloys. Its compounds correspond to those of arsenic, but it is more metallic than the latter in its chemical character.

BISMUTH resembles antimony closely. It finds use in many valuable alloys of low melting point. It is ordinarily a trivalent element, and as such is a base-former.

QUESTIONS

1. How much phosphorus may be obtained from 1000 kilos of calcium phosphate?

2. The gas density of phosphorus vapor at 300° is 62 and at 1040° it is 31. How many atoms are there in its molecule at each of these temperatures?

3. On the basis of Avogadro's hypothesis, calculate the gas density of phosphin.

4. In preparing the common acids from their salts could phosphoric acid be used instead of sulfuric acid? Why is it not used?

5. The skeleton of a man weighs about 10 pounds, three quarters of which is calcium phosphate. This would furnish phosphate for how many bushels of wheat? Wheat weighs about 60 lb. to the bushel, and contains about 1 % of calcium phosphate.

6. Compare the chemical behavior and properties of phosphorus, sulfur, and chlorin.

7. Compare the ways in which ammonia, phosphin, and hydrogen sulfid are formed in nature.

8. Compare the stability of the hydrids of the chlorin, sulfur, and phosphorus groups.

9. In the preparation of phosphin, what gases may take the place of hydrogen?

10. Write the chemical equation for the burning of phosphin. How many cubic centimeters of oxygen are required in the burning of 10 ccm. of phosphin?

11. Write the chemical equations for the burning of arsin and stibin. How much oxygen is required in the burning of 10 ccm. of each?

12. Ordinary sulfuric acid always contains arsenic compounds. Why? Suggest how you could detect the arsenic.

CHAPTER XXIV

THE CARBON GROUP

The group. The most important members of the carbon group are *carbon*, *silicon*, *tin*, and *lead*. Of these carbon has already been studied, and a review of its properties will serve to fix the type in mind. Though in physical properties carbon and silicon are non-metals and tin and lead are metals, yet chemically there are many points of similarity among the four. All act with similar valences and form corresponding compounds. The rare elements, *titanium* (Ti — 48), *germanium* (Ge — 72.5), *zirconium* (Zr — 90.6), *cerium* (Ce — 140), and *thorium* (Th — 232.5) belong to this group. The oxids of cerium and thorium are the material out of which incandescent mantles for gas lights are made.

SILICON (Si — 28) in the free state is an unfamiliar substance, but in its compounds it is very abundant and widely distributed, being next after oxygen the chief constituent of the earth's solid crust. It occurs as the dioxid, SiO_2, the anhydrid of silicic acid, salts of which form most of the commoner rocks.

The **element** silicon may be obtained in the free condition by the reduction of the oxid at high temperatures. The reaction does not take place readily, for silicon dioxid is one of the most stable substances known. Metallic magnesium or sodium can cause its decomposition, for the oxids of magnesium or sodium are somewhat more stable at high temperatures than the oxid of silicon.

$$4\,Na + SiO_2 \longrightarrow 2\,Na_2O + Si$$

Silicon exists in two, perhaps three, allotropic modifications. Amorphous silicon, corresponding to amorphous carbon, is a dark brown powder that readily takes fire when heated in the air and burns to the dioxid. Hydrofluoric acid and the alkalis dissolve it. Crystallized silicon is dark gray and hard, corresponding to the diamond. It is much less active than the amorphous form. A third allotropic form of silicon, corresponding to graphite, has been reported.

Hydrogen compounds. Silicon forms several hydrids which suggest the beginnings at least of the methane and ethylene series of carbon compounds, as the following table shows:

Methane	CH_4	SiH_4	Silico-methane
Ethane	C_2H_6	Si_2H_6	Silico-ethane
Propane	C_3H_8	Si_3H_8	Silico-propane
Ethylene	C_2H_4	Si_2H_4	Silico-ethylene

Silicon monoxid, SiO, made by heating the dioxid with silicon in the electric furnace, finds use as a very permanent brown pigment.

Silicon dioxid, SiO_2, commonly called *silica*, is found to a slight extent in the animal and vegetable kingdoms. It occurs in many grasses. The skeletons of certain microscopic animals are nearly pure silica. Large deposits of this material, called *infusorial* or *diatomaceous earth*, occur in various parts of the world. It is used for a variety of purposes. Mixed with washing soda and soap, it is found in most scouring soaps, furnishing the "grit" which does the scouring. Being very porous, it is often used as an absorbent. Dynamite is nitroglycerine soaked up in diatomaceous earth or sawdust.

In the mineral world silicon dioxid occurs in three forms.

1. **Quartz**, or *rock crystal*, the commonest form of silicon dioxid, occurs in the well-known, transparent, six-sided crystals (see frontispiece), which are very hard and are sometimes of great size and beauty. When tinged by traces of foreign matter, it is called *amethyst*, *milky quartz*,

smoky quartz, etc. Quartz is an important constituent of granite and other rocks, and when finely broken forms *sand* and *sandstone*.

2. *Tridymite* is a rare mineral, distinguished from quartz by its different crystalline structure, hardness, etc. It is found in many rocks.

3. **Amorphous silica** includes *agate*, *onyx*, *flint*, *chalcedony*, *jasper*, and similar minerals. Agate is silica deposited from its solution in alkaline water. The banded structure which agate shows when polished is caused by its method of formation, for as the supply of water varies from season to season layers of agate of different color and texture are formed.

Many agates and chalcedonies are more or less porous, and by utilizing this property it has been found possible to color them artificially. They are boiled in a sugar solution which is absorbed in different proportions by the layers of agate. The agates are then soaked in sulfuric acid, which chars the sugar and thus colors the layers brown and yellow.

Pure **silicon dioxid** in all its forms is a colorless solid, insoluble in water and most acids, the exception being hydrofluoric acid, which acts on it with the formation of water and silicon fluorid:

$$\mathbf{SiO_2} + 4\,HF \rightarrow 2\,H_2O + \mathit{SiF_4}$$

It is somewhat soluble in alkaline water especially when heated and under pressure, and hence occurs in many hot springs, around whose outlets it often forms large deposits as the water cools and evaporates. Yellowstone National Park is famous for its beautifully colored formations of this character.

By the use of an oxygen blast or electric furnace, silica may be melted and fashioned into tubes, dishes, flasks, and other laboratory apparatus. This ware is very durable; for it does not soften in a

Bunsen flame and does not crack even though plunged into water when white-hot. This last result is due to the fact that silica practically does not expand when heated. It is unequal expansion and contraction which causes glass and similar materials to crack when suddenly heated or cooled.

Silicic acids. As carbon is the prevailing element in the organic world because of the many compounds which it forms with hydrogen, oxygen and other elements, so silicon is the principal element in the inorganic world because of the number and variety of silicon compounds and their great abundance. Silicon dioxid is the anhydrid of all the acids of silicon. Of these a number apparently exist, for salts of several different acids of silicon are found in nature. The following are typical:

Mineral	Formula	Acid	Name	How Formed
Olivine	$MgFeSiO_4$	H_4SiO_4	Orthosilicic acid	$H_4SiO_4 - 0\,H_2O$
Mica	$KH_2Al_3(SiO_4)_3$	H_4SiO_4	Orthosilicic acid	$H_4SiO_4 - 0\,H_2O$
Pyroxene	$MgSiO_3$	H_2SiO_3	Metasilicic acid	$H_4SiO_4 - 1\,H_2O$
Serpentine	$Mg_3Si_2O_7$	$H_6Si_2O_7$	Disilicic acid	$2\,H_4SiO_4 - 1\,H_2O$
Feldspar	$KAlSi_3O_8$	$H_4Si_3O_8$	Trisilicic acid	$3\,H_4SiO_4 - 4\,H_2O$

Although these salts are well known, when the attempt is made to prepare the acids corresponding to them, nothing of definite composition results. The silicic acids are unstable and lose water, and nothing of a constant composition can be obtained except SiO_2. When a solution containing **silicates** is treated with acids, a clear jelly or an opaque, gelatinous mass may be formed, and finally a white powder, SiO_2, as the mass is heated. The acids of silicon are among the weakest acids known. They do not taste sour or turn litmus red. They dissociate so little that comparatively few ionic reactions of silicates are known.

Sodium and potassium silicates are soluble and each separates from solution as a glassy mass. Hence each is called "*water glass.*" Salts of other metals are insoluble. Silicates of aluminum, iron, calcium, magnesium, sodium, and potassium form the common rocks and constitute the largest part of the earth's crust so far as we know anything about it.

Common rocks and minerals. *A mineral is any naturally occurring substance having a definite composition.* A *rock* may consist of a mixture of minerals and need not have a definite composition.

Granite is a more or less coarse mixture of quartz, feldspar, mica, and pyroxene. *Basalt* and *porphyry* are rocks formed of the same minerals, but the components are more finely divided and less readily distinguishable by the eye. Both are formed by fusion; basalt cooled quickly, forming small crystals; granite more slowly, giving rise to larger crystals. A large part of all igneous rock has a composition similar to granite and basalt.

Weathering. By the action of water, frost, plant roots, and carbon dioxid, these rocks are broken up into fragments which are washed down into the streams. The particles of quartz are larger and heavier and are deposited soonest by the water, forming *sand*, which, subjected to the action of pressure and water containing silica, is cemented together, forming *sandstone*, one of the commonest building stones. The feldspar is decomposed by carbonic acid into potassium carbonate, K_2CO_3, a part of the silica separates out, and *kaolin*, $H_2Al_2(SiO_4)_2 \cdot H_2O$, is formed. The latter is very finely divided, and when deposited by water becomes mixed with other substances forming first *clays*, then *slates* and *schists*.

Soil consists of decomposed rock. Underlying any field is solid rock (Fig. 63), above this, partly broken and decomposed rock, and finally the soil, consisting of clay and sand mixed with partly decayed vegetable material called *humus.* Clay is very finely divided, packs close, and does not let water pass through it readily. Sand does not pack and is readily permeable by water. An ideal soil for any plant may be made by mixing sand, clay, and humus in the proper proportions. *Loam* is a mixture of sand and clay in proportions well suited to plant growth.

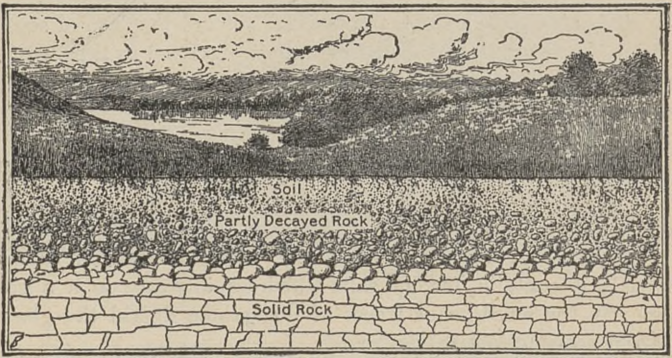


FIG. 63.

Glass is a mixture of calcium silicate with sodium or potassium silicate, having approximately the composition $CaSi_3O_7 . Na_2Si_3O_7$. It is formed by heating a mixture of sand, limestone ($CaCO_3$), and sodium sulfate (or carbonate) to a high temperature, when the following reaction takes place:

$$CaCO_3 + Na_2SO_4 + 6\,SiO_2 \rightarrow CaSi_3O_7 . Na_2Si_3O_7 + CO_2 + SO_3$$

The volatility of carbon dioxid and sulfur trioxid at high temperatures causes this reaction to take place and run to completion. The formation of igneous rocks by volcanic action or in other ways is a similar reaction. At ordinary temperatures, when a silicate is treated with sulfuric acid, or carbonic acid, it is slowly decomposed and the reaction goes the other way.

1. *Crown glass* consists of sodium and calcium silicates in the proportions indicated by the formula in the preceding equation. It softens at a much lower temperature than Bohemian glass, and for this reason is called *soft glass.* It is used for window and plate glass, but, being appreciably soluble in hot water, acids, and alkalis, it is not used for chemical apparatus.

2. *Bohemian glass* contains potassium silicate in place of sodium silicate. It softens less readily than crown glass and so is called *hard glass.* A variety is Jena glass. It is attacked but little by reagents and finds its chief use in laboratory glassware.

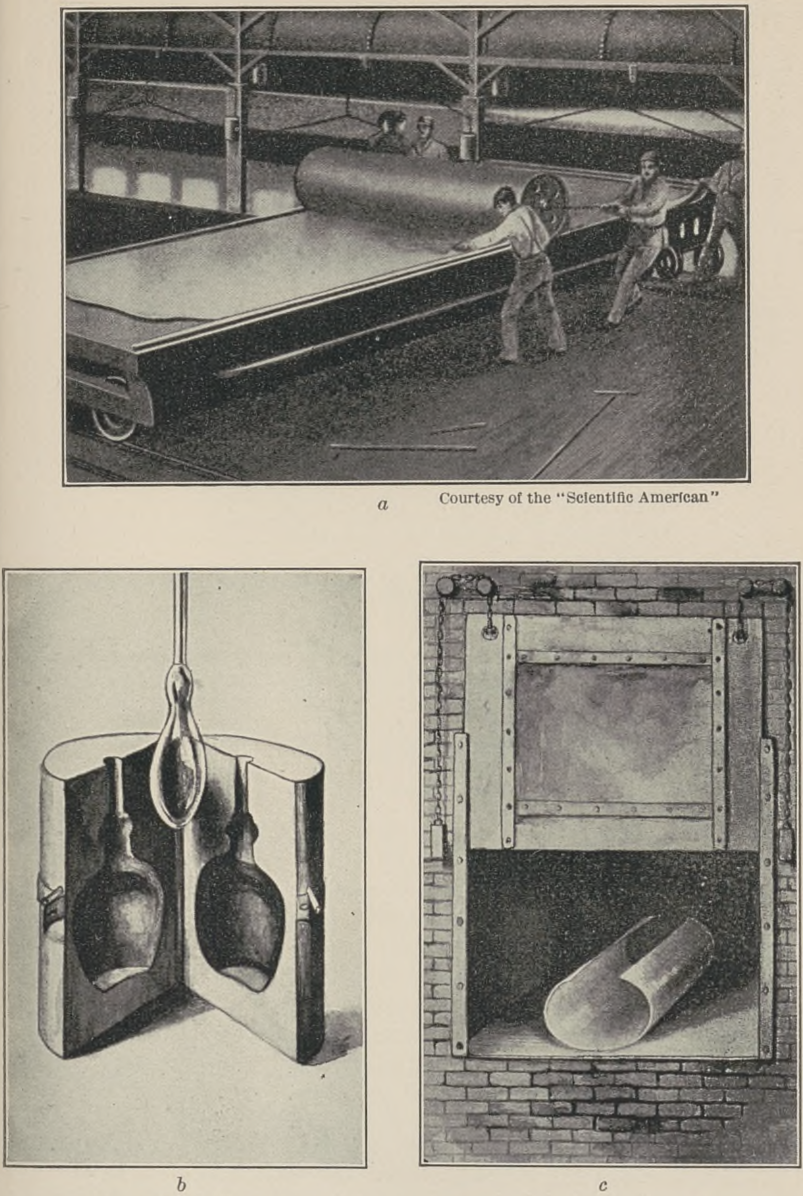
3. *Flint glass* consists of silicates of lead and potassium. It is softer, fuses readily, and is attacked by reagents considerably; but its brilliancy makes it valuable for cut glass, optical goods, and artificial gems.

4. *Bottle glass* is impure crown glass. Being made from common materials, it contains ferrous salts which usually give to it a green color. By the addition of traces of manganese dioxid the glass is rendered nearly colorless.

Glass owes its usefulness to a combination of three qualities: it is colorless and transparent; it is little soluble in water; when heated, it softens gradually like wax to a plastic mass that may be worked into any desired shape.

Glassware. In the manufacture of glassware, a mass of viscous material is removed from the melting pot on the end of a tube and then "blown" by the breath or compressed air into any desired shape. In making bottles the portion of glass on the tube is placed inside a mold and then blown into shape (*b*, Fig. 64). *Window glass* is blown into a large bubble, which by swinging is elongated into a cylinder. The ends are removed, the cylinder is cut open lengthwise, and, while heated in an oven (*c*, Fig. 64), the glass is spread out flat. *Plate glass* is poured onto a large table and rolled out into the desired thickness by heated rollers (*a*, Fig. 64). After cooling, both surfaces are ground down and polished. *Cut glass* is molded into shape, the design cut on by an emery wheel, and the whole finally polished. *Enamel* is an easily fusible glass, usually containing tin or lead oxid, and borax.

Glass is very brittle unless it is *annealed* by being allowed to cool slowly. The so-called "toughened glass" is made by heating ordinary glass very hot and then plunging it into hot oil. The surface of this glass is very hard, but if it is scratched, the object is liable to fly to pieces.



Courtesy of the "Scientific American"

Fig. 64. — The Manufacture of Glass

(a) Rolling out plate glass.
(b) Blowing a glass bottle.

Hydrofluoric acid dissolves all varieties of glass, forming fluorids, as the equation shows. (See p. 230).

$$Na_2Si_3O_7 \cdot CaSi_3O_7 + 28\,HF \longrightarrow 2\,NaF + CaF_2 + 6\,SiF_4 + 14\,H_2O$$

Silicon fluorid, SiF_4, is a heavy, pungent gas, fuming in the air. It is decomposed by water into silicic and hydrofluoric acids as the equation shows:

$$SiF_4 + 4\,HOH \longrightarrow 4\,HF + Si(OH)_4$$

Silicon carbid, SiC, or carborundum, is made by heating sand and coke in an electric furnace. The material is piled between walls of brick (*A*, Fig. 65) loosely laid together to contain the mass. Part way into the material carbon electrodes extend from the metal holders, *B*,*B*, which are connected with the dynamo, but the remainder of the distance the current traverses a layer of coke, the great resistance of which produces a very high temperature, causing the reaction to take place.

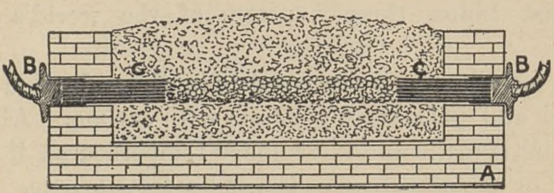


FIG. 65.

$$SiO_2 + 3\,C \longrightarrow SiC + 2\,CO$$

After the current has passed for several hours, the cooled mass is torn apart and steel-blue crystals obtained from the interior portions.

Carborundum is extremely hard and is used as a cutting agent or abrasive. It is manufactured into "grindstones," wheels, and the like by being powdered, sifted to uniform size, mixed with cement, pressed into shape, and baked. The finest powder is used for polishing.

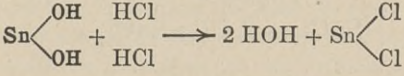
Other uses of silicon compounds. Water glass is used to preserve eggs, to fireproof cloth and wood, and in manufacturing ornamental building stone. It fills the pores of eggshells, thus preventing the access of bacteria and oxygen, both of which hasten decomposition of organic matter. Wood or cloth soaked in water glass takes on a thin coating of silicate which protects it from the air, thus hindering combustion. Some materials, such as gypsum, are too soft and porous to be satisfactory building materials. If the stone is soaked in water glass and then heated, it becomes hard and firm. By adding to the water glass salts of various metals, beautiful color effects resembling onyx are obtained.

TIN (Stannum, Sn — 119) has been known since very early times. The great tin mines of Cornwall, England, were worked in the time of Julius Cæsar, and to gain possession of them was one of the reasons why the Romans thought it worth while to conquer Britain. These mines are producing today. The only tin ore, *tinstone* or *cassiterite*, SnO_2, is found in but few other localities. From the East Indies three quarters of the world's supply comes.

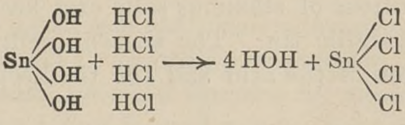
The metallurgy of tin consists in the reduction of the purified and pulverized tinstone with carbon. Although the metal is malleable at ordinary temperatures, if heated to 200° or cooled below – 40°, it becomes brittle. In the second case the change is due to the formation of an allotropic form known as amorphous or gray tin, the transition point between the brittle modification and the malleable form being 20°. It is possible that a third modification is formed above 200°.

Tin is a soft, silver-white metal that melts at 233°. It is not acted on by air or water at ordinary temperatures. For this reason it is used mainly as a covering for other metals. *Tin plate* is sheet iron covered with metallic tin, so that the strength of the iron is combined with the durability of the tin. Tin alloys are useful also. *Solder* is an alloy with usually an equal amount of lead. *Bronze* is an alloy of tin and copper and often other metals. It is very hard and tough and has generally been the first metallic substance used by early man in place of his stone implements. *Britannia metal* contains tin and antimony.

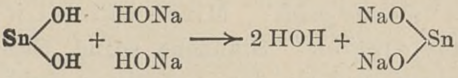
Compounds. Tin forms with oxygen stannous oxid, SnO, and stannic oxid, SnO_2, which resemble in formula carbon monoxid and carbon dioxid. Corresponding to these oxids of tin are the hydroxids, stannous hydroxid, $Sn(OH)_2$, and stannic hydroxid, $Sn(OH)_4$, or, when it has lost part of its water, $(HO)_2SnO$. In chemical compounds tin acts as a metal rather than a non-metal, and these oxids and hydroxids show more tendency to combine with acids to form salts of tin than to combine with bases to form compounds where tin plays the part of an acid-forming element. Nevertheless it may play either part, as the following equations indicate :



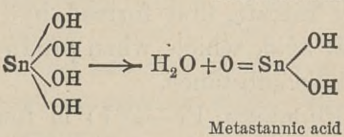
Stannous chlorid



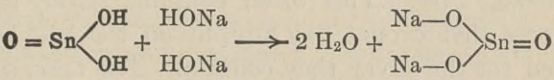
Stannic chlorid



Sodium stannite



Metastannic acid



Sodium stannate (meta)

In an analogous way the metal dissolves either in strong acids or in strong bases, as the equations indicate :

$Sn + H_2SO_4 \rightarrow H_2 + SnSO_4$ Stannous sulfate
$Sn + 2\ HONa \quad H_2 + (NaO)_2Sn$ Sodium stannite

Stannous chlorid, $SnCl_2 \cdot 2\,H_2O$, made by dissolving the metal in hydrochloric acid, is the most important tin salt. It is used in the dyeing industry and as a reducing agent, for it unites very readily with non-metallic elements and passes into the *stannic* condition. The oxygen of the air is sufficient to effect this change. The reaction may be written as the action of oxygen on hydrochloric acid, liberating chlorin, which then unites with stannous chlorid as the equations show:

$$\mathit{O} + 2\,\mathrm{HCl} \rightarrow 2\,\mathit{Cl} + \mathrm{H_2O}$$
$$\mathrm{SnCl_2} + 2\,\mathit{Cl} \rightarrow \mathrm{SnCl_4}$$

To prevent such oxidizing action it is necessary to add acid to solutions of stannous salts and keep them in contact with metallic tin. The nascent hydrogen liberated by the action of the acid and the tin keeps the solution reduced.

Stannic sulfid, SnS_2, is of a golden yellow color and is known as "*mosaic gold.*" Mixed with oil it is used as a gilding preparation. **Stannous sulfid, SnS,** is brown.

With nitric acid tin does not give a stable nitrate, for the stannic nitrate, first formed, hydrolizes and produces metastannic acid, which, when produced in this way, is a very insoluble substance.

LEAD (Plumbum, Pb—207) is found most commonly in *galena*, PbS. This often contains silver, and many lead ores that do not pay a profit on the lead alone are worked for the silver they contain. The main sources of lead in the United States are in the Rocky Mountain mining districts, where it is associated with silver, and in Illinois, Missouri, and neighboring states.

Lead compounds are easily reducible, and when fairly pure lead ores are used the processes are simple.

The galena is moderately heated in a furnace with access of air and thus oxidized partly to lead oxid and partly to lead sulfate.

$$2\,\mathrm{PbS} + 3\,O_2 \rightarrow 2\,\mathrm{PbO} + 2\,SO_2$$
$$\mathrm{PbS} + 2\,O_2 \rightarrow \mathrm{PbSO_4}$$

As soon as the oxidation is about half completed, the supply of air is shut off and the temperature of the furnace is raised. Under these conditions the unaltered lead sulfid acts on the oxid and sulfate, forming sulfur dioxid and metallic lead.

$$\mathrm{PbS} + 2\,\mathrm{PbO} \rightarrow 3\,\mathrm{Pb} + SO_2$$
$$\mathrm{PbS} + \mathrm{PbSO_4} \rightarrow 2\,\mathrm{Pb} + 2\,SO_2$$

Another process consists in heating the lead ore with metallic iron, which combines with the sulfur and leaves the lead in the free state. The lead ore may also be roasted to the oxid, which is then reduced with charcoal in the usual way.

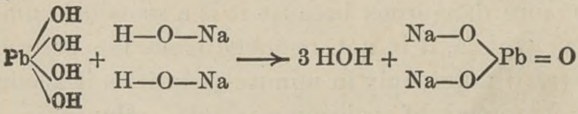
Properties. Lead is a soft, heavy, bluish-white metal, which melts at 327°. A freshly cut surface has a bright luster which soon becomes dimmed by oxidation. The metal cannot be drawn into wire, as it lacks tenacity, but it is very malleable and may be rolled into sheets, in which form it is largely employed. Lead, heated nearly to its melting point, is pressed through ring-shaped openings, thus making seamless water pipes. The metal is also used in storage batteries. When alloyed with a small proportion of arsenic, lead becomes harder and more fusible. This alloy is used in making shot. *Type metal* is an alloy of lead with antimony.

Lead and its compounds are poisonous, and its action is the more dangerous because it is a so-called cumulative poison; that is, it is not removed from the body readily, and even if taken only in minute quantities it accumulates until symptoms of poisoning result. Hence its use in water pipes may be a source of danger. Pure water has little or no effect on lead, but air and water together corrode it slowly, forming lead hydroxid, which is somewhat soluble. This process is hastened by the presence of ammonium salts such as often occur in drinking water, but is hindered or entirely prevented by carbonates or sulfates, which form coatings of insoluble carbonate or sulfate of lead. Lead poisoning is often called *saturnine poisoning*, for lead was by the ancients considered sacred to Saturn.

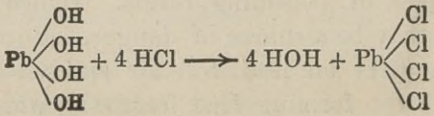
Oxids. In chemical conduct lead closely resembles tin. When it is heated in the air at not too high a temperature, it is converted into lead oxid, PbO. This is a yellow powder commonly called *litharge*, largely used in the preparation of glass, paints, and lead salts. Under proper conditions a brown oxid, PbO_2, may be obtained. It is used as an oxidizing agent in match heads, for it parts with half its oxygen rather readily. Another oxid of lead, Pb_3O_4, known as *red lead* or *minium*, is prepared by heating litharge in air. It is used in paint.

To the two oxids, PbO and PbO_2, correspond the hydroxids $Pb(OH)_2$ and $Pb(OH)_4$ or, after it has lost the elements of water, $(HO)_2PbO$. In properties as well as in composition these compounds of lead suggest the analogous compounds of other members of this group, especially those of tin. In both valences lead, like tin, acts both as an acid-former and as a base-former.

The tetravalent oxid and hydroxid dissolve in alkalis to form *plumbates* or salts of *plumbic acid*. Under proper conditions they dissolve in acids also, giving rise to a series of unstable salts in which lead is acting as a metal. The following equations illustrate typical reactions:



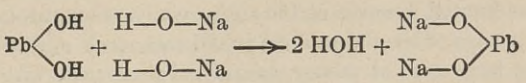
$$\mathrm{Pb}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix} + \begin{matrix}\mathrm{H{-}O{-}Na}\\ \mathrm{H{-}O{-}Na}\end{matrix} \longrightarrow 3\,\mathrm{HOH} + \begin{matrix}\mathrm{Na{-}O}\\ \mathrm{Na{-}O}\end{matrix}{>}\mathrm{Pb} = \mathrm{O}$$

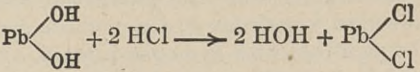


$$\mathrm{Pb}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix} + 4\,\mathrm{HCl} \longrightarrow 4\,\mathrm{HOH} + \mathrm{Pb}{<}\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{matrix}$$

Tetravalent compounds of lead are generally unstable and tend to break down into the divalent form.

The divalent hydroxid or oxid of lead is soluble in bases, forming *plumbites* or salts of *plumbous acid*, and dissolves in acids as well, forming a series of stable lead salts. The equations illustrate typical reactions:





The ordinary **lead compounds** are those in which lead is acting as a divalent metal. Salts of this character are generally insoluble, the common exceptions being the nitrate and the acetate. Lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$, is a colorless substance with a sweet taste. It is known as *sugar of lead.* Nitric acid is the only common acid readily dissolving lead.

Lead paints. When lead is exposed to the air, oxygen and water first form the hydroxid, which is later converted into carbonate. The product is not usually a normal salt, but rather a basic carbonate, $Pb_3(OH)_2(CO_3)_2$, in which a part of the lead hydroxid is not neutralized by carbonic acid. Under the name of *white lead* it is extensively used in the paint industry, and is made on the large scale by exposing lead to the action of carbon dioxid, dilute acetic acid or vinegar being used as a catalyzer.

Lead sulfate, $PbSO_4$, is an insoluble white substance also used as a pigment. Commercially it is made by roasting galena at a very high temperature, when a basic lead sulfate, Pb_2OSO_4, sublimes. It is known as "*sublimed white lead.*"

Lead chromate, $PbCrO_4$, is made by adding a solution of a chromate to a solution of a lead salt. It is deep yellow and is much used as a pigment under the name of *chrome yellow*. Chrome orange is a basic lead chromate, Pb_2OCrO_4.

Lead paints gradually turn dark, owing to the formation of *lead sulfid*, PbS, which is black like galena. Sulfur compounds are present in the air in small quantities wherever soft coal, oil, gas, or tallow candles are burned, because of the sulfur which these substances contain. Paintings of the old masters in old cathedrals darkened in this way, and a large sum of money was offered to any one who could restore them to their original colors. A young man won the prize by applying his chemical knowledge to the problem before him. He washed over the paintings with hydrogen peroxid, converting black lead sulfid into white lead sulfate, thus brightening them materially.

Some of the most important properties of the elements belonging to the carbon group are set down in tabular form.

THE CARBON GROUP

	CARBON	SILICON	TIN	LEAD
React. wt.	12	28	119	207
Melt. pt.	3500?	1200	233	327
State	solid	solid	solid	solid
Boil. pt.	3500?	2500?	1600	1500
Valences	2,4	2,4	2,4	2,4
Hyd. comp.	CH_4	SiH_4	*	*
Oxids	CO CO_2	SiO SiO_2	SnO SnO_2	PbO PbO_2
Hydroxids	$(HO)_2CO$	$(HO)_2SiO$	$(HO)_2Sn$ $(HO)_2SnO$	$(HO)_2Pb$ $(HO)_2PbO$
Character	weak acid	weak acid	weak base or weak acid	weak base or weak acid

* The simple compounds, SnH_4 and PbH_4, are unknown; but derivatives of them, $Sn(CH_3)_4$ and $Pb(CH_3)_4$, are known.

SUMMARY

SILICON is found in nature in silica and silicates. It is the most important element in minerals, and in many of its compounds suggests carbon.

Silicon dioxid, SiO_2, *silica*, is often found crystallized as quartz, and amorphous, as flint, agate, etc. It makes up the largest part of sand, and is extensively found in other ways. It is a colorless, insoluble solid that is not easily acted on by any common substances except hydrofluoric acid and molten alkalis.

Silicic acids as known in their salts are of several different forms. The acid H_2SiO_3 corresponds to carbonic acid, H_2CO_3. The silicates form many rocks. They are not generally acted on by water and other substances, except after long intervals of time, in which case "weathering" of rocks is the result. Soil is formed of decomposed rock mainly. It consists of clay, sand, and partially decomposed vegetable matter called humus.

Glass is a mixture of calcium or lead silicate with potassium or sodium silicate. According to its composition it may be classified as crown, Bohemian, flint, and bottle glass. It is useful because it is colorless and transparent, softens when heated, and is little soluble in ordinary reagents.

TIN is found in *cassiterite* or *tinstone*, SnO_2, which is reduced by hot charcoal. Tin is a white, crystalline metal used mostly in its alloys, as solder and bronze, and as a covering for other metals, as in tin plate. Chemically it is both metal and non-metal.

LEAD is found principally in *galena*, PbS, from which it is obtained by a roasting process. It is a soft, bluish white metal, used in sheet form, in pipes, and in alloys. It is not attacked by acids as easily as other common metals. Its oxids are *litharge*, PbO; *minium*, Pb_3O_4; and the peroxid, PbO_2. Important salts are the acetate, called *sugar of lead;* the carbonate and sulfate, used as *white lead:* and the chromate, *chrome yellow.* Chemically lead resembles tin.

QUESTIONS

1. Compare the composition, manner of formation, and properties of the oxids of carbon, silicon, tin, and lead so far as you have been informed concerning them.

2. How is such a weak acid as H_2CO_3 able to decompose such stable compounds as the silicates, as when weathering of rocks takes place?

3. How much metal should be obtained from 1 ton of "tin stone" if this ore runs 90 % pure?

4. What important changes would be noticed in our daily life if tin were to cease to exist; if lead should cease to exist?

5. Is there any lead in a "lead pencil"? Look up the origin of the name.

6. A certain ore runs 90 % of galena. Calculate the amount of lead that should be obtained from a ton of this ore.

7. Why should not a laboratory room be painted with white lead? What pigment might be used? (See p. 324.)

8. Write equations showing the action of (*a*) bromin water on stannous chlorid; (*b*) nascent hydrogen on stannic chlorid. How could you make nascent hydrogen and how must it be used?

9. White lead is sometimes mixed with barium sulfate. How could you detect this adulteration?

10. What is a mineral? Are the following substances minerals (*a*) quartz; (*b*) water; (*c*) granite; (*d*) mercury; (*e*) soil; (*f*) coal oil?

CHAPTER XXV

THE BORON-ALUMINUM GROUP

The group. Boron and aluminum are the only common elements in this group, the other members, *scandium* (Sc — 44), *gallium* (Ga — 70), *yttrium* (Y — 89), *indium* (In — 115), *lanthanum* (La — 139), and *thallium* (Tl — 204), all being very rare elements. Boron is a weak acid-former; the members of this group possessing higher reacting weights are base-formers; aluminum acts in both ways. All show a characteristic valence of 3.

BORON (B — 11) does not occur in nature in the free condition, but is found mainly in *tincal*, or native borax, $Na_2B_4O_7 \cdot 10\ H_2O$, large deposits of which occur near Death Valley, California. Magnesium and calcium borates also occur.

The element may be obtained by the reduction of its oxid, which, being very stable, like silicon dioxid, requires the use of metallic sodium, magnesium, or aluminum. Two allotropic forms are known. Amorphous boron is a chestnut-brown powder. Crystallized boron is a colorless, hard, transparent substance. When heated in air, the element burns to the trioxid, and may also unite with nitrogen to form a nitrid, BN.

Boric acid. Corresponding to the oxid, B_2O_3, is the hydroxid, $B(OH)_3$, which possesses slight acid properties and is called *boric* or *boracic acid.* On heating, boric acid loses water and is converted into *metaboric acid*, HBO_2. Further heating yields *tetraboric acid*, $H_2B_4O_7$, and finally the anhydrid, B_2O_3, as the following equations show:

$$B(OH)_3 \rightarrow H_2O + HBO_2$$

$$4\ HBO_2 \rightarrow H_2O + H_2B_4O_7$$

$$H_2B_4O_7 \rightarrow H_2O + 2\ B_2O_3.$$

All the boric acids are very weak, dissociating so little that a saturated solution possesses only a slight acid taste and colors litmus but slowly. Borates are generally insoluble, salts of the alkali metals being the only exceptions. Boron imparts a green color to a Bunsen flame.

Borax, $Na_2B_4O_7 . 10\,H_2O$, *is the most important boron compound.* Since the difference in composition between boric and tetraboric acid is simply a difference in the proportions of water and acid anhydrid in the composition of each, borax is readily obtained from boric acid and *vice versa.* Both reactions are carried out commercially.

$$Na_2B_4O_7 + H_2SO_4 + 5\,H_2O \rightarrow Na_2SO_4 + 4\,B(OH)_3$$
$$4\,B(OH)_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + CO_2 + 6\,H_2O$$

Uses. Borax or other salts of boric acid are important constituents of enamels, ordinary bath tub enamel being tin metaborate. Another important use of borax is in softening water for laundry purposes, a result accomplished by precipitating the calcium and magnesium ions as insoluble borates.

Molten borax and boric oxid have the power of combining with metallic oxids, thus converting substances which often are almost infusible and insoluble into metaborates which are readily fusible and soluble, at least in acids. Such a substance is called a *flux.* In obtaining metals from their ores, a flux is often added to make the whole mass fusible and thus aid the process.

Metaborates are often intensely colored, and by fusing with borax, tests for compounds of certain metals may be obtained, the color produced indicating whether the substance is present or not.

ALUMINUM (Al—27) receives its name from *alum*, one of its compounds known long before the element itself was isolated. Next after oxygen and silicon it is the most abundant of the elements. In company with other elements it unites with the silicic acids to form a great number of compounds which occur in common rocks (pp. 289 and 290). Aluminum is also found in *corundum*, Al_2O_3, and *bauxite*, $Al_2O(OH)_4$. In Greenland there are large deposits of *cryolite*, Na_3AlF_6.

Because of the many uses to which the metal could be put if its price were lower, numerous but unavailing efforts have been made to utilize clay and other common aluminum compounds in the commercial preparation of the element; but aluminum compounds are very firmly held together, and all ordinary and cheap reducing agents fail of the desired end. The production of aluminum at a cost that will permit its use in everyday life is an important problem.

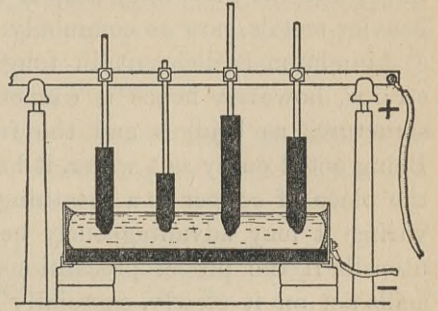


FIG. 66.

Preparation. The metal was formerly obtained by the reduction of aluminum chlorid by metallic sodium. This method is now superseded by the cheaper electrolytic process. Bauxite is heated to drive off its water and is thus converted into the oxid, Al_2O_3. This is dissolved in melted cryolite and a heavy current of electricity is passed through the mixture, which is contained in large iron receivers (Fig. 66). Aluminum oxid, rather than cryolite, is decomposed. The receiver is made the negative pole and the metal is deposited in it. Being heavier than cryolite, the molten metal sinks to the bottom of the box and may be drawn off. The positive pole consists of rods of carbon dipping into the molten mixture. The oxygen going to the positive pole unites with the carbon, forming carbon monoxid, which burns about the electrodes. The glowing receivers and flickering blue flames make an aluminum manufactory a most interesting spectacle at night.

Properties. Aluminum is a light, white metal, malleable, ductile, and capable of assuming a bright polish. In large pieces it is acted on by air and water only slowly, for a coating of insoluble oxid or hydroxid is formed which prevents further action. The facts that aluminum does not rust in the air and is so much lighter than other metals possessing desirable properties, have aroused much interest in the possibility that it may replace some of the heavier metals, now so commonly used.

Aluminum is deficient in toughness and resistance to strains, however, hence it cannot displace steel in such structures as bridges and the framework of buildings. Being acted on by salt water, it has thus far failed to take the place of copper as a sheathing for ships. In electric wiring it may advantageously be used, and for cooking utensils if the proper precautions are taken. Vegetable acids act on it slowly, especially in the presence of air or sodium chlorid. Hence it is best not to polish aluminum dishes, lest the protective coating of oxid be removed.

Many of its defects are removed by alloying aluminum with other metals, and it is probable that in this way it will find its chief application. The cost of obtaining the metal (at present about 20 cents a pound) has thus far been one of the chief obstacles to its employment.

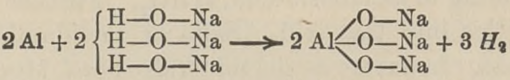
Though ordinarily stable in air, at high temperatures aluminum burns readily to the oxid, especially if the metal is finely divided. During the reaction a large amount of heat is liberated. The great heat of combustion of aluminum is utilized for the production of high temperatures by mixing powdered aluminum with ferric oxid or other oxids. When the mixture is ignited, a vigorous reaction takes place according to the equation:

$$2\,\mathrm{Al} + \mathrm{Fe_2O_3} \rightarrow \mathrm{Al_2O_3} + 2\,\mathrm{Fe}$$

Temperatures as high as 3500° may be obtained with this mixture, which is known as *thermit*, or the *Goldschmidt mixture.*

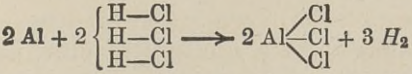
The Goldschmidt mixture is used in welding heavy iron and steel work. Thermit ignited in a crucible, produces a mass of iron which is run into a mold previously built around the two ends which are to be welded. The liquid iron is so hot that the solid iron softens sufficiently to produce a firm joint. Fig. 67 *a* shows the process in operation welding steel rails together and *b* shows the weld produced on a steel car truck. The excess of metal shown in the latter picture is afterwards cut away. A broken engine frame, drive wheel, or shaft is frequently mended without taking the machine apart.

In **chemical character** the element acts as both acid-former and base-former, dissolving in both alkalis and acids as the equations show:



$$2\,\mathrm{Al} + 2\left\{\begin{array}{l}\mathrm{H{-}O{-}Na}\\ \mathrm{H{-}O{-}Na}\\ \mathrm{H{-}O{-}Na}\end{array}\right. \longrightarrow 2\,\mathrm{Al}\left<\begin{array}{l}\mathrm{O{-}Na}\\ \mathrm{O{-}Na}\\ \mathrm{O{-}Na}\end{array}\right. + 3\,H_2$$

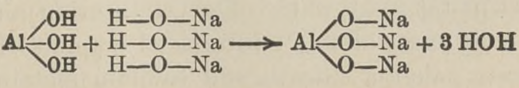
Sodium aluminate



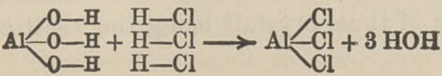
$$2\,\mathrm{Al} + 2\left\{\begin{array}{l}\mathrm{H{-}Cl}\\ \mathrm{H{-}Cl}\\ \mathrm{H{-}Cl}\end{array}\right. \longrightarrow 2\,\mathrm{Al}\left<\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{array}\right. + 3\,H_2$$

Aluminum chlorid

In an analogous way aluminum hydroxid acts as an acid in the presence of a base, and in the presence of an acid it acts as a base, dissolving in either reagent as the equations indicate:



$$\mathrm{Al}\left<\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{array}\right. + \begin{array}{l}\mathrm{H{-}O{-}Na}\\ \mathrm{H{-}O{-}Na}\\ \mathrm{H{-}O{-}Na}\end{array} \longrightarrow \mathrm{Al}\left<\begin{array}{l}\mathrm{O{-}Na}\\ \mathrm{O{-}Na}\\ \mathrm{O{-}Na}\end{array}\right. + 3\,\mathrm{HOH}$$

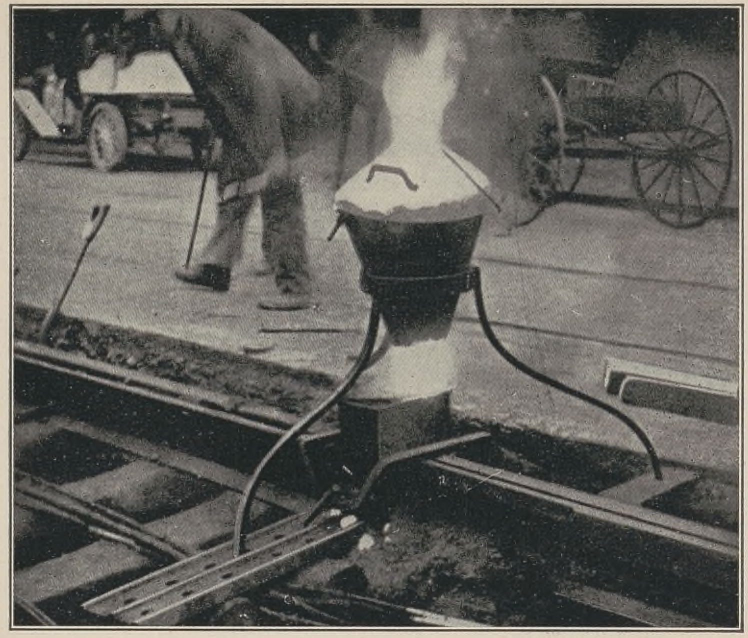


$$\mathrm{Al}\left<\begin{array}{l}\mathrm{O{-}H}\\ \mathrm{O{-}H}\\ \mathrm{O{-}H}\end{array}\right. + \begin{array}{l}\mathrm{H{-}Cl}\\ \mathrm{H{-}Cl}\\ \mathrm{H{-}Cl}\end{array} \longrightarrow \mathrm{Al}\left<\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{array}\right. + 3\,\mathrm{HOH}$$

Aluminum oxid, Al_2O_3, occurs in nature as the mineral *corundum*, which when pure is colorless, but it may be yellow, brown, or black, owing to impurities. Being very hard, under the name of *emery* it is used as a grinding and polishing agent. *Ruby* is transparent corundum colored by traces of chromium oxid, and *sapphire* is corundum tinged blue by cobalt oxid. Artificial emery, called *alundum*, is made by heating to very high temperatures the minerals hydrargyllite, $Al(OH)_3$, bauxite, $Al_2O(OH)_4$, or diaspore, $AlO(OH)$, all of which decompose and yield the oxid. Rubies and sapphires are manufactured in the same way from pure oxid, traces of chromium or cobalt oxid being added. They can scarcely be distinguished from the natural gems.

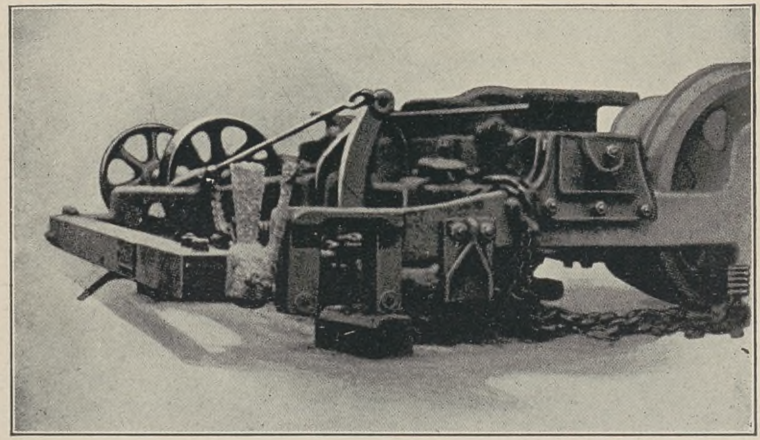
Aluminum hydroxid, $Al(OH)_3$, may be prepared as an insoluble, gelatinous substance by adding a solution of a hydroxid to a solution of an aluminum salt. On heating, it loses water and is converted into the compound $HAlO_2$, corresponding to metaboric acid, HBO_2. Further heating converts this into the oxid. Salts of metaluminic acid, $HAlO_2$, occur in nature as the minerals *spinel*, $Mg(AlO_2)_2$, and *chrysoberyl*, $Be(AlO_2)_2$, both of which are used as gems.

Cement is made from a mixture of clay, *i.e.* aluminum silicate, and limestone, $CaCO_3$, in such proportions that the final product has the composition: CaO, 60 – 65 %; Al_2O_3, 10 – 15 %; and SiO_2, 20 – 25 %. The limestone and clay are powdered, mixed, and heated together, and the resulting "clinker," again finely ground, is cement. When wet, it takes up water of crystallization and there results a solid mass of finely interlaced crystals of aluminum silicate, calcium silicate, and calcium metaluminate, the formation of these crystals being the "setting" of the cement.



a

Courtesy of the Thermit Co.



b

Courtesy of the Thermit Co.

Fig. 67.—Thermit in the Industries

(*a*) Welding steel rails; "pouring the charge."

(*b*) Steel car truck mended with thermit. The excess of metal shown in the picture is afterwards cut away.

Alum. If solutions of potassium sulfate and aluminum sulfate are mixed, none of the ordinary indications that a chemical change has taken place are noticed. The mixed solutions give all the reactions for aluminum, potassium, and sulfates. That is, all the ordinary ions are present; aluminum, $\overset{+++}{Al}$, potassium, $\overset{+}{K}$, and sulfate, $\overset{=}{SO_4}$. If the solution is evaporated, crystals are deposited, not of potassium and aluminum sulfates separately, but of one substance having the composition $KAl(SO_4)_2 \cdot 12\,H_2O$. Such a substance is often called a *double salt*, but there is no more significance to this term than there would be in calling sulfuric acid a double oxid because it may be formed by the union of the oxids of sulfur and hydrogen; or limestone, $CaCO_3$, a double oxid because it is formed by the union of calcium oxid, CaO, and carbon dioxid. Chemical combination takes place in all such cases. In the formation of alum and other so-called double salts, union does not take place in dilute solution, but only when the solution nears the point of saturation.

Alum is a white substance with a slightly sour, astringent taste. When heated, it loses its water and forms a substance with very different properties, known as *burnt alum.* Only slowly does burnt alum take up water and become alum again.

Just as we have seen that sulfur may replace oxygen in the formation of thiosulfates and similar substances, so the potassium in alum may be substituted by similar univalent elements such as sodium, lithium, rubidium, cæsium, silver, copper, and the ammonium radical. Furthermore, the aluminum may be replaced by other weakly-basic trivalent elements such as iron, chromium, and manganese. The sulfur may be replaced also by selenium and tellurium. From this a whole series of bodies result, all of which have the same crystal form, the same amount of "water of crystallization," and much the same properties. They are all called *alums.* The formulas for some of the commoner alums follow.

$KAl(SO_4)_2 \cdot 12\ H_2O$	Potash alum
$NH_4Al(SO_4)_2 \cdot 12\ H_2O$	Ammonia alum
$KFe(SO_4)_2 \cdot 12\ H_2O$	Potash iron alum
$NH_4Fe(SO_4)_2 \cdot 12\ H_2O$	Ammonia iron alum
$KCr(SO_4)_2 \cdot 12\ H_2O$	Potash chrome alum

Dyes and Mordants. Since aluminum is a very weak base-forming element, its salts hydrolize considerably. Especially is this true of aluminum acetate, for acetic acid is a weak acid. Hydrolysis of this salt gives rise to aluminum hydroxid, particularly on heating, as the equation indicates:

$$Al(C_2H_3O_2)_3 + 3\ HOH \rightarrow \mathbf{Al(OH)_3} + 3\ H(C_2H_3O_2)$$

Advantage of this fact is taken in dyeing fabrics.

A *dye* is an intensely colored substance capable of being fixed on fabrics. Dyes are generally either weak acids or weak bases. The former unite with many metals, giving highly colored insoluble salts, and the latter combine with several organic acids to form compounds of similar character. These salts are known as *lakes* and are used as water-color pigments. The substance with which a dye unites in this way is called a *mordant.*

Fabrics of animal origin, such as silk and wool, are composed of substances which contain within their molecules both acid (-COOH) and basic ($-NH_2$) radicals. Dyes unite with these groups chemically and in this way become firmly fixed to the fabric. Vegetable materials, such as cotton, linen, etc., do not contain these radicals and dyes do not unite with them readily. Hence these goods are *mordanted;* that is, they are soaked in solutions of the acids or of the salts of the metals which are mordants. Salts that hydrolize readily are ordinarily used, for by running the goods over hot rollers it is possible to drive off the acid and leave the base deposited all through the fiber. With this an acid dye will unite, forming an insoluble, highly colored precipitate, or lake, all through the fabric, which gives much the same effect as if the vegetable material were itself colored. Salts of aluminum, tin, iron, lead, and many others are used as mordants, as well as tannic acid and other organic substances.

Ultramarine, a silicate of aluminum and sodium containing sulfur, is found in nature as *lapis lazuli*, valued for its splendid blue color. It is used extensively as a pigment and is now manufactured by heating together sand, aluminum oxid, sodium sulfate, and sulfur. The color of the artificial product is even brighter than that of the mineral. By varying treatment different colors are now produced, such as green, violet, and red.

Porcelain. *Kaolin* is hydrogen aluminum silicate $H_2Al_2(SiO_4)_2 \cdot H_2O$, formed by the decomposition of feldspar. When heated, kaolin does not melt, but forms a hard, porous mass. If it is mixed with some fusible silicate, such as feldspar, when heated the fused material penetrates the pores of the kaolin and yields a hard, semitransparent substance known as porcelain. This is the basis of the manufacture of all grades of porcelain, from the finest china to ordinary earthenware, which differ mainly in the purity of the materials used and the excellence of the workmanship.

For *fine china* the materials must be very pure, finely powdered, and thoroughly mixed. The mass is then worked up into the desired shapes, which are allowed to dry and are afterward baked in a kiln. The porcelain thus made is without a glaze. This is supplied by dipping the unglazed ware into water containing in suspension finely divided feldspar. On again heating in a kiln, the coating of feldspar melts, forming a transparent, glassy surface.

In *china painting* only such coloring matters can be used as are not injured by firing in the kiln, such as the oxids of cobalt, copper, iron, manganese, and other elements. These colors are mixed with a flux, and with them the desired design is painted on the porcelain. On heating, the flux melts and the colors are permanently attached to the ware.

Earthenware is made like porcelain, but impure materials are used and less care is taken. The glaze is usually applied when the first firing is nearly complete, by throwing into the kiln a small quantity of common salt. This is volatilized, and when the vapors come in contact with the pottery, by the aid of the water vapor present a fusible silicate of aluminum and sodium is formed that melts and gives the glaze. Sometimes lead oxide is used; this forms a fusible lead silicate glaze.

Bricks and porous ware are made by heating impure kaolin or clay unmixed with feldspar. The porous mass thus obtained is usually of a red color from the presence of iron compounds. Owing to impurities, common bricks are fusible at a high temperature. *Fire brick* is made of clay mixed with quartz (sand). *Vitrified brick* is heated until it begins to fuse, hence it is harder than ordinary brick.

SUMMARY

BORON occurs in boric acid, borax, and as magnesium and calcium borates. *Boric acid* is found in nature and may be prepared by the action of an acid on borax. It is used as an antiseptic and preservative, but chiefly in making *borax*, $Na_2B_4O_7 . 10\ H_2O$. The latter is the most important boron compound. It is used in "softening" water and is a constituent of many enamels.

ALUMINUM is found widely distributed in rocks such as *granites*, *clays*, *feldspars*, *micas*, and the like. It is prepared with difficulty, the usual method being the electrolysis of the oxids dissolved in molten cryolite. It is a light, white metal not appreciably corroded by the atmosphere, finding use both alone and in alloys. Chemically it acts both as base-former and as acid-former.

The **oxid**, Al_2O_3, is formed when the metal burns, a large amount of heat being liberated in the reaction. This is taken advantage of in the production of high temperatures by the *thermit* mixture. Aluminum oxid occurs naturally as *corundum*, *emery*, *ruby*, and *sapphire*.

The **hydroxid**, $Al(OH)_3$, is used as a mordant in dyeing, for it forms insoluble compounds with dyestuffs.

The **alums** are chemical compounds formed by the combination of the sulfate of aluminum or some similar trivalent metal with the sulfate of potassium or some other univalent metal.

The silicates are the most abundant aluminum compounds, being the commonest rock-forming minerals. *Cement* is formed by igniting a mixture of clay and calcium carbonate or limestone. *Ultramarine* occurs naturally as *lapis lazuli* and is also made artificially for use as a pigment. *Kaolin* is formed by the weathering of feldspar. When the decomposition products are mixed with foreign substances, clay results. *Porcelain* is made by mixing kaolin, feldspar, and water into paste, which is then moulded into shapes which are dried and fired. Earthenware, bricks, etc. are made of impure kaolin or clay.

DYES are highly colored substances capable of being fixed on fabrics. Most dyes are either weak acids or bases, and combine chemically with silk or wool to form salts; for animal fabrics contain both $-COOH$ and $-NH_2$ groups within their molecules. Vegetable fabrics, such as cotton or linen, do not contain these groups, hence many dyes do not unite with them readily. Such goods are *mordanted: i.e.*, soaked in solutions of (*a*) metallic salts with which acid dyes unite, or (*b*) weak acids with which basic dyes unite. In either case insoluble precipitates, known as *lakes*, are formed all through the fabric, giving it a color.

QUESTIONS

1. How much aluminum is contained in a mass of clay weighing one ton, considering the clay to be pure kaolin?

2. If aluminum is worth 30 cents a pound, how much would the aluminum in one ton of clay be worth? Why is not the clay worth as much as the aluminum?

3. How is aluminum obtained? Is the method of electrolysis used in decomposing the more stable or less stable compounds?

4. An iron pan weighs 8 pounds. If the iron were replaced by aluminum, bulk for bulk, what would be the saving in weight? (Take the specific gravity of aluminum as 2.5 and that of iron as 8.)

5. What care must be taken in using kitchen utensils made of aluminum?

6. How could you prove that alum contains aluminum; that it contains the sulfate radical?

7. Explain why alum has an acid reaction with litmus, while borax reacts alkaline.

8. Ordinary bauxite contains about 90 per cent. of $Al(OH)_3$. What weight of bauxite will be needed to produce 100 pounds of aluminum?

9. Do you think alum could be obtained from ordinary earth? Suggest a method by which this problem could be put to a practical test.

10. What other elements besides aluminum act either as acid-formers or base-formers?

11. If borax sells for 10 cents a pound, how much does it cost, when used as a flux, *i.e.* anhydrous.

12. If solutions of borax and nitric acid are mixed, what reaction will take place? Will it run to equilibrium or to completion? Why?

CHAPTER XXVI

THE CALCIUM-MAGNESIUM GROUP

The group. The elements belonging to this group are *beryllium*, *magnesium*, *calcium*, *zinc*, *strontium*, *cadmium*, *barium*, *mercury*, and *radium*. Some of these contribute much more to the welfare of man than others, and on this account are often said to be more important. With the exception of *radium* (Ra — 226), none of them can be considered as really rare. Beryllium and zinc may act as acid-formers as well as base-formers, but the other elements possess metallic properties only. All show prevailing valences of 2.

BERYLLIUM (Be — 9) occurs in nature as *beryl*, $Be_3Al_2(SiO_3)_6$, (see frontispiece) and as *chrysoberyl*, $Be(AlO_2)_2$, both of which are used as gems. Particularly clear specimens of beryl, when colored by chromium, are known as *emeralds*. Beryllium salts have a peculiar sweetish taste, and on this account the element was often called *glucinum*, from the Greek adjective meaning sweet. In chemical properties it most closely resembles magnesium, although it shows some resemblances to aluminum as well.

MAGNESIUM (Mg — 24) is widely distributed in nature, being found especially in *magnesite*, $MgCO_3$; *dolomite* $(CaMg)CO_3$;* and together with other metals forms many

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* The expression $(CaMg)CO_3$ means that the bivalent calcium may be partly replaced by bivalent magnesium, the two together always occurring in the right proportions to replace the two atoms of hydrogen in carbonic acid, H_2CO_3. Similarly, $(MgCa)SiO_3$ means that the magnesium may be partly replaced by calcium. As might be expected, this frequently occurs in nature in the formation of minerals.

of the complex silicates which enter into the composition of ordinary rocks. Compounds of this character are *asbestos*, $(MgCa)SiO_3$, and *talc*, $H_2Mg_3Si_4O_{12}$. All of these minerals are insoluble. Soluble compounds, such as the chlorid, $MgCl_2$, and the sulfate, $MgSO_4$, are found in sea water, in mineral water, and in salt beds.

Metallic magnesium is prepared by the electrolysis of *carnallite*, $KCl . Mg Cl_2 . 6 H_2O$, after it has been fused and the water driven off. In electrolyzing this material, metallic potassium does not separate until after all the magnesium has been obtained. It is usually found in commerce in the form of ribbon or powder, and is a light, silver-white metal. It is not altered in dry air, but in moist air it becomes covered with a film of oxid. It decomposes water in much the same way as sodium, except that the action is much slower. When heated in the air, it burns with an intense white light, and hence is used in signaling and in fireworks. As the light of burning magnesium is rich in chemically active rays, it is much used in photography in the form of ribbon, and in *flash-light* powders. These latter consist of the finely powdered metal and potassium chlorate. The mixture possesses the characteristics of an explosive, and should be handled as such.

Magnesium hydroxid, $Mg(OH)_2$, is a strong but quite insoluble base.

Magnesium oxid, MgO, known as *magnesia*, is quite generally used in suspension in water in preference to the hydroxid. It is very resistant to heat, hence is used as a lining for crucibles and other vessels subjected to high temperatures. A mixture of magnesium oxid and magnesium chlorid sets to a hard, firm mass, and is *magnesium cement.* Mixed with wood pulp and similar materials, it is used as artificial stone for floors, etc.

Magnesium chlorid, $MgCl_2 . 6 H_2O$, is a very deliquescent substance. It is present in table salt to a slight extent, causing it to cake in moist weather. It hydrolizes at the temperature of boiling water, forming magnesium hydroxid and hydrochloric acid. This action prevents the use of sea water for boiler purposes because the acid corrodes the boilers, pipes, and cylinders.

Magnesium sulfate, $MgSO_4 \cdot 7 H_2O$, is *Epsom salt*, so named because it is present in the water of the famous medicinal spring at Epsom, England.

Magnesium and its compounds closely resemble calcium and its compounds.

CALCIUM (Ca—40) is found in nature abundantly distributed in carbonates, sulfates, silicates, and phosphates. By reason of the number and value of its compounds, it is one of the most important of the elements.

Metallic calcium is obtained from its chlorid by electrolysis. It is similar to magnesium, but is more active chemically, decomposing water more readily. It is a strong base-former, and is always bivalent.

Calcium carbonate, $CaCO_3$, is the commonest compound of calcium. When amorphous, it is called *limestone*. This forms deposits of great extent and thickness. When subjected to pressure and moderate heat, it becomes finely crystalline, and is then known as *marble*. Large crystals are *calcite*, which, when very pure and transparent, are called *Iceland spar*. Another crystalline form is *aragonite*. Limestone is used as a building material, as a flux in the reduction of metals from their ores, and in the manufacture of lime. The skeletons and shells of invertebrate animals* are generally composed of calcium carbonate. Deposits of shells and corals, cemented together by the

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* The hard parts of insects, crabs, and similar animals, are composed of an organic substance like horn. It is called *chitin*.

action of sea water, are found in many localities. This rock is known as *coquina.* From this material the buildings of St. Augustine, Florida, are largely constructed.

Though insoluble in pure water, calcium carbonate dissolves to a considerable extent in water containing carbon dioxid in solution, owing to the formation of a soluble acid calcium carbonate, or calcium bicarbonate, $CaH_2(CO_3)_2$. As the atmosphere and the soil always contain carbon dioxid, natural water invariably contains more or less dissolved carbon dioxid. If the soil is underlaid by limestone deposits, the water trickles along cracks in the rock, enlarging them by slowly dissolving the calcium carbonate. In this way *caves* are formed.

Sometimes water containing calcium carbonate drips slowly from the roof of a cave. In this case there may gradually be formed a deposit of calcium carbonate, which hangs from the roof and is called a *stalactite.* Where the water falls on the floor of the cave, there is a similar deposit called a *stalagmite.* Stalactites are formed somewhat after the manner of icicles. (See Fig. 68).

Hard water. Water containing calcium or magnesium salts curdles a soap solution and makes washing difficult, and hence is called "hard" water. (See p. 219.)

In limestone regions hard water contains calcium bicarbonate. When this is heated, carbon dioxid is driven out and insoluble calcium carbonate is formed. Since boiling removes calcium bicarbonate from solution, the water no longer precipitates soap, and is said to be "soft." Hardness caused by the presence of calcium bicarbonate is said to be *temporary*, for it may be so easily removed by boiling.

In some regions the water contains calcium or magnesium sulfate in solution. This water, also, precipitates soap solution and so is hard. As the dissolved substances cannot be removed by boiling, the hardness is said to be

Courtesy of Seeley & Co.

FIG. 68. — INTERIOR OF A CAVE SHOWING STALACTITES AND STALAGMITES

permanent. To soften water of this character, chemical treatment is necessary. *Boiler scale* is the crust which forms on the inside of teakettles and steam boilers. It consists largely of calcium carbonate and sulfate. It is a poor conductor of heat, hence wastes coal.

Calcium oxid, CaO, commonly called *quicklime*, is made in immense quantities by heating limestone in furnaces called *limekilns*, when the following reaction takes place:

$$CaCO_3 \rightarrow CaO + CO_2$$

Lime is a hard, white substance that does not fuse even in the flame of the oxyhydrogen blowpipe. Exposed to the air, it slowly absorbs carbon dioxid and becomes converted into the carbonate again. In this condition it is said to be *air-slacked.*

Calcium hydroxid, $Ca(OH)_2$, commonly called *slacked lime*, is made by treating quicklime with water. Great heat is evolved, and fires have sometimes been traced to this source. The chemical change is expressed by the equation

$$CaO + H_2O \rightarrow Ca(OH)_2$$

The product is a white powder somewhat soluble in water. The solution is known as *limewater* and has a strong alkaline taste and reaction. Exposed to the air, slacked lime absorbs carbon dioxid and is converted into the carbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

In the world of industry lime serves many useful purposes, as in making mortar, plaster, cement, and bleaching salt. It is used to remove the hair from skins before they are tanned, and as "lime cartridges" in coal mines. Instead of blasting powder, the drill holes are filled with lime, and water is then introduced. In slacking, lime expands greatly, exerting a tremendous pressure and bringing down the coal without the danger of fire or explosion.

Mortar is a mixture of freshly slacked lime, sand, and water. *Plaster* usually contains hair, in addition, to make the material hold together better. The first setting of mortar and plaster seems to be due to the drying out of the pasty slacked lime and the consequent cementing of the sand grains together. The subsequent permanent hardening is caused by the absorption of carbon dioxid with the formation of calcium carbonate. This process may occupy years.

Calcium sulfate, $CaSO_4$, is found in nature as the mineral *anhydrite*, but more commonly as *gypsum*, $CaSO_4 . 2\,H_2O$. The fibrous variety of gypsum is called *satin spar*, and the finely crystallized variety, *alabaster*. When gypsum is heated in the air to 110–112°, it loses about three fourths of its water and crumbles to a white powder called *plaster of Paris*. This, mixed with water, forms a soft paste that quickly solidifies, the hardening being due to the absorption of water and the reforming of gypsum crystals that closely interlace and form a hard, firm mass. If gypsum is heated to 200°, it loses the whole of its water and is valueless for casts, as it does not harden again except after a long time. Besides the use just mentioned, gypsum is valuable as a land fertilizer, as a cement, and as a filling for writing paper. A gypsum crystal is shown in the frontispiece.

Calcium phosphate, $Ca_3(PO_4)_2$, is found in the mineral *phosphorite*, and in *apatite*, which usually contains some fluorid and has the composition $3\,Ca_3(PO_4)_2 . CaF_2$. It is the chief mineral constituent of the bones of vertebrate animals. It is a white substance, insoluble in water, but soluble in acids. It is used in the preparation of phosphorus and phosphoric acid and as a fertilizer.

Phosphorus is a necessary ingredient in the food of plants, as we have seen (p. 276). The neutral calcium phosphate, obtained from bone ash or phosphate rock, is insoluble and so is taken up only slowly by plants. In the manufacture of fertilizers phosphate rock is treated with sufficient sulfuric acid to convert it into the mono- and di-acid calcium phosphates according to the equations:

$$Ca_3(PO_4)_2 + H_2SO_4 \rightarrow CaSO_4 + 2\,HCaPO_4$$

(secondary calcium phosphate)

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 \rightarrow 2\,CaSO_4 + H_4Ca(PO_4)_2$$

(primary calcium phosphate)

The mixture of gypsum and acid calcium phosphates contains the phosphorus in a form that is readily taken up by plants. It is manufactured and sold under the name of "*superphosphate of lime*," and when mixed with other plant foods is valuable as a fertilizer.

Calcium fluorid, CaF_2, occurs in nature as *fluor spar*, and is the chief source of hydrofluoric acid and other fluorin compounds. A crystal of fluor spar is shown in the frontispiece.

Calcium chlorid, $CaCl_2$, may be obtained anhydrous by heating the product resulting from the treatment of lime or limestone with hydrochloric acid. It readily absorbs water and passes into the very deliquescent crystal form, $CaCl_2 \cdot 6\,H_2O$. For this reason anhydrous calcium chlorid is used as a drying agent in desiccators. Its solution is the "brine" used in the manufacture of artificial ice by the ammonia process.

Calcium carbid, CaC_2, is made by heating lime and coke in an electric furnace. The commercial article is a heavy, dull gray substance which liberates acetylene when treated with water.

$$CaO + 3\,C \rightarrow CO + CaC_2$$

$$CaC_2 + 2\,HOH \rightarrow Ca(OH)_2 + C_2H_2$$

STRONTIUM (Sr — 88) occurs chiefly in the minerals *celestite*, $SrSO_4$, and *strontianite*, $SrCO_3$, alone or associated with calcium. It resembles calcium and barium in its properties, being intermediate between those two elements. It imparts a brilliant crimson color to a flame. Strontium chlorate, $Sr(ClO_3)_2$, or nitrate, $Sr(NO_3)_2$, mixed with powdered charcoal, is used in the manufacture of red fire.

BARIUM (Ba — 137) is found mostly as the sulfate, $BaSO_4$, in the mineral *barite* or *heavy spar*. Like calcium and strontium, it is strongly basic and acts with a valence of 2. *Barium oxid*, BaO, and *hydroxid*, $Ba(OH)_2$, resemble the corresponding compounds of calcium. The solution of the hydroxid in water is alkaline like limewater; it is called *baryta water* and finds use in the laboratory. *Barium sulfate* is a very insoluble substance and may be precipitated, by the addition of a solution containing the barium ion, from solutions containing even traces of sulfates. This is known as a test for sulfates. Conversely, by adding a solution of a sulfate to a solution of a barium salt, a test for barium may be made.

Barium salts color a flame green. In solution they give the barium ion, $\overset{++}{Ba}$.

In addition to the common oxids, the metals of this group form the dioxids CaO_2, SrO_2, and BaO_2. There is reason to believe, however, that in these compounds the metals retain their ordinary valence of 2. Barium dioxid is prepared by heating barium oxid to about 500° in a current of air, when oxygen is absorbed according to the equation:

$$2\,BaO + O_2 \longrightarrow 2\,BaO_2$$

When heated to about 1000°, the dioxid decomposes into barium oxid and oxygen. The Brin's process for obtaining oxygen from the air depends on these two reactions.

When barium dioxid is treated with dilute sulfuric acid, insoluble barium sulfate is precipitated and a solution of hydrogen dioxid is obtained. This reaction is carried out on the large scale in the manufacture of hydrogen dioxid.

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

ZINC (Zn — 65) is found in nature chiefly as *sphalerite* or *blende*, ZnS, but nearly all the zinc mines contain ores of other metals, especially lead. The main supply of zinc in the United States comes from Missouri and neighboring states, and from New Jersey and Pennsylvania.

To obtain the metal, blende is first roasted until the zinc sulfid is changed to zinc oxid. The roasted ore is then mixed with powdered charcoal and heated in retorts. As zinc boils at 918°, the reduced metal is converted into vapor, which passes into iron receivers and is condensed. At first the vapor, coming in contact with the cold receivers, is chilled suddenly, yielding a fine powder known as *zinc dust*, analogous to the flowers of sulfur. Later, when the receivers become heated, the zinc condenses to a liquid which solidifies in molds and is then called *spelter*.

Zinc is a bluish white, moderately hard metal, malleable and ductile. Because of its stability in the presence of air and water, it finds extensive use in the form of thin sheets of the metal and also in the manufacture of *galvanized iron*. Sheet iron and iron wire are dipped into molten zinc and become coated with a thin layer of the metal which protects the iron from rust. *Brass* is an alloy containing usually about 1 part of zinc to 2 of copper. It is hard, malleable, ductile, and may be cast, hence it finds many uses.

Zinc is stable in the air at ordinary temperatures because a thin layer of oxid forms readily and protects the metal from further action. It melts at 420° and at a higher temperature takes fire and burns to the oxid, ZnO.

Compounds. Commercial zinc reacts with most dilute acids, liberating hydrogen and forming salts in which zinc acts as a base-former. The element is attacked by strong bases also, with the evolution of hydrogen and the formation of soluble zincates in which zinc acts as an acid former.

$$Zn + 2\,HCl \rightarrow H_2 + ZnCl_2 \qquad \text{Zinc chlorid}$$
$$Zn + 2\,NaOH \rightarrow H_2 + (NaO)_2Zn \qquad \text{Sodium zincate}$$

Zinc oxid, ZnO, is used as a pigment and known as "*zinc white.*" Since zinc sulfid is white, zinc paints are not turned dark by sulfur compounds as lead paints are. Hence, the former are used largely for inside work in buildings where gas, oil, and coal are burned, for these substances contain appreciable amounts of sulfur.

Zinc sulfate, $ZnSO_4 \cdot 7\,H_2O$, is known as *white vitriol* and is used to kill molds and insects on fruits and vegetables, also as a mordant in dyeing.

Zinc chlorid, $ZnCl_2 \cdot 6\,H_2O$, is used in preserving from decay railroad ties and other wooden articles which come in contact with the ground.

Electric batteries. Zinc, coupled with copper (or carbon) is commonly used in electric batteries. The elements are usually immersed in dilute sulfuric acid. The copper is unaffected by the acid, but the zinc, known as the *positive* element, dissolves in the acid, forming zinc sulfate. In this reaction a large amount of heat is set free, but when the zinc and the copper (or carbon) are connected by a wire, a part of the energy is converted into electrical energy and we say that a current of electricity flows through the circuit.

When two metals are connected in such a way as to generate a current of electricity, the positive metal dissolves much more rapidly than if immersed in the acid and not connected with the copper or carbon. *Pure zinc* is not appreciably dissolved by dilute sulfuric acid, but when connected with copper and immersed in the same acid the action is rapid. If pure zinc is used in batteries, there is no action except when the circuit is closed. Commercial zinc contains as impurities small particles of iron, carbon, etc., which set up small electric currents and cause the metal to dissolve as soon as immersed in the acid. To prevent this so-called *local action* in batteries, it is customary to *amalgamate* the zinc with mercury. Mercury dissolves zinc and covers over the impurities, and thus exposes an even, clean surface of metal to the action of the acid. When so amalgamated, zinc is attacked by the acid only when the circuit is closed.

CADMIUM (Cd—112) is an element closely resembling zinc. It is usually found associated with zinc and is separated from it by distillation. Cadmium sulfid, CdS, when prepared artificially is bright yellow and is used as a pigment under the name of *cadmium yellow*.

MERCURY (Hydrargyrum, Hg—201), often called *quicksilver*, is sometimes found in free condition, but the chief source is *cinnabar*, HgS. The famous cinnabar mines at Almaden in Spain have been worked for more than twenty centuries. They still yield a large fraction of the world's total production of mercury, and show no signs of giving out. Other important deposits occur in Austria and in California. Mercury ores are easily reduced. Cinnabar is roasted; the sulfur is converted into sulfur dioxid, while the mercury is vaporized and afterwards condensed.

Fig. 69 shows the plan of a cinnabar furnace. The coarse ore is loosely piled in the flue over a fire, the fine ore being heated in pans. The heat from the fire and the sulfur burning in the ore volatilizes the mercury which is condensed in the chambers as shown. The sulfur dioxid passes up the stacks into the atmosphere.

Mercury is the only metallic element that is liquid at ordinary temperatures, bromin being the liquid non-metal. It is a heavy, silver-white metal freezing at – 39° to a malleable solid. It boils at 357°, giving a vapor that contains only one atom to the molecule, a general property of metals. When heated in the air for a long time, it is gradually converted into red *mercuric oxid*, HgO, which on higher heating decomposes into the elements. The metal is dissolved by nitric acid and by hot sulfuric acid, but hydrochloric acid has no action on it.

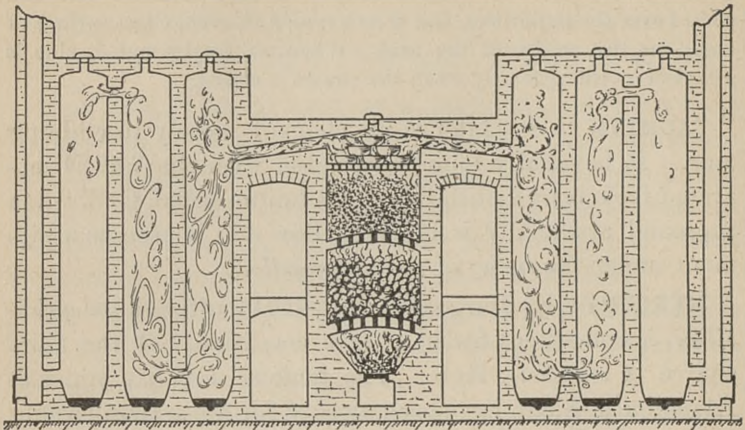

Fig. 69.

Since hydrochloric acid is one of the strongest acids and yet does not attack mercury, the action of nitric acid and hot concentrated sulfuric acid on mercury is to be explained as due to their oxidizing properties. The following equations suggest the various steps in the reaction:

(1) $2\,HNO_3 \rightarrow H_2O + N_2O_2 + 3\,O$

(2) $Hg + O \rightarrow HgO$

(3) $HgO + 2\,HNO_3 \rightarrow Hg(NO_3)_2 + H_2O$

To use the 3 atoms of oxygen represented in (1) will require 3 atoms of mercury, and 3 molecules of mercuric oxid will be formed. This will require 6 molecules of nitric acid to dissolve the mercuric oxid, hence equation (4) is often written to express this change. It must be regarded only as a summary of the different steps in the process, which are better represented by the simple equations.

(4) $3\,Hg + 8\,HNO_3 \rightarrow 3\,Hg(NO_3)_2 + N_2O_2 + 4\,H_2O$

Similar equations may be written to express the action of nitric acid on copper and silver.

Mercury is used in scientific instruments, such as thermometers and barometers. Its greatest usefulness depends on the fact that it readily dissolves many other metals, forming alloys known as *amalgams*. For this reason it is used in many mining operations, where it readily takes up the gold and silver, thus separating them from great masses of mineral matter. The two metals are then easily obtained by distilling off the mercury.

Compounds. Mercury forms two series of salts, one of which contains a larger proportion of mercury than the other. The former are called mercurous compounds; the latter, mercuric compounds.

Mercuric salts may be derived from the red oxid of mercury, HgO, by the action of acids. Typical mercuric salts have the formulas $HgCl_2$, $Hg(NO_3)_2$, $HgSO_4$, etc. It will be noticed that they correspond in formula with the salts of other metals of the group. They give rise to the mercuric ion, $\overset{++}{Hg}$, when in solution.

Mercurous salts contain proportionately twice as much mercury, and may be represented by the formulas Hg_2Cl_2, $Hg_2(NO_3)_2$, Hg_2SO_4, etc. It might seem that some of these formulas might preferably be divided and written $HgCl$ and $HgNO_3$, but it has been found that mercurous salts contain two atoms of mercury in the molecule. They give rise to the mercurous ion $(\overset{+}{Hg})_2$, consisting of two atoms of mercury each carrying a positive charge.

Many mercuric salts are soluble; all common mercurous salts except the nitrate are insoluble. Mercuric salts are more stable than mercurous salts. Exposed to the air, the latter become oxidized to the mercuric condition. On the other hand, strong reducing agents convert mercuric salts into the mercurous form.

Mercuric chlorid, $HgCl_2$, commonly called *corrosive sublimate*, is manufactured commercially by subliming a mixture of mercuric sulfate and sodium chlorid.

$$HgSO_4 + 2\,NaCl \rightarrow Na_2SO_4 + \mathit{HgCl_2}$$

It is a white, crystalline, soluble substance. It acts as a violent poison and in dilute solution is a valuable germicide and disinfectant.

Mercurous chlorid, Hg_2Cl_2, commonly called *calomel*, is used in medicine. Together with mercuric chlorid it may be obtained by the action of chlorin on mercury. Since it is insoluble, it may also be obtained as a precipitate by adding a solution of a mercurous salt to a solution of a chlorid. On the large scale it is prepared by subliming a mixture of mercuric chlorid and mercury.

$$HgCl_2 + Hg \rightarrow Hg_2Cl_2$$

By oxidation in the presence of hydrochloric acid, mercurous chlorid is readily converted into mercuric chlorid. Conversely, reducing agents change mercuric chlorid to mercurous. When stannous chlorid, $SnCl_2$, is the reducing agent, chemical action takes place according to the equation:

$$SnCl_2 + 2\,HgCl_2 \rightarrow SnCl_4 + \mathbf{Hg_2Cl_2}$$

A larger proportion of stannous chlorid gives metallic mercury.

$$SnCl_2 + HgCl_2 \rightarrow SnCl_4 + \mathbf{Hg}$$

These facts are the basis of a test for either mercury or tin.

Mercuric sulfid, HgS, may be prepared as a black precipitate by treating a solution of mercuric chlorid with hydrogen sulfid. On heating, the precipitate changes to a red color which is permanent and resembles the color of cinnabar. By carefully treating mercury with sodium sulfid, a more brilliant product is obtained which is the pigment *vermilion*.

Study of the group. A detailed study of the elements of this group will indicate that, while each member of the group shows considerable similarity to all the others, nevertheless each element has an individuality of its own, and the resemblances between some elements are much closer than between others. Barium, strontium, and calcium are so closely alike in properties that in chemical analysis their separation is brought about only with some difficulty. In a general way these elements resemble zinc, cadmium, and mercury, but the latter show greater similarities among themselves than they do to barium, strontium, and calcium.

Two types of elements exist within the group. The main class, consisting of beryllium, magnesium, calcium, strontium, and barium, are strong base-forming elements of low density which show a constant valence. The members of the second type are heavy metals, much weaker base-formers, whose valence is not constant. In mercuric salts mercury shows a valence of two; in mercurous compounds it is said to have a valence of one. Zinc and cadmium form compounds of both types, though rarely the latter. The division of the group into two branches is shown in Fig. 70. Similar branching in other groups will be noticed later. (See pp. 398 and 399.)

CALCIUM-MAGNESIUM GROUP

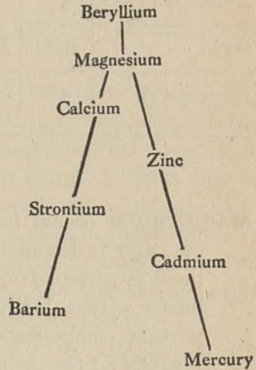

FIG. 70.

The elements, beryllium, magnesium, calcium, strontium, barium, and radium are known as the *alkaline earths* because in properties they stand midway between the aluminum group known as the *earths* and the sodium group known as the *alkalis*.

MAGNESIUM—CALCIUM GROUP

	Be	Mg	Ca	Zn	Sr	Cd	Ba	Hg
At. wt.	9	24	40	65	88	112	137	201
Melt. pt.	800°	633°	760°	420°	800°	320°	850°	−39°
Boil. pt.		1120°		918°		778°		357°
Spec. grav.	1.8	1.75	1.85	7.2	2.5	8.7	3.8	13.6
Valence	2	2	2	2 (1)	2	2 (1)	2	2 (1)
Action on H_2O	4*	5	6	3	7	2	8	1
Oxid	BeO	MgO	CaO	ZnO	SrO	CdO	BaO	HgO
Basic prop.	4*	5	6	3	7	2	8	1

SUMMARY

MAGNESIUM occurs in many rocks, as *dolomite, magnesite, asbestos,* etc., and is found in sea water as magnesium chlorid. The element is prepared by electrolysis. It is a light, whitish metal that burns with a brilliant white light useful in photography. Important compounds are the oxid, *magnesia,* MgO; the hydroxid, $Mg(OH)_2$; the carbonate, $MgCO_3$; and the sulfate, $MgSO_4 . 7 H_2O$.

CALCIUM is found in compounds, such as limestone, marble, gypsum, etc., which are of great importance.

Calcium carbonate, $CaCO_3$, is found pure in *calcite,* also in marble, limestone, shells, etc. It is used as a building stone, in making lime and mortar, and as a flux. Though insoluble in pure water, it dissolves to a slight extent in water containing carbonic acid. In this way it is removed by underground water, and caverns are formed. Water containing calcium carbonate is "hard," but as the hardness can be removed by boiling it is said to be "temporary."

Calcium oxid, or *quicklime,* CaO, is obtained by roasting limestone in kilns.

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* The figures denote the order in which the elements stand, the number 8 indicating the possession of a property in greatest degree, while 1 indicates the least.

Calcium hydroxid, or *slacked lime*, $Ca(OH)_2$, is made by treating quicklime with water. On exposure to the air it becomes converted into calcium carbonate. It finds many uses, especially in making mortar. This is a mixture of slacked lime, sand, and water. The final setting of the mortar is due to the conversion of its lime into the carbonate.

Calcium sulfate is found in nature usually as *gypsum*, $CaSO_4 \cdot 2\,H_2O$. When heated to about 110° this loses water, and is converted into *plaster of Paris*. Water containing gypsum or magnesium sulfate in solution is said to be "permanently hard."

Calcium phosphate, $Ca_3(PO_4)_2$, is found in bones and as a mineral. It is an essential ingredient of productive soils, and is used in preparing fertilizers.

STRONTIUM and **BARIUM** resemble calcium, and form corresponding compounds.

ZINC occurs chiefly as the sulfid, *blende*, which is roasted to the oxid and then reduced with carbon. It is stable in the atmosphere, hence is used to protect other metals as in galvanized iron. It is also used in batteries and in alloys, brass being the most important. Chemically, zinc acts both as base-former and as acid-former. The oxid, known as *zinc white*, is used in making paints which are not darkened by sulfur compounds as lead paints are. The chlorid is used for preserving wood; and the sulfate, *white vitriol*, as a mordant and for killing insects and molds.

CADMIUM closely resembles zinc. Its sulfid, CdS, is the pigment cadmium yellow.

MERCURY, or *quicksilver*, occurs native and as the sulfid cinnabar, HgS. It is rather inactive chemically, and is used in scientific instruments and in the mining of gold and silver, with which it readily amalgamates. It forms two series of salts, *mercuric* and *mercurous*, in which it acts with valences of 2 and 1 respectively. The most important compounds are mercuric chlorid, or *corrosive sublimate*, $HgCl_2$, and mercurous chlorid, or *calomel*, Hg_2Cl_2.

QUESTIONS

1. Write the reaction taking place when magnesium flash-light powder is set on fire.

2. Why must dry magnesium chlorid be used in the preparation of metallic magnesium?

3. The average family uses 20 tons or over of water in a year, one-tenth of which is used with soap. If the water is hard and contains 0.1% of calcium sulfate, what is the approximate value of the soap wasted each year, supposing soap to be $NaC_{18}H_{35}O_2$? (A 5-cent cake of soap weighs about 10 ounces and often contains 40% of water.)

4. When limestone is "burned," what burns? How could you make quicklime from slacked lime? What is air-slacked lime?

5. Would limestone be completely converted into lime if heated in a closed tube? Why?

6. In making lime, steam or air is frequently blown into the kiln to hasten the process. Why does this aid the reaction?

7. Limewater on standing in the air loses its basic reaction. Explain.

8. Using equations, explain the chemical changes which are involved in testing for carbon dioxid by means of limewater. Could barium hydroxid be used in place of limewater in this test?

9. What is the difference in composition and properties between mortar and cement? What is concrete? Compare the setting of mortar with the setting of plaster of Paris.

10. What substances must be avoided when galvanized iron vessels are in use?

11. Why does not the growth of forests cause land to become exhausted as wheat-raising does?

12. For kitchen use, how may hardness be removed from water?

13. Phosphate rock is worth $6 per ton; superphosphate of lime ($CaH_4(PO_4)_2$), $25 per ton; waste sulfuric acid from oil refineries may be purchased for $6 a ton. If the cost of labor is 25% of the cost of materials, how much profit is there in the manufacture of superphosphate?

14. Does the preparation of corrosive sublimate appear to be a reaction between ions? Why does the reaction not reverse?

15. What weight of zinc is contained in 1 ton of blende running 80% ZnS?

16. Why does a surgeon frequently dip his hands in a solution of corrosive sublimate when performing an operation?

17. (*a*) The gas density of the vapor of mercury is 100. What is the formula for its molecule?

(*b*) The specific gravity (referred to air) of the vapor of zinc is 2.36. Calculate the formula for its molecule.

18. Why is nitric acid a better solvent for mercury, copper, and silver than hydrochloric or sulfuric acids? Why does hot, concentrated sulfuric acid dissolve all of these metals readily?

CHAPTER XXVII

THE ALKALI METALS

The group. The term *alkali* as applied to these elements signifies that they are strong base-formers. The group includes the abundant elements, *sodium* and *potassium*, *lithium*, which is less common, and *rubidium* and *cæsium*, which are very rare. These elements are the most reactive of metals, combining readily with most non-metals to form stable compounds. The constituents of the atmosphere, water, carbon dioxid, and oxygen, all attack these metals readily, and hence they are never found free in nature.

The various feldspars, which are among the principal constituents of granite and other igneous rocks, are the primary sources of sodium and potassium (Fig. 71 *a*). By the weathering of these rocks the alkali metals are changed to carbonates, which, being soluble, become mixed with the solutions of chlorids and sulfates of other elements extracted from the earth and are converted into alkali chlorids and sulfates.

Salts of potassium are necessary for the existence of plant life, and a considerable portion of the potassium salts are absorbed by vegetation.

Sea water. Most of the sodium salts wash out of the soil and collect in the ocean or in salt lakes. Ocean water contains about 3½ per cent of solid material in solution, four fifths of which is sodium chlorid, with sulfates and chlorids of potassium, magnesium and calcium making up the balance.

Photo by H. M. Tenney

b Courtesy of the "Scientific American"

FIG. 71. — SOURCES OF THE ALKALIS

(*a*) Kearsarge Pinnacles. Granite rocks, like the Southern Sierra Nevada Mountains, are the primary sources of the alkali metals and their compounds.

(*b*) Making salt, San Francisco Bay. Salt lakes and the ocean are the secondary sources of the alkalis.

Salt deposits. Practically all the salts of sodium and potassium used in commerce are obtained by the evaporation of sea water. This may be carried out on a relatively small scale by man, as when the water of Great Salt Lake, or from other similar sources, is led into shallow ponds and evaporated by the heat of the sun (see Fig. 71 *b*); or on a large scale when lakes and seas have dried up in past geological time and left salt deposits such as exist in New York, Michigan, Kansas, and other places in this country, and notably at Stassfurt in Germany where the deposit is nearly a mile in thickness. In the latter place one layer consists of *carnallite*, $MgCl_2 . KCl . 6H_2O$. When heated, this salt melts in its own water of crystallization, and on cooling, potassium chlorid crystallizes from the solution. From this source most of the potassium salts of commerce are derived. Formerly the largest source was potassium carbonate obtained from wood ashes. Salts of sodium, such as the sulfate, nitrate, carbonate and borate, occur in various localities.

Sodium and potassium resemble each other so closely that what is said of the properties of the one applies in general almost equally well to the other. Hence, compounds of these elements will not be treated separately.

Ammonium salts resemble potassium salts quite as closely as those of sodium do. One general reaction of ammonium salts serves to separate them from the others. When an ammonium salt is treated with a strong base, such as sodium or calcium hydroxid, the weak base, ammonium hydroxid, is formed and ammonia is liberated.

$$\overset{+}{N}H_4 . \overset{-}{Cl} + \overset{+}{Na} . \overset{-}{OH} \rightarrow \overset{+}{Na} . \overset{-}{Cl} + NH_4OH$$
$$NH_4OH \rightarrow \mathit{NH}_3 + H_2O$$

Important ammonium salts will be considered along with the corresponding sodium and potassium compounds.

Sodium (Natrium, Na — 23) has already been described (p. 121), and its properties should be reviewed at this time.

Potassium (Kalium, K — 39) was first prepared by Sir Humphry Davy by means of the electrolysis of molten potassium hydroxid exactly as he obtained sodium. The electrical method is still in use to-day, the chlorid being frequently used instead of the hydroxid, which is more expensive. Metallic potassium is little used industrially.

Potassium is a silver-white metal melting at 62° and boiling at 667°, its vapor being of a greenish color. At ordinary temperatures it is soft like wax and may be cut with a knife. It is the lightest of all metals, except lithium, its specific gravity being 0.875. In clean, dry air it remains for some time unaltered, but in moist air it soon becomes covered with the hydroxid and carbonate. When thrown on water it liberates hydrogen, and the liquid after the reaction contains potassium hydroxid. So much heat is evolved that the hydrogen catches fire and burns with a flame colored violet or pink by traces of potassium.

Lithium (Li — 7) is an element that closely resembles sodium and potassium. It is the lightest of known metals, its specific gravity being 0.59. In traces lithium compounds are widely distributed in nature, but they rarely occur in quantity. *Lithium carbonate*, Li_2CO_3, is used in medicine as *lithia water* or *lithia tablets*.

Oxids. Since the alkali metals are univalent, one would expect them to form oxids of the type Na_2O. Such compounds are known, but more important are the dioxids like Na_2O_2. *Sodium dioxid*, or *peroxid*, is a heavy, straw-colored powder which is a good oxidizing agent. It reacts with water to form sodium hydroxid and hydrogen peroxid, as the equation shows.

$$Na_2O_2 + 2\,H_2O \rightarrow 2\,NaOH + H_2O_2$$

Fused sodium peroxid is used as a source for oxygen in accordance with the preceding equation; for the heat of the reaction decomposes the hydrogen peroxid into water and oxygen. Under the name of "*oxone*" it is sold for this purpose.

Sodium hydroxid, NaOH, often called *caustic soda* or *soda lye*, is prepared by the decomposition of water by metallic sodium, when an especially pure product is desired. It may be prepared also by treating sodium carbonate with slacked lime.

$$\overset{+}{Na_2} \cdot \overset{=}{CO_3} + \overset{++}{Ca} \cdot (\overset{-}{OH})_2 \rightarrow 2\,\overset{+}{Na} \cdot \overset{-}{OH} + CaCO_3$$

On a commercial scale sodium hydroxid is now prepared by the electrolysis of sodium chlorid. In the Castner process (Fig. 72), the anodes, *A*, *A*, are placed in a salt solution in the two outer compartments and the cathode, *C*, in water. A layer of mercury seals these compartments at the bottom. The mercury is free to flow from one compartment into the others, but it prevents the mixing of the solutions. In the outer compartments (where chlorin is liberated at the anodes), the mercury acts as an intermediate cathode; and the sodium, dissolving in it, is protected from the action of water and of chlorin. In the middle compartment, the mercury acts as an intermediate anode. Here the sodium dissolves out of the mercury as fast as it dissolves in it in the outer compartments. It reacts with the water, and a solution of sodium hydroxid results. By means of the cam, *E*, the mercury is periodically run out of the outer compartments into the middle one, and *vice versa*.

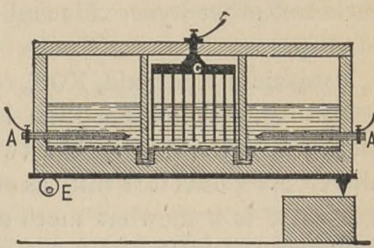

Fig. 72.

When this solution becomes sufficiently concentrated it is evaporated to dryness and the fused sodium hydroxid cast in sticks or other forms.

A large per cent of the cost of manufacture lies in this evaporation of water. The following modification, known as the Acker process, seems nearly ideal theoretically. Molten salt, instead of a solution is used, and melted lead takes the place of mercury as a cathode. The sodium dissolves in the lead as it did in the mercury, and the resulting alloy is decomposed by superheated steam, thus avoiding all excess of water. Commercially this process has not yet proven successful.

The chlorin, obtained as a by-product, is ordinarily used in making bleaching salt.

Sodium hydroxid is a white, deliquescent solid. It is a powerful base and is used in the laboratory for the preparation of other hydroxids and commercially in the making of soap.

Potassium hydroxid, KOH, often called *caustic potash* or *potash lye*, resembles sodium hydroxid, is made by similar methods, and ordinarily the two may be used interchangeably. As a base it is fully as effective as sodium hydroxid, but as it is somewhat more expensive than the latter, it finds less use in the industries.

Ammonium hydroxid, NH_4OH, known as the volatile alkali, in distinction from sodium and potassium hydroxids, which are not volatile, has already been considered (p. 152). It is a much weaker base than sodium hydroxid.

Sodium nitrate, $NaNO_3$, often called *Chili saltpeter*, is found in large deposits in the rainless regions of Chili, where it is mined and then purified by crystallization from water. The mother liquors contain sodium iodid and iodate, which are used in the manufacture of iodin. Sodium nitrate forms colorless, transparent crystals. For the manufacture of gunpowder it is not as satisfactory as the potassium salt, for it absorbs water vapor from the air and causes the powder to become moist. It is used as a fertilizer and in making nitric acid and potassium nitrate.

Potassium nitrate, KNO_3, is commonly called *niter* or *saltpeter*. Along with sodium nitrate, it is always in process of formation in the soils of warm countries, where animal matter is decomposing under the influence of certain bacteria. It is made on "saltpeter plantations" by allowing masses of animal and vegetable matter mixed with wood ashes to decompose in the dark, the proper bacteria being present. The potassium nitrate is then dissolved out and purified by crystallization. Much of the potassium nitrate of commerce is made by bringing together solutions of potassium chlorid and sodium nitrate. Potassium nitrate readily yields its oxygen when heated, and is used as an oxidizing agent in chemical operations; also in fire-works and gunpowder.

In **converting sodium nitrate into potassium nitrate,** a saturated solution of the former is treated with the calculated amount of solid potassium chlorid. By the combination of the ions present in this solution, $\overset{+}{\mathrm{Na}}$, $\overset{+}{\mathrm{K}}$, $\overset{-}{\mathrm{NO_3}}$, and $\overset{-}{\mathrm{Cl}}$, there is the possibility of forming $NaNO_3$, KNO_3, $NaCl$, or KCl, and all four substances are present in solution. But all are not equally soluble (see p. 64), and if the solution is concentrated, one substance will soon be present in larger quantities than can remain in solution and will begin to separate. This substance is sodium chlorid, for the solubility of salt does not increase greatly as the temperature rises, as is the case with the other three substances. Therefore, on evaporating the solution a considerable amount of salt separates out. The removal of $\overset{+}{\mathrm{Na}}$ and $\overset{-}{\mathrm{Cl}}$ ions leaves $\overset{+}{\mathrm{K}}$ and $\overset{-}{\mathrm{NO_3}}$ ions in solution, which unite to form KNO_3. Potassium nitrate is the least soluble compound at low temperatures and crystallizes out when the solution is cooled.

The process depends on an equilibrium reaction and never runs to completion, but by adding more $NaNO_3$ and KCl and repeating the operation, it is possible to bring about the continuous removal of salt at higher temperatures and of potassium nitrate at low temperatures.

Gunpowder is an intimate mixture of charcoal, potassium nitrate, and sulfur. Its explosive power depends on the rapid oxidation of the charcoal by the potassium nitrate, which is mostly converted into potassium sulfid. Thus a large volume of gas is suddenly liberated, and at the temperature of the combustion this immediately attempts to expand to a bulk several hundred times as great as that occupied by the gunpowder. It thus exerts a tremendous pressure and an explosion results. The decomposition of gunpowder, when burning in an open space, is approximately represented by the equation

$$2\,KNO_3 + S + 3\,C \longrightarrow K_2S + N_2 + 3\,CO_2$$

The requirements of this equation correspond very nearly to the usual composition of gunpowder:

Potassium nitrate, 75 %; sulfur, 12 %; charcoal, 13 %.

Sodium chlorid, $NaCl$, occurs in solid form as *rock salt.* When the deposits are of sufficient purity, it is mined in the solid form, but it is more often obtained by flooding the mines with water and after a time pumping out the brine, from which on evaporation the salt crystallizes in colorless, transparent cubes. The salt of commerce always contains foreign materials, chiefly magnesium chlorid which has not been entirely removed in the process of manufacture. This substance is deliquescent and causes the salt to pack together on moist days. Salt is essential to the life of man and animals. On account of its abundance it is the material from which all other compounds of sodium are usually made.

Potassium chlorid, KCl, is found alone and with other potassium compounds in the celebrated mines at Stassfurt. It resembles sodium chlorid, being a white substance crystallizing in cubes and possessing a salty taste. It is the chief source of other potassium compounds, and is also of importance as a fertilizer, for which purpose it is sold under the name of "muriate of potash."

Ammonium chlorid, NH_4Cl, commonly called *sal ammoniac*, is obtained commercially by neutralizing the ammonia water of the gas works with hydrochloric acid and then purifying the product. It is a colorless, crystalline solid with a sharp, salty taste. When heated it is decomposed into ammonia and hydrogen chlorid, but on cooling these recombine so that the substance seems to sublime without change.

$$\mathrm{NH_4Cl} \longleftrightarrow NH_3 + HCl$$

The use of ammonium chlorid in battery cells depends on the fact that it acts on zinc as the equation shows:

$$\mathrm{Zn} + 2\,\mathrm{NH_4Cl} \rightarrow \mathrm{ZnCl_2} + 2\,NH_3 + H_2$$

The zinc is thus dissolved and a current results. This action takes place only when the circuit is closed.

Potassium chlorate, $KClO_3$, is a crystalline substance having a cooling, salty taste. Under the name *chlorate of potash* it is used in medicine. Since it readily parts with its oxygen, it finds use in the preparation of that gas, in making fireworks, and in general as an oxidizing agent.

It may be prepared by passing chlorin into a hot, concentrated solution of potassium hydroxid, when a hypochlorite is first formed, which then decomposes and gives a chlorate. (See p. 94.) As potassium compounds are expensive, a saving is effected by boiling a solution of bleaching powder, which is thereby converted into calcium chlorate. When a concentrated solution of potassium chlorid is added to this, the slightly-soluble potassium chlorate forms and separates from solution.

Of late potassium chlorate has been prepared on the large scale by the electrolysis of a solution of potassium chlorid. The potassium that separates at the cathode reacts with water and is converted into the hydroxid. This reacts with chlorin liberated at the other pole. In any method of preparation the potassium chlorate is purified by recrystallization.

Potassium bromid, KBr, and **potassium iodid, KI,** are made by treating a solution of potassium hydroxid with the proper halogen, evaporating the liquid, and heating the residue. The reactions are exactly analogous to the reactions of chlorin under the same conditions. A hypobromite and a hypoiodite are first formed, then a bromate and an iodate, and finally on heating a bromid and an iodid with the liberation of oxygen. They are white, salty substances, crystallizing in cubes, and find use in medicine and in photography.

Sodium carbonate, Na_2CO_3, commonly called *soda*, is sometimes found in nature, but is prepared artificially in large quantities. Next to sulfuric acid, the manufacture of soda is the world's most extensive chemical industry. The starting point is salt, the cheapest sodium compound, and one of two methods is followed, the first chiefly in America, the second almost exclusively in Europe.

1. The *Solvay* or *ammonia-soda process* is carried out as follows: A saturated solution of salt is further saturated with ammonia and later with carbon dioxid under pressure, the following reactions taking place:

(*a*) The carbon dioxid converts the ammonium hydroxid into acid ammonium carbonate, HNH_4CO_3.

$$NH_4OH + H_2CO_3 \rightarrow HNH_4CO_3 + H_2O$$

(*b*) Acid sodium carbonate is much less soluble than any other substance which can be formed from the reagents present. Hence the ions of sodium chlorid react with those of acid ammonium carbonate to form acid sodium carbonate, $HNaCO_3$, which is precipitated.

$$\overset{+}{Na}\,.\,\overset{-}{Cl} + \overset{+}{H}\,.\,\overset{+}{N}H_4\,.\,\overset{=}{C}O_3 \rightarrow \overset{+}{N}H_4\,.\,\overset{-}{Cl} + \mathbf{HNaCO_3}$$

(*c*) If sodium carbonate is required, the hydrogen sodium carbonate is heated, when it decomposes as any acid carbonate does.

$$2\,\mathbf{HNaCO_3} \rightarrow \mathbf{Na_2CO_3} + H_2O + CO_2$$

Formerly, the by-products formed in commercial processes were commonly thrown away as "waste." To-day they are converted into something that can be used, and thus an enormous saving to the world has been brought about.

In the Solvay process this saving is accomplished as follows:

The carbon dioxid given off in (*c*) is one-half the total amount. It is collected and used again in (*a*).

The ammonium chlorid is heated with slacked lime, and the ammonia thus obtained is used over again in (*a*).

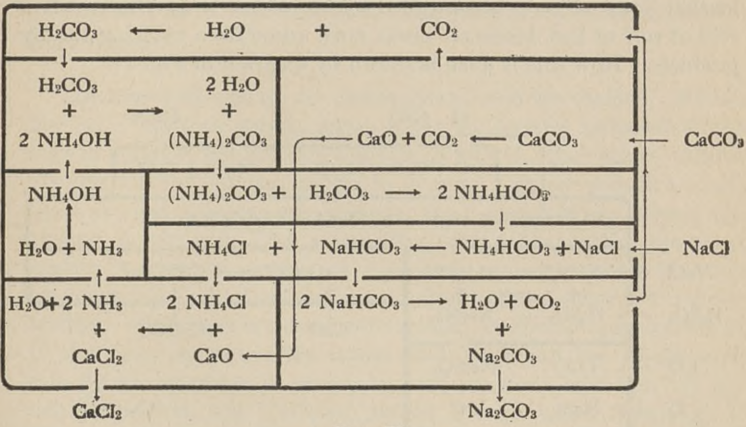

FIG. 73.

Fig. 73 shows how the by-products are utilized. Note that the ammonia never leaves the factory, but continually circulates from one process to another.

2. The *Le Blanc process* consists of three reactions:

(*a*) Salt is treated with sulfuric acid in furnaces, thus forming sodium sulfate.

$$2\,NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\,HCl$$

(*b*) Sodium sulfate is heated with charcoal or coal dust, when reduction to sodium sulfid takes place.

$$Na_2SO_4 + 4\,C \rightarrow Na_2S + 4\,CO$$

(*c*) Sodium sulfid is treated with limestone, and calcium sulfid and sodium carbonate are formed.

$$Na_2S + CaCO_3 \rightarrow CaS + Na_2CO_3$$

When the resulting mass is treated with water, sodium carbonate dissolves out and is purified by crystallization. In practice (*b*) and (*c*) are united by heating a mixture of sodium sulfate, charcoal or coal, and limestone.

The Solvay process is much cheaper than the Le Blanc, hence the market price of soda is controlled by the former. Le Blanc soda is sold at cost or less, hence all profit must come from utilizing the by-products. How this is done is shown by diagram in Fig. 74.

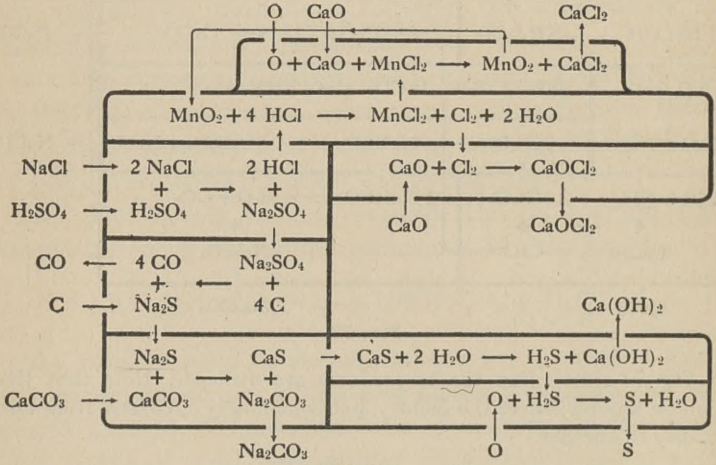

FIG. 74.

The hydrochloric acid given off in the treatment with sulfuric acid is dissolved in water and converted into bleaching salt.

The carbon monoxid produced in the second reaction is piped under the furnaces and burned to produce heat.

The calcium sulfid is decomposed by carbon dioxid in the presence of water, calcium carbonate and hydrogen sulfid being formed. The hydrogen sulfid is burned to water and sulfur by admitting a supply of air insufficient for complete oxidation.

Sodium carbonate crystallizes from solution in large crystals having the formula $Na_2CO_3 . 10H_2O$, which soon effloresce and fall to a powder having the composition $Na_2CO_3 . H_2O$. Because of hydrolysis, sodium carbonate gives to its solutions an alkaline reaction. It is often called *washing soda* in distinction from acid sodium carbonate or sodium bicarbonate, which is known as *baking soda*. Soda is used in making soap and glass, and in "softening" water, its action in the latter case being the precipitation of calcium and magnesium salts as insoluble carbonates.

The **household uses** of the carbonates of soda are various. Besides the use of washing soda to soften water for laundry purposes, advantage is taken of the alkaline reaction of soda in other ways. Alkalis dissolve fat and animal matter in general. Hence soda is a constituent of most cleaning preparations; for it dissolves any grease, converting it partially into soap, after which the earthy matter is readily removed by water. A little soda added to water in which meat is boiling will dissolve some of the fiber and cause it to become tender. When soda is treated with an acid, it liberates carbon dioxid. If the soda be intimately mixed with flour and the whole made into dough by water to which an acid has been added in the correct proportion, the liberated carbon dioxid causes the dough to rise and become light, especially when the gas expands in the heated oven. The bicarbonate gives twice as large a volume of gas for the same amount of sodium present, and is generally used in place of soda.

Baking powder is universally used. It consists of bicarbonate of soda and some acid substance to act upon it and cause it to yield carbon dioxid. A good baking powder has about the following composition:

Acid potassium tartrate, *i.e.* "cream of tartar"	8 ounces
Bicarbonate of soda	4 ounces

In this the "cream of tartar" acts on the bicarbonate to form carbon dioxid, water, and sodium potassium tartrate, or Rochelle salt. Acid calcium phosphate and alum are cheaper and are often substituted for "cream of tartar"; but the action is similar in all cases, as the equations show:

$$HNaCO_3 + HK(C_4H_4O_6) \rightarrow NaK(C_4H_4O_6) + H_2O + \mathit{CO_2}$$
$$2\ HNaCO_3 + H_4Ca(PO_4)_2 \rightarrow HCaPO_4 + HNa_2PO_4 + 2\ H_2O + 2\ \mathit{CO_2}$$
$$6\ HNaCO_3 + 2\ NH_4Al(SO_4)_2 \rightarrow 3\ Na_2SO_4 + (NH_4)_2SO_4 + 2\ Al(OH)_3 + 6\ \mathit{CO_2}$$

Of the products left in the bread, Rochelle salt and calcium phosphate are probably less harmful than aluminum hydroxid. When sour milk and baking soda are used, it is the lactic acid, formed in the fermentation of the milk sugar, which decomposes the carbonate. An ideal baking powder would consist of sodium bicarbonate and hydrochloric acid, as the products would certainly be harmless. Sometimes the bicarbonate is used alone without acid, as in soda biscuits; it is mixed with the dough, and when the latter is baked the bicarbonate decomposes according to the equation given above. Of course washing soda is left in the product, and sometimes this imparts an objectionable taste and injures the digestion as well. It is to avoid the formation of washing soda that an acid substance is added to the baking soda in making baking powders.

Potassium carbonate, K_2CO_3, resembles sodium carbonate and is made from potassium chlorid by similar processes. Together with sodium and potassium sulfates, it is left in the ash when wood and other vegetable products burn, and from this it gets its common name, *potash.* It is largely used in making glass and soap. Potassium bicarbonate, known as *saleratus*, may be used interchangeably with sodium bicarbonate, but a somewhat larger amount is required.

Ammonium carbonate, $(NH_4)_2CO_3$, is a white substance that easily decomposes into ammonia, carbon dioxid, and water. Under the name of *sal volatile* it is used in smelling salts. It is prepared by heating ammonium chlorid with limestone, ammonium carbonate subliming out of the mixture.

$$2\ NH_4Cl + CaCO_3 \rightarrow CaCl_2 + \mathit{(NH_4)_2CO_3}$$

Sodium phosphate. There are three sodium phosphates: *trisodium phosphate*, Na_3PO_4; *disodium phosphate*, HNa_2PO_4; and *monosodium phosphate*, H_2NaPO_4. Trisodium phosphate is unstable, and on exposure to the air absorbs water and carbon dioxid and is converted into disodium phosphate, which is the substance commonly called *sodium phosphate*. Crystals of the latter have the composition $HNa_2PO_4 . 12\,H_2O$, and it finds use in medicine and in the laboratory.

Sodium sulfate, Na_2SO_4, occurs native in some localities and is formed as a by-product in the manufacture of nitric acid. It finds its chief use in making glass. It separates from solution in large crystals having the composition $Na_2SO_4 . 10\,H_2O$. It is then known as *Glauber's salt*, and finds use in medicine.

Sodium thiosulfate, $Na_2S_2O_3 . 5\,H_2O$, is known as *hypo* (see p. 249), and finds use in photography and in bleaching industries.

Sodium sulfite, $Na_2SO_3 . 7\,H_2O$, and **acid sodium sulfite, $NaHSO_3$,** are formed by the action of sulfur dioxid on sodium hydroxid. They are used as disinfectants and preservative agents, and the acid salt is used in making wood pulp for paper. Wood consists mainly of cellulose, stiffened and strengthened by a resinous substance called *lignin*. Acid sodium sulfite dissolves out the lignin and leaves the cellulose.

Borax, $Na_2B_4O_7 . 10\,H_2O$, and **potassium cyanid, KCN,** are important substances previously considered.

Ammonium sulfid, $(NH_4)_2S$, is best obtained in solution by passing hydrogen sulfid into ammonia water. It is a colorless solid, but in solution it gives a greenish, ill-smelling liquid much used in chemical analysis for the preparation of sulfids. If it is exposed to the action of the air, oxidation slowly takes place and sulfur is set free.

This sulfur dissolves in the remaining ammonium sulfid and gives a liquid known to chemists as *yellow ammonium sulfid.* It contains the polysulfids of ammonium containing 2, 3, 4, and 5 atoms of sulfur in the molecule ; such as $(NH_4)_2S_2$, $(NH_4)_2S_3$, etc. It is used in analysis.

Detection. Since compounds of sodium and potassium are for the most part readily soluble, it is no easy task to recognize the presence of compounds of these elements in solution by adding some reagent that will cause a characteristic precipitate. They may be recognized, however, by the colors which they impart to a Bunsen flame. Sodium gives a yellow flame, potassium a pinkish lavender, lithium a crimson.

If both sodium and potassium are present together, the intense yellow of the sodium will completely hide the paler flame of the potassium. Potassium may be made visible in the presence of sodium by looking through blue glass or a bottle filled with blue liquid, which will absorb the yellow rays but permit the lavender flame of the potassium to reach the eye.

Another method is to examine the flame with a spectroscope. In this case each element gives separate and distinct lines which permit the detection of an element in the presence of others. Ammonium salts are detected by boiling with a strong base. If ammonium salts are present, ammonia is liberated. (See p. 335.)

SUMMARY

THE ALKALI GROUP. The elements of this group strongly resemble one another. Soluble compounds are produced in nature by the weathering of rocks and, excepting such as are absorbed by plants, find their way to the sea. By the evaporation of sea water these salts are obtained. The metals are strong base-formers and act with an unvarying valence of 1. The ammonium radical, NH_4, forms similar compounds.

SODIUM is found in many compounds, the most important of which is common salt.

The metal is obtained by electrolysis of the chlorid or hydroxid. It is a light, lustrous, very active metal, rapidly tarnishing in the air. It decomposes water with the liberation of hydrogen and the formation of the hydroxid.

Sodium hydroxid, $NaOH$, *known as caustic soda or soda lye*, is obtained by electrolysis of sodium chlorid or by treating sodium carbonate with slacked lime. It is a white deliquescent substance which is one of the strongest bases. It is much used in soap making.

Sodium carbonate, Na_2CO_3, known as *soda*, is prepared from salt either by the Le Blanc or the Solvay process. It finds many important uses, as in making soap and glass and in cooking and cleaning.

Acid sodium carbonate, $HNaCO_3$, known as *baking soda*, is the product first formed by the Solvay process. It is an ingredient of baking powder and is used in cooking.

Sodium chlorid, $NaCl$, *salt*, is used in the preparation of practically all other sodium compounds, thus making it very important in the industries. It is essential to animal life.

Sodium nitrate, $NaNO_3$, *Chili saltpeter*, is found in Chili and is used as a fertilizer and in making nitric acid and potassium nitrate.

Sodium tetraborate, $Na_2B_4O_7 . 10 H_2O$, or *borax* is another important compound as are also the *sulfate*, $Na_2SO_4 . 10 H_2O$, *Glauber's salt;* the *sulfite*, Na_2SO_3; *thiosulfate*, $Na_2S_2O_3$, "hypo"; and the phosphates, Na_3PO_4 and HNa_2PO_4.

POTASSIUM is widely distributed in nature in compounds similar to those of sodium. It is essential to plant life and was formerly obtained as the carbonate from wood ashes. The main supply of potassium compounds is the Stassfurt deposit.

Metallic potassium is similar to sodium and is similarly prepared.

Potassium hydroxid, KOH, *caustic potash* or *potash lye*, is similar to sodium hydroxid in preparation and properties.

Potassium carbonate, K_2CO_3, *potash*, is similar to sodium carbonate in properties. It is prepared by the Le Blanc process from potassium chlorid.

Acid potassium carbonate, $HKCO_3$, *saleratus*, cannot be prepared by the Solvay process from potassium chlorid for saleratus is much more soluble than baking soda. It is used in cooking.

Potassium chlorid, KCl, is obtained from the Stassfurt deposits, where it occurs chiefly as *carnallite*, $KCl . MgCl_2 . 6 H_2O$. Potassium chlorid is used as a fertilizer and is the material from which practically all other potassium compounds are made.

Potassium nitrate, KNO_3, *niter* or *saltpeter*, is found in India and is made from sodium nitrate by heating in solution with potassium chlorid. It is a good oxidizing agent and is used in making explosives and fireworks.

Potassium bromid, KBr; *iodid*, KI; *cyanid*, KCN; *chlorate*, $KClO_3$; and *acid tartrate*, $HKC_4H_4O_6$, or *cream of tartar*, are important salts.

AMMONIUM salts most closely resemble potassium salts.

Ammonium hydroxid, NH_4OH, is a weak base already considered.

Ammonium carbonate, $(NH_4)_2CO_3$, is used as "smelling salts" and in chemical analysis.

Ammonium chlorid, NH_4Cl, "sal ammoniac," is made by neutralizing ammonia water with hydrochloric acid. It is used in "dry batteries" and as a fertilizer.

Ammonium sulfid, $(NH_4)_2S$, is used in analysis.

Detection. Potassium compounds color a flame pinkish lavender, sodium compounds intense yellow. Looked at through a spectroscope, each flame gives distinct lines that make it possible to detect one element in the presence of another which, in the ordinary flame, may completely hide it. Ammonium compounds may be detected by boiling them with a strong base Ammonia will be liberated if ammonium salts are present.

QUESTIONS

1. In what respects do the alkaline earths resemble the alkalis?

2. Which do you judge to be the most important of the compounds of sodium? of potassium? of ammonium? Why?

3. (*a*) Any lake which has no outlet will become salt. Why?

(*b*) Why does table salt become moist and cake in damp weather?

4. How much sodium hydroxid may be obtained by the electrolysis of 1000 pounds of salt?

5. Explain the chemical changes taking place when sodium is prepared by the electrolysis of sodium hydroxid.

6. Write the chemical equations for the changes taking place when sodium is exposed to the air.

7. Why is sodium nitrate and not potassium nitrate used in the preparation of nitric acid?

8. How much sodium carbonate crystals, $Na_2CO_3 . 10 H_2O$, may be obtained from one ton of pure salt, $NaCl$?

9. In purchasing soda, if the clerk offers you your choice of large clean crystals or the fine powder, which would you take? Why?

10. What is the difference (*a*) between Epsom salt and Glauber's salt; (*b*) between baking soda and baking powder; (*c*) between washing soda and baking soda; (*d*) between soda and caustic soda; (*e*) between soda and potash?

11. If the equation given on page 340 be taken as correct, what will be the volume under standard conditions of the gases generated by the burning of 1 gram of gunpowder. If the gases are not allowed to expand and the temperature of combustion of gunpowder is 1638°, what pressure will be produced? (Assume sp. gr. of gunpowder $= 1$.)

12. If saleratus is substituted for baking soda in cooking, why is it necessary to use a little more of the former?

13. "Muriate of potash" sells for $50 per ton for fertilizer purposes. Assuming that half the price is due to cost of manufacture, transportation, and legitimate profits, what is the highest price that could be paid for carnallite?

14. How could you distinguish between $NaCl$, KCl, and NH_4Cl?

15. How could you distinguish between KF, KCl, KBr, and KI?

16. Why does $NaHCO_3$ react alkaline when $KHSO_4$ reacts acid to litmus?

CHAPTER XXVIII

THE COPPER GROUP

The group. *Copper*, *silver*, and *gold*, constitute the second type of elements belonging to the sodium group. Their resemblance to the alkali metals is not marked, although they are capable of acting with a valence of 1, forming compounds whose formulas correspond to those of the alkali metals. Further, silver and copper form alums, $AgAl(SO_4)_2 \cdot 12\,H_2O$ and $CuAl(SO_4)_2 \cdot 12\,H_2O$, thus showing similarity to the alkali metals as the formula for potash alum, $KAl(SO_4)_2 \cdot 12\,H_2O$, indicates.

The three metals are found free in nature as well as in combination, and are often associated with one another in their ores. They are heavy, soft, malleable metals, but little affected by water or air. They act as weak base-formers, but are much more important in the metallic state than in their compounds. They are all readily obtained from their compounds by the action of reducing agents, especially at higher temperatures. Furthermore, these metals are displaced from solutions of their salts by many other metals.

Replacement or potential series. To illustrate this peculiar action of the replacement of one metal by another: If a piece of iron or zinc is immersed in a solution of copper sulfate or other salt of this metal, copper is precipitated and the iron or zinc dissolves, forming iron or zinc sulfate as the equations show.

$$Fe + CuSO_4 \rightarrow FeSO_4 + Cu \qquad Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

If we write ionic equations and then simplify them, the real action will become more apparent.

$$\mathrm{Fe} + \overset{++}{\mathrm{Cu}} \,.\, \overset{=}{\mathrm{SO_4}} \rightarrow \overset{++}{\mathrm{Fe}} \,.\, \overset{=}{\mathrm{SO_4}} + \mathrm{Cu} \qquad \mathrm{Zn} + \overset{++}{\mathrm{Cu}} \,.\, \overset{=}{\mathrm{SO_4}} \rightarrow \overset{++}{\mathrm{Zn}} \,.\, \overset{=}{\mathrm{SO_4}} + \mathrm{Cu}$$

$$\mathrm{Fe} + \overset{++}{\mathrm{Cu}} \rightarrow \overset{++}{\mathrm{Fe}} + \mathrm{Cu} \qquad \mathrm{Zn} + \overset{++}{\mathrm{Cu}} \rightarrow \overset{++}{\mathrm{Zn}} + \mathrm{Cu}$$

The explanation of this action is that iron and zinc tend to take on an electrical charge and pass into the ionic condition more readily than copper does. Hence, when metallic iron comes in contact with copper ions, the charge passes to the iron, which goes into the ionic condition, while the copper separates as metal. The sulfate ions do not enter the reaction.

Replacement Series

Potassium
Sodium
Barium
Strontium
Calcium
Magnesium
Aluminum
Zinc
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
Hydrogen
Arsenic
Antimony
Bismuth
Copper
Mercury
Silver
Platinum
Gold
Carbon

The relative readiness with which each element goes into the ionic condition has been determined and is shown by the following series, the elements which enter the ionic condition most readily being first in order. Consequently, under proper conditions any metal in this list will be displaced from solutions of its salts by every metal above it and will replace every metal standing below it in the list. This is known as the *Replacement*, or *Potential Series* of the elements; for it is found that the *potential*, or *electromotive force*, of an electric battery depends upon the relative positions of the two elements in this series. The farther they are apart, the greater is the potential of the current produced.

Hydrogen, it will be noticed, occupies an intermediate position in the list. Metals standing above it displace it from its compounds, and may therefore be expected to act on acids or water with the evolution of hydrogen. Such metals are not found free in nature. Metals standing below hydrogen in the series do not replace it. We may expect to find such metals free in nature, for they do not act on water at all, and not on acids with the evolution of hydrogen. If any action with acids takes place, it is usually an oxidation of the metal at the expense of a part of the acid, followed by a secondary reaction in which the oxid is dissolved by the excess of acid. (See pp. 246 and 326.)

Metals standing high in this series form stable compounds from which the element is obtained only with difficulty. Metals low in the series are readily obtained from their compounds, which are relatively unstable.

The ability of some metals to replace others recalls the similar action of chlorin in replacing bromin, iodin, and other elements. The explanation in both cases is identical. Chlorin tends to go into the ionic condition more readily than bromin and the other elements do, the only difference being that we are here dealing with minus and not plus charges of electricity.

The other non-metallic elements do not ordinarily form simple ions.

REPLACEMENT SERIES FOR NON-METALS

Fluorin
Chlorin
Bromin
Oxygen
Iodin
Sulfur

In many of the arts and industries advantage is taken of the ability of one element to replace another in its compounds.

COPPER (Cuprum, Cu—64) is found native in the region about Lake Superior and also occurs in several ores such as *chalcocite*, Cu_2S, *chalcopyrite*, $CuFeS_2$; the basic carbonates — *malachite*, $CuCO_3 . Cu(OH)_2$, and *azurite*, $(CuCO_3)_2 . Cu(OH)_2$; *chrysocolla*, $CuSiO_3$, and *cuprite*,

Cu_2O. The United States produces about two thirds of the world's supply of copper, Montana, Arizona, and Michigan being the leading producers.

Metallurgy. The processes of extracting copper from its ores vary considerably, depending on the nature of the ore. The main ore deposits consist of sulfids of iron and copper and other metals in small amounts. A typical method of handling such ores is to mix with coke and sand and heat in blast furnaces.* This treatment largely separates the iron from the copper by burning iron sulfid to sulfur dioxid and iron oxid, and causing the latter to unite with the sand to form iron silicate — "slag" * — which is drawn off and rejected. The copper sulfid, together with some iron sulfid, melts and concentrates at the bottom of the furnace. This "matte," as it is called, is then poured into a "converter" * in which a blast of air is forced through it to burn out the sulfur and leave the crude metal known as "blister copper."

"Blister copper," about 96 % pure, is refined by electrolysis. It is attached to the positive pole of a dynamo and hung in a solution of copper sulfate. When a current of suitable strength is passed, pure copper is deposited on the cathode. As fast as this action takes place, the sulfate group, SO_4, liberated at the anode, dissolves copper out of the crude product, forming copper sulfate and making the process continuous.

Traces of gold and silver contained in the ores are not dissolved from the crude metal in this process, but fall to the bottom as "anode mud." By proper treatment of this material, gold and silver to the value of millions of dollars are recovered annually. By the oxidation of sulfid ores, copper sulfate is formed and dissolves in the

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* For explanation of the terms used in this description consult paragraphs on the metallurgy of iron (p. 368).

water which collects in mines. Copper is obtained from this source by precipitation by means of scrap iron.

Copper is a lustrous metal possessing an old rose color. Its specific gravity is 8.9. It melts at 1045° to a greenish-blue liquid. Next to silver it is the best conductor of electricity and is much used for this purpose. It is one of the toughest of metals, and may be rolled into thin sheets or drawn into fine wire. Alloyed with other metals, as with tin in *bronze*, copper has been used from very ancient times. *Brass*, the alloy with zinc, is the most important alloy in the industrial world to-day.

Copper dissolves with ease in nitric acid (see p. 326), but only with difficulty even in concentrated hydrochloric or sulfuric acid, forming the corresponding cupric salts. In dry air it is not affected, but in moist air it sometimes becomes covered with a green layer of the basic carbonate. Its soluble compounds are injurious hence the use of copper in kitchen utensils should be avoided.

Compounds. Copper forms two series of compounds. In *cupric* compounds, which are commoner, copper has a valence of 2, as in cupric chlorid, $CuCl_2$, the formula of which is fixed by its vapor density. In *cuprous* compounds it appears from the results of analysis that each copper atom is capable of uniting with only one atom of a univalent element. Thus the composition of cuprous chlorid might be represented by the formula $CuCl$, and its molecular weight would then be $63.6 + 35.5 = 99.1$. But the gas density of cuprous chlorid vapor is 99, which corresponds to a molecular weight of 198 for the compound. The formula for cuprous chlorid must be doubled, therefore, and written $(CuCl)_2$.

Copper compounds are in most cases characterized by their colors. Cupric salts in the hydrated condition are blue or green, and become white or yellow when they lose "water of crystallization."

Oxids. The oxids of copper are cuprous oxid, Cu_2O, and cupric oxid, CuO, both of which occur in nature. Cuprous oxid may be obtained as a red or yellow powder by reducing cupric solutions by means of grape sugar, and is used to impart a ruby color to glass. Cupric oxid is obtained when copper is heated in air. It is a black substance that is easily reduced, and is extensively used in chemical operations.

When a solution of cupric salt is treated with a solution of a hydroxid, cupric hydroxid is formed; this is unstable, and when heated it decomposes, yielding cupric oxid. The equations are:

$$\overset{++}{\mathrm{Cu}} \,.\, \overset{=}{\mathrm{SO}_4} + 2\,\overset{+}{\mathrm{Na}} \,.\, \overset{-}{\mathrm{OH}} \rightarrow \mathrm{Cu(OH)_2} + \overset{+}{\mathrm{Na}_2} \,.\, \overset{=}{\mathrm{SO}_4}$$

$$\mathrm{Cu(OH)_2} \rightarrow \mathrm{CuO} + \mathrm{H_2O}$$

Most copper compounds dissolve in ammonia water owing to the union of copper with ammonia. This radical $(Cu.\ 4\ NH_3)$ forms salts just as copper does. They are all very soluble and are characterized by a deep blue color that is often used as a "*test for copper*."

Copper sulfate, $CuSO_4$, is formed in copper mines by the natural oxidation of the sulfids of copper. Artificially it is made by the same process or by the action of sulfuric acid on copper or its compounds. In the common crystal form it is called *blue vitriol*, or *bluestone*, and has the composition $CuSO_4 . 5\ H_2O$. It is used in calico printing, in battery cells, in spraying plants, in copper plating, and in the preparation of pigments. When heated, copper sulfate crystals lose their water and are changed into a dirty white powder, which, when brought in contact with water, regains the original blue color. This reaction is used as a *test for water*.

A crystal of copper sulfate is shown in the frontispiece.

Copper has a poisonous effect on living things, and is therefore used in spraying fruit trees and plants to kill insects, fungi, etc. *Bordeaux mixture* is very commonly used for this purpose. It is made by mixing slacked lime with copper sulfate solution; it contains cupric hydroxid and calcium sulfate. The growth of vegetable organisms in reservoirs is prevented by the addition of traces of copper salts.

SILVER (Argentum, Ag — 108) occurs native and as the chlorid, or *horn silver*, $AgCl$, but its chief ore is the sulfid, Ag_2S, which is usually found associated with the sulfids of lead, copper, and other metals. Much of the silver produced in this country is obtained from the smelting of lead, copper, and gold ores. The mountainous country of western America is the greatest silver-producing region in the world.

The purer silver ores are reduced by first roasting with salt, whereby the silver is converted into the chlorid; this is then treated with metallic iron, when ferrous chlorid and metallic silver result.

$$2\,AgCl + Fe \rightarrow FeCl_2 + 2\,Ag$$

The mass may then be treated with mercury, which dissolves any silver or gold, forming an amalgam, but leaves other metals unaffected.

The reduction of lead ores containing silver results in an alloy containing much lead and a little silver. On cooling this molten alloy, crystals of pure lead are formed, which may be removed from time to time. This process, known as the *Pattinson process*, results finally in an alloy rich in silver. To this a little zinc is added, and the molten mass is then well churned. Silver, being more soluble in zinc than in lead, leaves the lead almost entirely and dissolves in the zinc, forming an alloy which floats on the lead and may be removed from it. The latter part of the operation is known as the *Parke process*. From the last alloy the silver is obtained by heating, when the zinc is oxidized and vaporized.

Silver is a white metal with a bright luster and a specific gravity of 10.5. Of all metals it is the best conductor of heat and electricity. It is not acted on by air, water, or oxygen, but sulfur even in traces produces a blackening due to the formation of sulfid. When silver is melted, it absorbs oxygen; but no chemical union seems to occur, and the gas is given off again on cooling, the phenomenon being known as "*spitting.*" It reacts readily with nitric acid and concentrated sulfuric acid (see p. 246), but is only slightly acted on by hydrochloric acid.

The silver used for coins is alloyed with 10% of copper. Sterling silver is 92.5% silver and 7.5% copper. This does not sensibly affect its color, but renders it hard enough to stand use without undue wear. As molten silver contracts on cooling, coins of this metal cannot be cast, but must be stamped into shape by heavy machinery. "Oxidized silver" is made by dipping the metal in a solution of sodium sulfid, the darkening being due to the formation of black silver sulfid, Ag_2S.

Compounds. Silver acts with a valence of 1, its compounds suggesting cuprous rather than cupric compounds, but the formulas are not doubled. Under the influence of light, silver salts are easily reduced by organic matter. Hence silver compounds exposed to dust and light generally turn black because of reduction to metallic silver, which, when finely divided, is black. Because of this reaction solutions of silver salts are often used for indelible ink. Most of the latter, however, consist of finely divided carbon.

Silver nitrate, $AgNO_3$, is the only common soluble salt of silver. It is a colorless, crystalline substance formed by dissolving the metal in nitric acid. In solid form it has slight caustic action and is used in surgery under the name of "*lunar caustic.*"

Silver chlorid, AgCl, is a heavy, white substance, forming as a curdy precipitate whenever a solution containing the silver ion, $\overset{+}{Ag}$, is added to a solution containing the chlorin ion, $\bar{\mathrm{Cl}}$. It is so insoluble that traces of either element may be detected by the other, and this reaction is known as a *test* for silver or for chlorids. Exposed to the action of light, silver chlorid darkens owing to a partial reduction. Silver bromid and iodid act in the same way. Upon this fact is based the use of silver in photography.

In **photography** a silver compound, usually the bromid, is precipitated in a solution of gelatine or glue and the liquid then poured over a sheet of glass, a film of celluloid, or a sheet of paper, and allowed to dry and harden in the dark. When exposed in a camera, an image of the object photographed is formed on the plate or film. This is then immersed in a solution of a mild reducing agent known as the *developer*. During this process those portions of the plate which received the strong light from the object are reduced to black, opaque, metallic silver, while that portion of the image which was in comparative darkness remains unchanged. The plate is then placed in the *fixing bath*, a solution of sodium thiosulfate, or "*hypo*." This dissolves the unchanged silver bromid, thus preventing "*fogging*" when the plate is brought into the light. In the *negative* thus prepared a representation of any object or scene is produced, the lights and shadows, however, being reversed (Fig. 75 *a*). To print the picture, another plate or sheet of paper, coated with gelatine and a silver salt, is placed beneath the negative in a printing frame and then exposed to light, developed, and fixed exactly as in the case of the negative. In this *print* the light and shade appear in their true values (Fig. 75 *b*). Some silver prints are *toned* by being placed in a solution of gold chlorid. The silver precipitates the gold and a different colored picture is obtained. These, in brief are the processes employed in photography, though many other modifications

Fig. 75. — Photography

(*a*) The plate, or negative.
(*b*) The print, or positive.

are in use. Blue prints depend upon the action of light in iron salts. (See p. 376.)

GOLD (Aurum, Au — 197) is a very widely distributed element, being found in traces in sea-water. In rocks it is usually found free. The metal is so valuable that often a tenth of an ounce of gold in a ton of ore may be recovered at a profit. The most productive gold fields are in California, Nevada, Alaska, Mexico, Australia, and South Africa, but mines are worked in nearly all localities.

Gold mining is a simple process, consisting for the most part in washing away the rock material from the heavy gold with which it is associated. (See Fig. 76.) In this way the gold is concentrated in a small mass of material. This process has taken place in nature on a large scale, and beds of gravel formed in this way have been found very rich in gold. The water carrying these *concentrates* is run through sluices in the bottom of which are *riffles*; *i.e.*, boxes containing copper plates covered with mercury which dissolves the gold. By heating the resulting alloy the mercury may be vaporized, leaving the gold behind.

Deposits containing too little gold to be handled in this way are treated by the *chlorination* or *cyanid process*. The finely pulverized ore is treated in the former with dilute chlorin water, in the latter with dilute potassium cyanid. Both of these reagents dissolve the gold as the following equations indicate. From the resulting solutions the precious metal may be obtained by electrolysis or by replacement with iron, zinc, or copper.

$$\mathrm{Au} + 3\,Cl \rightarrow \mathrm{AuCl_3}$$

$$2\,\mathrm{Au} + 4\,\mathrm{KCN} + O + \mathrm{H_2O} \rightarrow 2\,\mathrm{KAuC_2N_2} + 2\,\mathrm{KOH}$$

Native gold is never pure, but is always alloyed with varying amounts of other metals, chiefly silver. The gold obtained by the use of mercury contains silver. The two metals may be "parted," or separated, by treating the alloy with aqua regia, when the gold dissolves as auric chlorid, $AuCl_3$, and the silver forms the insoluble chlorid $AgCl$. On filtering and adding a reducing agent to the filtrate, metallic gold is precipitated.

Another method consists in boiling the alloy with concentrated sulfuric acid or with nitric acid, when the silver dissolves and the gold remains unaffected. The process is not satisfactory unless the alloy contains at least three quarters silver. If less silver is present, the alloy is melted and the requisite amount added. This is known as *quartation*. From the silver sulfate solution obtained in "parting" gold, the silver is recovered by introducing sheets of copper. The silver is replaced and the copper dissolves. From this source much of the copper sulfate of commerce is produced.

An electrolytic process for the separation of silver and gold has recently been perfected and is now used in the United States mints.

Gold is a yellow metal with a bright luster. It is quite soft, and is the most malleable of metals. Gold leaf has been made that is only 0.000002 mm. in thickness. The specific gravity of gold is 19.3, nearly twice that of silver. It combines directly with chlorin, and therefore dissolves in aqua regia, but air, water, and most ordinary reagents do not affect it. It is precipitated from solutions of its salts by most reducing agents. The purple powder obtained by adding a solution of stannous chlorid to a solution of a gold salt is used as a pigment under the name of *purple of Cassius*.

Because of its rarity and its properties, gold is used for coinage and for ornaments and jewels. Pure gold, however, is too soft and would soon become worn away. Hence it is usually alloyed with copper. United States gold coins consist of an alloy of 90 % gold and 10 % copper. The composition of the gold used in jewelry is stated in *carats*, pure gold being 24 carats fine.

Compounds. Gold forms compounds of two types, in which the element shows valences of 1 and 3. As a class they are unstable, however, and tend to decompose into the metal when heated slightly. *Auric chlorid*, $AuCl_3$, the most common of the simpler gold salts, is used in

Fig. 76. — Hydraulic Gold Mining in California

toning photographs. In gold plating the double cyanid of potassium and gold, $KAuC_2N_2$, is used, and similar salts are used in silver and copper plating. The object to be plated is connected with the cathode, and sheets of metal, — gold, silver, or copper, as the case may be, — are made the anode. (See Fig. 77.) The anode dissolves as rapidly as metal is deposited on the cathode.

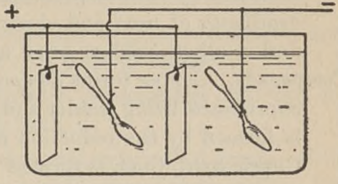


FIG. 77.

SUMMARY

THE COPPER GROUP, consisting of copper, silver, and gold, is considered as the second type of the alkali group. In some of the compounds produced, these elements resemble the alkali metals, but in general the resemblance is slight. These elements are heavy metals, found free in nature. They are not strong base-formers, and their compounds are not very stable.

THE REPLACEMENT OR POTENTIAL SERIES. Because of the readiness with which the different elements tend to go into the ionic condition and take on a charge of electricity, it has been found possible to arrange them in series, any member of which is displaced from its salts by any metal above it, while it will replace any metal standing below it in the series. This is known as the *Replacement Series;* or, because it has been found that the potential of an electric current depends upon the distance in this series between the two elements, it is known as the *Potential Series.*

Hydrogen stands below the middle of the series, hence will be replaced by all the metals above it. Such metals will act on acids (frequently on water also) and liberate hydrogen, hence they are not found free in nature. They form stable compounds from which they may be obtained only with difficulty. Metals standing below hydrogen in the series do not liberate hydrogen from acids or water. They form compounds from which the metal is readily obtained, hence are found free in nature.

Copper, silver, and gold stand near the bottom of the series, while the alkali metals stand at the top.

COPPER is found free in nature and in a number of compounds, chief of which are the sulfids, carbonates, and silicates. The metal is obtained by various processes, depending on the ore. It is a fine conductor of heat and electricity and is used in electrical work and in alloys, such as brass and bronze.

Compounds. Copper forms a *cuprous* and a *cupric* series of compounds, cupric salts being stabler and more common. Cuprous oxid, Cu_2O, is formed by the reduction of cupric compounds by grape sugar. Cupric oxid, CuO, is formed by heating copper.

Cupric sulfate crystallizes as the hydrate, $CuSO_4 \cdot 5H_2O$, called blue vitriol or bluestone. It is the common starting point in making many other copper compounds.

SILVER is obtained mostly from Ag_2S, often associated with PbS. In the latter case, the two metals are reduced together and are then separated by Pattinson's and Parke's processes. Silver is used for ornaments, coins, etc. Its compounds are sensitive to the action of light, especially in the presence of organic matter, and are therefore used in photography. Silver nitrate, $AgNO_3$, is used in medicine as *lunar caustic*.

GOLD is usually found native. Its separation from the rocky material which accompanies it is accomplished by mechanical processes, such as agitating the crushed material with water and then taking out the heavy gold with mercury; or by chemical means, as in the chlorination and the cyanid processes. Gold resists the action of most chemicals, and its attractive appearance, scarcity, and durability make it valuable. In its compounds it acts with valences of 1 and 3. Auric chlorid, $AuCl_3$, is commonly met with, as is also the double cyanid $KAuC_2N_2$, used in electroplating.

QUESTIONS

1. Compare copper, silver, and gold in their physical and chemical properties.

2. To what properties do silver and gold owe their value? If they should become cheaper, to what additional uses could each be put?

3. What is formed when copper dissolves in each of these substances: nitric acid; concentrated sulfuric acid; aqua regia?

4. Why do dilute solutions of all copper salts have the same color? The dry salts often differ in color.

5. Why do solutions of blue vitriol, $CuSO_4 . 5 H_2O$, react slightly acid to litmus?

6. What is sterling silver; oxidized silver; german silver?

7. Why are silver spoons tarnished by eggs and mustard, and silver coins by matches in the pocket or a piece of rubber?

8. Explain the action of (*a*) light in photography; (*b*) the developer; (*c*) "hypo"; (*d*) the toning bath.

9. A silver dollar contains 10 % alloy and weighs 26.5 grams. How much is the silver in it worth? How could you separate it from the copper?

10. Why would you not expect silver to decompose water?

11. An electric current that will deposit 6.3 grams of copper in a given time will deposit what amount of silver in the same time?

12. Jewellers tell gold from brass by applying nitric acid. What is the reaction in each case? How would you expect 10 K gold to differ from 18 K gold in this test? (10 K means 10 carats; 18 K means 18 carats.)

13. Which metal would you expect to be more permanent in the atmosphere, zinc or tin? Why? Which would you expect to be more durable, galvanized iron or tin plates, if the coating of metal on the iron is the same thickness in each case?

CHAPTER XXIX

THE IRON GROUP

The iron group of metals differs in one important respect from all the other groups of elements. If all the elements are arranged in series according to their atomic weights, the members of any group of elements so far considered occur singly. The members of the iron group occur in threes, however. Taking as an illustration all the elements whose atomic weights lie between 50 and 60, vanadium, 51, belongs to the nitrogen group; chromium, 52, to the sulphur group; and manganese, 55, to the chlorin group; but *iron*, 56, *cobalt*, 59, and *nickel*, 59, are all in the iron group. So also *ruthenium*, 102, *rhodium*, 103, and *palladium*, 106; and later *osmium*, 191, *iridium*, 193, and *platinum*, 195, are members of the iron or platinum group, as it is often called.

Of these nine elements, iron, ruthenium, and osmium resemble one another; cobalt, rhodium, and iridium show similarities; and nickel, palladium, and platinum are silver-white metals which do not tarnish in the air and show other close resemblances.

Iron, nickel, and platinum are the important members of this group; the others are generally very rare. Pure cobalt ores are not often found but the element sometimes occurs in nickel ores, and in purifying the latter some cobalt is obtained. There is no industrial use for the metal, however, and so practically all of it finds its way into chemical laboratories where it is better known than many more common substances.

IRON (Ferrum, Fe—56) finds such varied and important uses that it may well be considered the most important mineral product of the earth. Without iron it is questionable whether the human race could have attained its present stage of development, and the people of this country owe much of their prosperity to the occurrence of rich and available deposits of iron ore within their boundaries.

Except in meteorites, iron occurs rarely in the free state. In combination it is found everywhere in rocks and soils and in mineral waters. Its most important compounds are the *oxids*, the *hydroxids*, and the *carbonate*, which are useful as ores. *Iron pyrites*, FeS_2, *copper pyrites*, $CuFeS_2$, and *arsenical pyrites*, $FeAsS$, are common iron minerals, yet are seldom used as ores; for the cost of obtaining iron from these compounds in a state of sufficient purity is too great.

Iron ores. *Hematite*, Fe_2O_3, when pulverized, forms a red powder which is used as a paint (Venetian red) and as a polishing agent (rouge). Extensive deposits are found in many states, Michigan and Alabama being the chief producers. It is an important ore.

Limonite is found in deposits in swamps and in strata that were in former ages marshy land, and is often called *bog iron ore*. It occurs in all soils as a brown stain, and often accumulates around springs. It is a soft, reddish-brown substance, resembling iron rust in composition, both these substances being ferric hydroxid, $Fe(OH)_3$, which has lost some water.

Magnetite, Fe_3O_4, is the ore richest in iron, but it is less common than the others. It is hard, black, glistening, and magnetic, being the natural magnet, called *lode-stone*. New York and New Jersey are the largest producers.

Siderite, or *spathic iron*, which is the carbonate, $FeCO_3$, is another valuable iron ore.

Reduction of iron ores. Theoretically, the metallurgy of iron is simple, the ore being reduced by means of coke or charcoal. On account of differences in the ores, many modifications are in use. Some ores must first be roasted in the air, to burn out any sulfur they may contain or to drive off water or carbon dioxid. In this process the ore is converted into the oxid, Fe_2O_3, and the roasted ores are then reduced in huge blast furnaces, which will often handle 1000 tons of ore a day. A simple form of blast furnace is shown in Fig. 78.

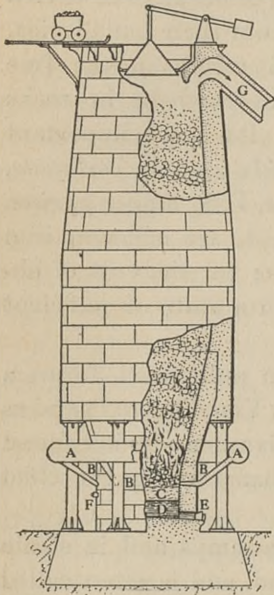


Fig. 78.

Into the top of the furnace loads of coke, iron ore, and a flux are dumped. A *flux* being a substance added for the purpose of combining with and removing the impurities of an ore, the nature of the flux required is determined by a chemical analysis of the ore. If the ore contains silicates or sand, limestone is added; and when limestone or dolomite is present, sand is used as the flux. The idea is to form an easily fusible silicate, which is known as the *slag*. The chemical action is as represented by the equation:

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$

The furnace, once lighted, is kept going night and day. The draft is aided by compressed air which enters through *A*, Fig. 78, and is led into the bottom of the furnace by the pipes, *B*, *B*, *B*, called *tuyères.* The carbon burns to carbon monoxid, which, being gaseous, penetrates the heated ore and reduces it.

$$Fe_2O_3 + 3\,CO \rightarrow 2\,Fe + 3\,CO_2$$

The reduced iron and the slag melt and sink to the bottom of the furnace, the slag, *C*, floating on the molten iron, *D*, and protecting it from oxidation by the blast. As the iron accumulates, it is drawn off at *E* from time to time into molds, where it solidifies as *pig iron.* The slag is drawn off at *F*. As the coke, ore, and flux are used up, fresh quantities are added at the top, and the process is thus made continuous. The life of a blast furnace ranges from 2 to 20 years.

Since the gas that escapes from the top of the furnace at *G* contains a considerable proportion of unaltered carbon monoxid, it is led away and burned. The heat evolved in its combustion is used to heat the air that is forced through the tuyères, or, often, to run gas engines.

Varieties of iron. *Pig iron* is usually about 90 % pure, and contains nearly 5 % carbon, about as much silicon, together with sulfur, phosphorus, manganese, and other impurities in small amounts. All forms of commercial iron contain some carbon, which affects the properties of the metal decidedly. This carbon is either free or combined. The carbon in combination is in the form of *iron carbid*, Fe_3C, and when such iron is treated with acids its carbon is given off in combination with hydrogen; but after the same treatment uncombined carbon is left as graphite. There are three main varieties of iron:

Cast iron, usually containing 2.5 to 3 % of carbon.

Steel, usually containing 0.5 to 1.5 % of carbon.

Wrought iron, containing usually less than 0.5 % of carbon.

These varieties pass into each other by insensible gradations as the amount of carbon varies.

Cast iron differs but little in its composition from the purer forms of pig iron. It is hard, rigid, and brittle, combining great firmness with little elasticity. Hence it is easily broken by a blow or too great a strain. When heated it does not soften gradually, but melts sharply when its fusion point (about 1200°) is reached; hence it cannot be welded. It expands on solidifying, and hence is used in castings. Much of its carbon is present in the form of graphite.

Wrought iron is made from pig or cast iron by oxidizing and thus removing a part of its carbon and other impurities, the process being technically known as *puddling*. The cast iron is melted in furnaces lined with oxids of iron and is subjected to the action of drafts of hot air while being continually stirred. Carbon, silicon, and phosphorus are gradually oxidized and pass off as gases or unite with the lining of the furnace to form slag. The mass of spongy wrought iron thus obtained is hammered or rolled into shape for commercial purposes.

Wrought iron differs considerably from cast iron in properties. It is soft, tough, fibrous, malleable, and ductile. As the temperature is raised, it grows continually more and more plastic until a liquid condition is reached at about 1600°. At a red heat it may be readily *welded*, *i.e.* joined by hammering or great pressure. The physical properties of the wrought iron are considerably influenced by the nature of the impurities in it. Thus, sulfur imparts the defect of being brittle when hot, and phosphorus renders it brittle when cold. Hence the removal of these substances is a matter of importance.

Steel, being intermediate in composition between cast iron and wrought iron, may be made from wrought iron by adding carbon, or from cast iron by oxidizing out a part of the carbon. Several processes are in use.

1. In the *cementation process*, bars of wrought iron are placed in boxes of fire brick, the spaces between the bars being filled with powdered charcoal. The whole is then heated for several days at a temperature considerably below the melting point of the iron. The iron takes up carbon and is converted into a steel of very fine quality, which is used for various kinds of instruments.

2. In the *open hearth process*, scrap iron and pig iron are melted in a reverberatory furnace in the proper proportions to form steel; or pig iron and an iron oxid ore are heated together, the oxygen from the ore burning the carbon and silicon from the cast iron. A reverberatory furnace (Fig. 79) is one in which the material is heated by reflection from the walls and roof of the furnace. The fire at *A* heats the ore at *B*, the gases then passing up the stack *D*. *C* is the charging hole. This process has come into extensive use because it is cheaper than the Bessemer process and the steel produced is superior in quality. A reverberatory furnace will make several hundred tons of steel in one charge, the time required being six to eight hours. A Bessemer converter will handle five to ten tons every twenty minutes.

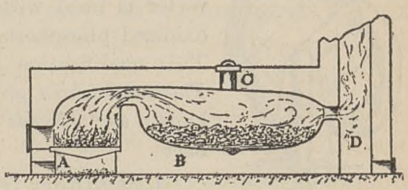


FIG. 79.

3. The *Bessemer process* is employed in the manufacture of the cheap steel used for rails. It depends on the fact that when a current of hot air is blown through molten pig iron, the heat produced by the oxidation of the impurities is sufficient to keep the whole mass liquid until it is entirely converted into steel or wrought iron. The operation is carried on in egg-shaped furnaces, called *converters* (Fig. 80), the compressed air entering

through *A* and being led through the pipe into the bottom of the converter. The process is continued until the cast iron is approximately changed to wrought iron. An iron rich in carbon, called *spiegel iron*, is then added in sufficient quantity to convert the wrought iron into steel, and the molten mass is then poured into molds, after which the hot metal may be rolled, drawn, or fashioned as desired.

The ordinary Bessemer process does not remove the phosphorus. To accomplish this end, the converter is lined with lime, which unites with the oxidized phosphorus, forming calcium phosphate. This modification is called the *basic lining* or *Thomas-Gilchrist process.* The calcium phosphate, known as "*Thomas slag,*" is used in making fertilizers.

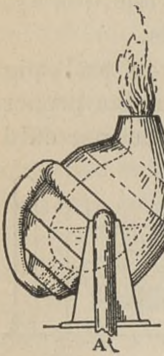


FIG. 80.

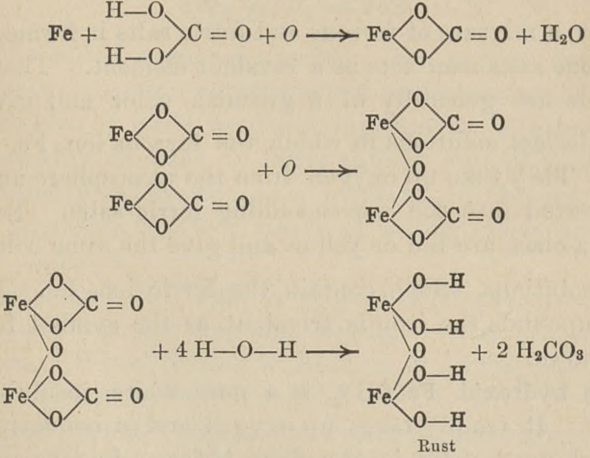
Steel differs from other varieties of iron mainly in its hardness and elasticity, which are regulated by a process called *tempering.* The steel is heated very hot and is then suddenly cooled by being plunged into water. After this treatment it is very brittle and elastic, and can be made so hard that it will cut diamond. For various uses the hardness and brittleness are partially removed by heating the steel moderately and then allowing it to cool.

Pure iron is not obtained by any of the commercial processes, the best grade being that used in piano wire, which contains about 99.7 per cent of iron. Pure iron may be made by reducing certain salts of the metal with hydrogen. It is a dark powder that inflames spontaneously in the air, if the temperature of the reduction has been kept low. In massive form it has a silver-white luster, a specific gravity of 7.84, and melts at about 2000°. Iron may be rendered magnetic, but it does not permanently retain its magnetism except in the case of steel.

When heated to a high temperature in air or oxygen, iron burns to the magnetic oxid, Fe_3O_4. The black scales which fly off from heated iron when the blacksmith hammers at his anvil, have this composition. The same product results from the action of red-hot iron on steam.

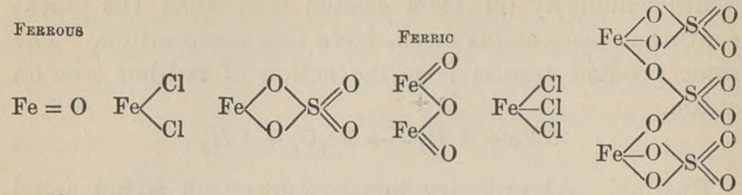
$$3\,\mathrm{Fe} + 4\,H_2O \rightarrow \mathrm{Fe_3O_4} + 4\,H_2$$

Rusting. At ordinary temperatures iron is not acted on by dry air, but in moist air it becomes converted into *rust.* Carbon dioxid acts as a catalytic agent and greatly hastens the action, which may be represented by the following equations:



Rusting is a most serious defect of iron, and to prevent it many devices are in use. In *galvanized iron* a coating of zinc, and in *tin plate* a covering of tin, protect the iron from corrosion. For the same reason iron is painted or varnished. Another preventive of rust is to expose the iron to superheated steam, whereby it becomes coated with a film of the oxid, Fe_3O_4, which serves as a protection.

Compounds of iron. The metal and its oxids, FeO and Fe_2O_3, dissolve readily in most acids, forming salts which are of two types, as the following typical formulas indicate:

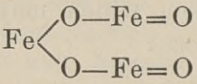


Ferrous

oxid chlorid sulfate

Ferric

oxid chlorid sulfate

The magnetic oxid of iron, Fe_3O_4, has the structure indicated by the formula  $Fe\begin{matrix} \diagup O-Fe=O \\ \diagdown O-Fe=O \end{matrix}$. On treatment with acids, a mixture of ferrous and ferric salts is formed.

In **ferrous** salts iron acts as a bivalent element. These compounds are generally of a greenish color and give rise to colorless solutions in which the ferrous ion, $\overset{++}{Fe}$, is present. They take up oxygen from the atmosphere and are converted into the corresponding **ferric** salts. The latter, as a class, are red or yellow and give the same color to their solutions, which contain the ferric ion, $\overset{+++}{Fe}$. In these compounds the iron is trivalent, as the symbol for the ion shows.

Ferrous hydroxid, $Fe(OH)_2$, is a pure white, insoluble substance. It readily takes up oxygen and is converted into a dark green body intermediate between ferrous and ferric hydroxids. So rapid is this action that, unless special precautions are taken, no indication of a white body is seen, but only the green precipitate is obtained. On standing in the air this is converted into **ferric hydroxid**, $Fe(OH)_3$, which appears as a red, flocculent precipitate when ferric solutions are treated with solutions containing hydroxyl ions.

Ferrous chlorid, $FeCl_2$, is obtained by treating iron with hydrochloric acid, the hydrogen which is liberated preventing the formation of ferric chlorid. When a solution is allowed to stand exposed to the air, it oxidizes to **ferric chlorid, $FeCl_3$**, yellow or red in color. The same change is brought about by the action of chlorin or other oxidizing agents. "*Tincture of iron*" is ferric chlorid dissolved in alcohol.

Ferrous sulfate, $FeSO_4 \cdot 7\,H_2O$, is a light green salt commonly called *green vitriol* and sometimes *copperas*. It is formed in large quantities by the oxidation of iron pyrites in the air.

$$FeS_2 + 2\,O_2 \rightarrow FeSO_4 + S$$

As mines commonly contain iron pyrites, ferrous sulfate is a common constituent of their drainage water. It may also be made by dissolving iron in sulfuric acid. It is readily oxidized to **ferric sulfate, $Fe_2(SO_4)_3$**, and finds extensive application as a mordant, in the manufacture of pigments, and as a means of killing molds and insects on plants.

Ferrous sulfid, FeS, is a black substance obtained by melting together iron and sulphur in the proper proportions. When treated with acids, it decomposes with the evolution of hydrogen sulfid.

Iron pyrites, FeS_2, or *fool's gold*, is found abundantly in nature as yellow, cubical crystals. It is used as a source of sulfur, but not to any extent as an iron ore.

Cyanogen compounds. When iron is heated with charcoal, refuse animal matter, and potassium carbonate, the residue on treatment with water yields **potassium ferrocyanid, $K_4FeC_6N_6$**, or *yellow prussiate of potash*. On treatment with chlorin this is changed to **potassium ferricyanid, $K_3FeC_6N_6$**, or *red prussiate of potash*. These substances are used in the industries, in making pigments and bluing. They are not poisonous, and hence do not contain the deadly cyanid ion, $\overline{\mathrm{CN}}$, but instead the complex ions, $(\mathrm{Fe}\overset{\equiv}{\overline{\mathrm{C}}}_6\mathrm{N}_6)$ and $(\mathrm{Fe}\overset{\equiv}{\mathrm{C}}_6\mathrm{N}_6)$.

Iron salts treated with ferrocyanid and ferricyanid give reactions much used as *tests* for iron, the colors produced being indicated by the diagram (Fig. 81).

Ferric ferrocyanid, $\mathrm{Fe_4(FeC_6N_6)_3}$, is *Prussian blue*; and **ferrous ferricyanid**, $\mathrm{Fe_3(FeC_6N_6)_2}$, is *Turnbull's blue*. Both are used as pigments.

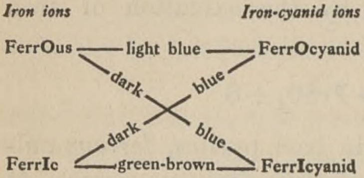


Fig. 81.

Blue prints. In the presence of reducing matter ferric salts are reduced to the ferrous condition by the action of light. Upon this reaction the process of making blue prints depends. A mixture of potassium ferricyanid with a ferric salt is applied to sheets of paper, coloring them brownish green. When exposed to light, the ferric salt is reduced to the ferrous condition. This unites with the ferricyanid to form ferrous ferricyanid, which is deep blue and insoluble. When the paper is immersed in water, the soluble mixture of salts washes away, leaving the paper white where no light has struck it, but deep blue where the light has acted.

With thiocyanates ferric salts produce a blood-red color much used as a test for ferric iron. Ferrous salts give no color with the reagent.

Nickel and **cobalt** are metals bearing a close resemblance to iron and to each other. The most striking difference is the colors of the hydrated salts, which with cobalt are generally red or pink, and in the case of nickel, green. Both metals are found in nature associated with sulfur and arsenic, and in meteors alloyed with iron. Like iron, they are magnetic.

Cobalt and its compounds find little industrial use, whereas nickel is in great demand. The latter is a white, hard metal, capable of taking a fine polish. It is not attacked by the atmosphere, hence is used in nickel-plating and in alloys. German silver consists of nickel, copper, and zinc. Five-cent coins of the United States, "nickels," are an alloy of nickel and copper. Of late years the importance of nickel has much increased, owing to its use in making certain kinds of hard steel such as are used in the construction of battleships, etc.

Cobalt chlorid, $CoCl_2 \cdot 6\ H_2O$, is a soluble red salt producing pink solutions. The "water of crystallization" may be driven off by gentle heating, thus forming the anhydrous chlorid, which is blue. Hence solutions of cobalt chlorid are sometimes used as a "sympathetic ink," changing color when warmed, but returning to the original shade as water is absorbed from the atmosphere. This color change may be used as a *test for water*.

Nickel sulfate, $NiSO_4 \cdot 7\ H_2O$, is the most important nickel salt.

PLATINUM (Pt — 195) is found associated with gold in many places, but the only sources of importance are in the Ural Mountains. In its natural state platinum is alloyed with the related metals *osmium*, *iridium*, *ruthenium*, and *rhodium*. All these metals are characterized by their great specific gravity, their extreme hardness, their high melting points, and their power of resisting the action of common reagents. Osmium and iridium are fusible only in the electric furnace. An extremely hard alloy of these metals is used in tipping gold pens.

Platinum is a grayish-white metal somewhat resembling steel in appearance. It is the most ductile of all metals, has a specific gravity of 21.5, and melts only in the flame of the oxyhydrogen blowpipe or in the electric furnace. It is not affected by air, water, or acids, but dissolves in aqua regia and chlorin water, and is somewhat acted on by molten caustic alkalis and their nitrates.

Finely divided platinum has to a remarkable degree the power of causing gases to condense on its surface. Thus it absorbs more than 200 times its volume of oxygen, and hence, by increasing the concentration, is often used to bring about oxidation, as in the manufacture of sulfuric acid by the contact process, and in automatic gas lighting appliances.

In the form of wire or foil, or made into crucibles and dishes, the metal is of great use to the chemist, as it is unaffected by most ordinary reagents and does not melt. Since it expands, when heated, to about the same degree as glass, it is largely used in incandescent lights as a means of conducting electricity through the glass bulb. The supply of platinum is not equal to the demand, and its market price has been constantly increasing.

Like copper, silver, and gold, platinum in its salts is not nearly so important as in the metallic condition. Platinum dissolves in aqua regia, forming *platinum chlorid*, $PtCl_4$. This unites readily with hydrochloric acid to form *hydrochlorplatinic acid*, H_2PtCl_6. The potassium and the ammonium salts of this acid, K_2PtCl_6 and $(NH_4)_2PtCl_6$, are rather insoluble and may be used as a means of precipitating potassium and ammonium ions from solution.

SUMMARY

THE IRON GROUP contains the elements in threes: iron, cobalt, and nickel; ruthenium, rhodium, and palladium; osmium, iridium, and platinum. Iron, nickel, and platinum are the most important.

IRON is widely distributed in compounds, and the chief ores are *hematite*, *limonite*, *magnetite*, and *siderite*. The ores are first roasted and are then mixed with carbon and a flux and reduced in blast furnaces. The carbon forms carbon monoxid, which reduces the ores, and the flux unites with impurities and forms slag. The molten iron is run into molds and called *pig iron*. Commercial iron always contains carbon, either free as graphite, or combined as iron carbid, Fe_3C.

Cast iron contains 2.5 % of carbon or more. It is hard and brittle and, because it expands on solidifying, it is used for castings.

Wrought iron contains 0.5 % of carbon or less. It is made by heating cast iron in air until its carbon is oxidized. It is malleable and tough and melts with difficulty.

Steel stands between cast iron and wrought iron in composition. It is made

(*a*) From wrought iron by the *cementation* process.

(*b*) By heating cast iron together with wrought iron or pure iron ores in the *Siemens-Martin* or open hearth process.

(*c*) By the *Bessemer* process, in which cast iron is first converted into wrought iron and the amount of carbon necessary to make steel is then added in the form of spiegel iron.

Steel is elastic, may be tempered, and forms permanent magnets. The metal is acted on rather easily by acids and other reagents. Its worst fault is rusting, which can be prevented only by a protective covering.

Compounds. Iron forms two series of compounds: *ferrous*, which are green and tend to oxidize; *ferric*, which are yellow or red and are stable. Ferric oxid, Fe_2O_3, is the commonest oxid, and is similar to rust in composition. Ferrous chlorid is formed when iron dissolves in hydrochloric acid. Ferrous sulfate, when crystallized, is known as *green vitriol* or *copperas*.

NICKEL is not readily attacked by the atmosphere, and so is used for plating other metals. It is important in making nickel steel.

PLATINUM is found chiefly in the Ural Mountains, and the supply does not equal the demand. It is used as a catalyzer in many processes, notably the contact process for sulfuric acid, in electric lights, and in laboratories in the form of wire, foil, crucibles, etc. Hydrochlorplatinic acid is the only important compound.

QUESTIONS

1. Why would you not expect iron to occur free in nature?

2. How many liters of hydrogen would result from the action of steam on 100 grams of iron?

3. Compare the composition and properties of the three varieties of iron. Why should cast iron, wrought iron, and steel, not be regarded as allotropic forms of the element?

4. Metallurgical processes may be divided into two distinct types. Iron and zinc illustrate one class; aluminum and sodium the other. State briefly these processes.

5. What is "roasting"? What ores require "roasting" and what is accomplished by this treatment?

6. What is a flux? If an iron ore is found in nature associated with quartz, what flux would you use? Suppose the iron ore "carries" dolomite, what would you use as a flux?

7. How much carbon would be required to reduce 1 ton of pure hematite? How much pig iron would be formed?

8. Write equations expressing the reactions taking place in making a blue print.

9. Write equations showing how you would prepare ferric sulfate from iron; ferrous sulfate from ferric oxid.

10. Which metal would you expect to be more permanent in the atmosphere, nickel or tin? Why?

CHAPTER XXX

THE CHROMIUM GROUP AND MANGANESE

The group. Four elements, *chromium* (Cr — 52), *molybdenum* (Mo — 96), *tungsten* (W — 184), and *uranium* (U — 239), belong to the second type of the sulfur group. They show marked differences from, and also strong similarities to, sulfur. In the free state these elements are much more metallic than sulfur and little resemblance can be noted. When the elements are highly oxidized, however, strong similarities are evident. Thus, chromic acid and sulfuric acid are much alike.

These elements unite with oxygen to form very stable compounds, from which the metals may be obtained only with difficulty. Their chief use is in alloys with iron in making hard, resistant steels. Incandescent bulbs with a filament of tungsten give much more light for the same amount of electricity than can be obtained from a carbon filament. All are comparatively rare. The most common one, chromium, will be considered in detail.

Manganese is an element which in many respects seems unlike any other known element, but is usually considered as belonging to the second type of the chlorin group. Since it shows some similarity to chromium, it will be considered along with the above elements.

CHROMIUM (Cr — 52) is found in nature chiefly in the minerals *crocoisite*, $PbCrO_4$, and *chrome iron ore* or *chromite*, $FeCr_2O_4$. The latter is the chief source from which chromium compounds are prepared. The name chromium comes from the Greek noun which signifies "color," for compounds of this element are generally highly colored.

Metallic chromium is obtained by the reduction of its oxid by carbon or aluminum at high temperatures, the Goldschmidt method being most satisfactory. Chromium oxid, Cr_2O_3, is mixed with aluminum filings and ignited. The aluminum unites with the oxygen and sets free chromium. The latter has a white, metallic lustre, is difficultly fusible, and is very hard.

Chromium shows four different valences, forming compounds very different in character. When the element shows a valence of 2, it acts as a base-former, giving rise to bodies which, when exposed to the air, oxidize rapidly to compounds of trivalent chromium; hence the former are rarely met with. Compounds of trivalent chromium are stable, green or purple in color, and in them the chromium acts as a weaker base-former than when it shows a valence of 2. These substances may be oxidized until the chromium shows a valence of 6, in which condition it acts as an acid-former, giving rise to chromic acid and its salts, which are yellow or red. Further oxidation forms perchromic acid, in which chromium shows a valence of 7. In these compounds oxygen acts true to its name of "acid-maker," for in proportion as chromium is oxidized, its compounds exhibit acid properties, as the following table shows:

PROPERTIES OF CHROMIUM

VALENCE	OXID	CHARACTER	TYPICAL COMPOUND
2	CrO	Base-former	$CrCl_2$, chromous chlorid
3	Cr_2O_3	Weak base-former	$CrCl_3$, chromic chlorid
6	CrO_3	Acid-former	H_2CrO_4, chromic acid
7	(Cr_2O_7)*	Strong acid-former	$HCrO_4$, perchromic acid

Base-forming chromium. *Chromic oxid*, Cr_2O_3, is a green powder much used in making paints. The corresponding hydroxid, $Cr(OH)_3$, is a greenish gray, gelatinous substance when obtained by precipitation from solutions of

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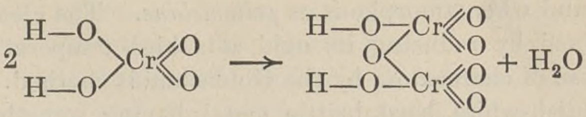
* Unknown.

chromium salts. By treating either of these substances with the appropriate acids, salts may be obtained. The sulfate, $Cr_2(SO_4)_3$, is used in tanning leather and as a mordant in dyeing. Since it takes up water from the air, it cannot be conveniently handled, and so is frequently converted into *chrome alum*, $KCr(SO_4)_2 . 12 H_2O$. This is a purple substance which is stable in the air, is isomorphous with ordinary alum, and crystallizes from solution in beautifully regular, eight-sided crystals. (See frontispiece.)

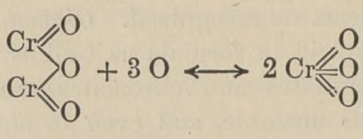
Acid-forming chromium. Strong oxidizing agents convert Cr_2O_3 into CrO_3, which is the anhydrid of chromic acid. It is a dark red, crystalline substance that is very soluble in water, uniting with it to form acids of which two common forms are recognized. *Chromic acid*, H_2CrO_4, is like sulfuric acid in formula as well as in many of its reations, and sulfates and chromates are isomorphous. The free acid is unstable, and even in aqueous solution separates water and forms dichromic acid, as the equation indicates:



Dichromic acid is only a little more stable than chromic acid. Whenever the attempt is made to get it from solution it gives up water as chromic acid does, and only the anhydrid results. For this reason the oxid, CrO_3, is sometimes called chromic acid. Dichromates of the alkali metals are orange-red substances, *potassium dichromate*, $K_2Cr_2O_7$, and *sodium dichromate*, $Na_2Cr_2O_7$, being the most important. With these exceptions few dichromates are known, for, as it is neutralized the acid takes up water and forms chromates rather than dichromates. *Potassium chro-*

mate, K_2CrO_4, and *sodium chromate*, Na_2CrO_4, are lemon yellow, soluble substances. Most other chromates are insoluble. All are highly colored, several being used as pigments. *Chrome yellow* is the insoluble lead salt, $PbCrO_4$, while *chrome orange* is $PbO . PbCrO_4$.

All of the highly oxidized compounds of chromium part with some of their oxygen quite readily, and hence are good oxidizing agents. The color changes from reddish yellow to green as they give up their oxygen and break down into compounds of base-forming, trivalent chromium. The color change is reversed as the latter are oxidized to the acid-forming state. The following equation expresses the essential change, the conditions of the experiment determining which way the reaction shall go:



MANGANESE (Mn — 55) occurs in nature chiefly as the dioxid, MnO_2, which when crystalline is known as *pyrolusite*, and when amorphous as *psilomelane*. The element is obtained by reducing its oxid at a high temperature by the use of charcoal or by the Goldschmidt method. It is a reddish-white, hard, brittle metal, having something of the appearance of cast iron. In its alloys, as *spiegel iron*, it is important in the steel industry.

Like chromium, manganese shows many valences, and the character of the compounds formed varies accordingly. When it shows a valence of 2, it acts as a base-former, giving rise to salts which are of a light pink color and are relatively stable. A few compounds are known in which manganese is trivalent and acts as a weak base-former, but they are unimportant. Manganese with a valence of 4 forms one compound, MnO_2, which will unite with either acids or bases, thus acting either as a base-former or as an acid-former. Manganese showing a valence of 6 forms manganic acid, H_2MnO_4, and its salts, which are generally unstable and of little importance. In permanganic acid, $HMnO_4$, and its salts, manganese shows a valence of 7 and acts as a strong acid-former. The change in character of the compounds as the element is oxidized is shown in the following table:

Properties of Manganese

Valence	Oxid	Character	Typical Compound
2	MnO	Base-former	$MnCl_2$, manganous chlorid
3	Mn_2O_3	Weak base-former	$MnCl_3$, manganic chlorid
4	MnO_2	Very weak base-former	$MnCl_4$, manganese tetrachlorid
		Very weak acid-former	$CaMnO_3$, calcium manganite
6	(MnO_3)*	Acid-former	H_2MnO_4, manganic acid
7	Mn_2O_7	Strong acid-former	$HMnO_4$, permanganic acid

Base-forming manganese. Of the salts of manganese acting as a metal, those in which the element is divalent are most important. These salts resemble those of ferrous iron, except that the color is pink.

The only compounds of trivalent manganese that need be mentioned are the brown manganese alums, such as $KMn(SO_4)_2 \cdot 12\,H_2O$.

Manganese dioxid, or black oxid of manganese, contains tetravalent manganese and is one of the most important compounds of this element. It is employed in the preparation of oxygen, in the manufacture of the inferior grades of glass to counteract the green color due to iron, and in the manufacture of colored glass to impart an amethyst shade. Its most important use, however, is in the preparation of chlorin.

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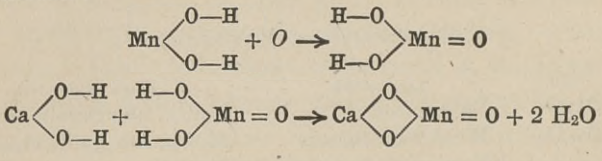
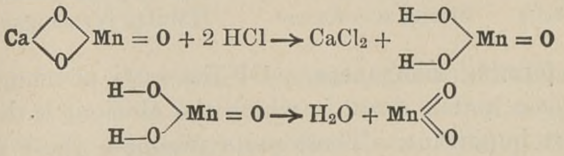
* Unknown.

In preparing chlorin, manganese is left in the form of sulfate or chlorid, compounds valueless so far as the further production of chlorin is concerned. Many processes have been devised with the object of economically transforming these manganous salts into some compound that may again be used. The most successful of these is *Weldon's process.* The manganous salts are treated with slacked lime, which converts them into manganous hydroxid. By the action of hot air this is oxidized to the tetravalent condition and then unites with more calcium hydroxid to form calcium manganite, as the equations indicate:



On treating calcium manganite with hydrochloric acid, manganous acid is set free, which then decomposes into water and manganese dioxid, the anhydrid of manganous acid, as the equations show:



By this process manganese may be used repeatedly to liberate chlorin. In calcium manganite, manganese is acting as a weak acid-former.

Tetravalent manganese acting as a base-former is known in a few compounds, such as $MnCl_4$. These are very unstable; $MnCl_4$ breaks down into $MnCl_2$ and chlorin. This is the reaction on which the production of chlorin from manganese dioxid and hydrochloric acid depends, as the equations indicate:

$$\mathbf{MnO_2} + 4\,HCl \rightarrow 2\,H_2O + MnCl_4$$
$$MnCl_4 \rightarrow MnCl_2 + Cl_2$$

Acid-forming manganese. When manganese is oxidized to a valence of 6, it forms *manganic acid*, H_2MnO_4, which resembles chromic acid. It is known only in its salts, all of which are bright green. One test for manganese is to heat it in a bead of sodium carbonate and potassium nitrate, when, if manganese is present, a green color develops. In this reaction the nitrate oxidizes the manganese to manganic acid, which unites with the sodium carbonate to form sodium manganate, as the equation shows:

$$\mathbf{Mn(OH)_2} + \mathbf{Na_2CO_3} + 2\ O \rightarrow \mathbf{Na_2MnO_4} + CO_2 + H_2O$$

Manganates are stable only in the presence of alkalis. When acidified, the manganic acid set free changes into permanganic acid according to the equation:

$$3\ H_2MnO_4 \rightarrow 2\ HMnO_4 + \mathbf{MnO_2} + 2\ H_2O$$

As this change occurs, the green color of the manganates gives place to the purple of permanganates. This change may be caused by the absorption of carbon dioxid from the air, hence solutions of manganates are known as "*chameleon liquids*."

In *permanganic acid*, $HMnO_4$, manganese is oxidized up to a valence of 7 and in this state forms a strong acid. It shows considerable similarity to perchloric acid, $HClO_4$. The acid and all of its salts are purple, and, since they part with their oxygen readily, they are strong oxidizing agents and are much used as disinfectants and deodorizers. *Potassium permanganate*, $KMnO_4$, is the most important salt. In acid solutions, permanganates liberate oxygen according to the following equation, the oxygen being taken up by the reducing matter present:

$$2\ KMnO_4 + 3\ H_2SO_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 3\ H_2O + 5\ O$$

Radioactivity. In 1896 it was noticed that uranium gives off some kind of a radiation that affects a photographic plate even when the latter is inclosed in a plateholder and wrapped in black paper to protect it from the action of light. Fig. 82 shows the way in which uranium affects a photographic plate wrapped in black paper when a key is laid on the paper and covered with uranium oxid which is also spread on the paper in the form of the letters as shown. The radiation does not pass through the metal and leaves the plate below it unaffected.

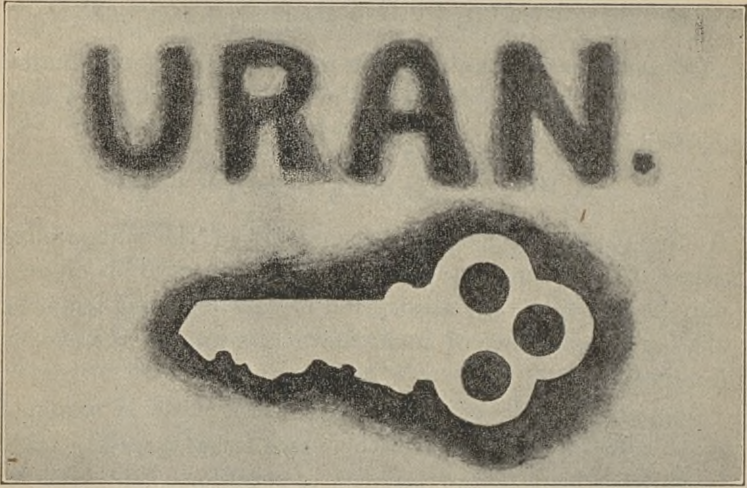


Fig. 82.

Professor and Madame Curie soon proved that this activity is due to a substance called radium, which is present in traces in all uranium compounds. From about a ton of uranium ore they separated about half a thimbleful of radium, and found that it is a million times more active than the original material. Furthermore, when the uranium ore is purified from radium, it no longer affects a photographic plate.

Radium is an element with an atomic weight of 226, closely resembling barium in its properties, and yet it has proved to be more interesting and wonderful than any element previously known. Radium chlorid looks much like ordinary salt, yet it sends off a radiation that affects a photographic plate and causes a body charged with electricity to lose its charge, even though it be insulated as perfectly as possible. It glows in the dark, is always warmer than the surrounding atmosphere, and gives off continually enough heat to melt its own weight of ice every hour.

Other substances possessing similar properties were soon discovered, among others, *thorium* and *actinium.* To this peculiar activity the name *radioactivity* is given, and the substances possessing these properties are said to be *radioactive.* Radioactivity was soon seen to be different from any ordinary chemical reaction, for the radiation is not increased at a white heat, and not slowed down at the temperature of liquid air.

An investigation of **thorium** revealed even more surprising results. Rutherford found it possible to separate from thorium compounds a substance called *thorium X*, which was very radioactive, while the thorium thus purified showed no activity. He was greatly disheartened, however, to notice that thorium *X* gradually lost its activity, and after a month was practically inactive. Imagine his surprise, however, to find that the thorium from which he had separated the thorium *X* had regained all its original activity in the same time, and more thorium *X* could now be separated from it. He repeated his work time and time again, always with the same result. Thorium is continually changing into thorium *X*, and this after a brief existence changes into something else, a gaseous substance which is radioactive for a time and then changes into solids which are not radioactive. This constant change of one substance, supposed to be an element, into another is something that the world had never known before, and it attracted universal attention.

Examination of the radiation soon gave a clew as to the nature of the process. It was found that there are **three kinds of radioactivity**, some substances possessing only one kind and others all three.

One form of radiation, called the *alpha ray*, has been proved to consist of particles of matter about four times the weight of the hydrogen atom, charged with positive electricity and traveling with about one tenth the speed of light.

Another form, known as the *beta ray*, consists of particles of matter charged with negative electricity and traveling with almost the speed of light. The latter particles are known as *electrons*, and they appear to be somewhat less than one two-thousandth the weight of a hydrogen atom.

The third form of radioactivity is called the *gamma ray;* it proves to be identical with the Roentgen or X-ray, and is thought to be due to vibrations of the ether, of a different character, however, from those of light. The *gamma* ray always accompanies the *beta* ray and seems to be caused by the latter.

Decomposition of atoms. That the change which causes radioactivity is connected with the atoms of thorium and other radioactive elements is indicated by the fact that the metal and every substance containing it is radioactive exactly in proportion to the amount of the element present. The atoms of radioactive substances are decomposing into particles, some about four times the weight of the hydrogen atom, others about two thousand times as small as the hydrogen atom. If the mind can form any picture of this change, it must be that of a most terrific explosion, for some of the particles are driven off with almost the speed of light. It is the impact of these particles which causes the heat and the glow.

The question naturally arises: Are the radioactive atoms blown entirely into electrons and other small particles, or is there a large part left from which the smaller particles have been expelled? If the latter supposition is true, and each radioactive element expels only one or at most a few *alpha* particles, its atomic weight should be lessened by four or more units. In this case we might expect to find

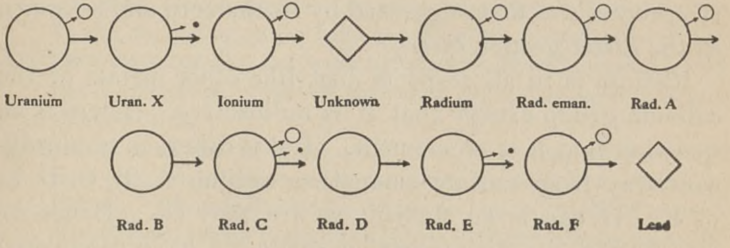


FIG. 83.*

that radioactive elements change into some of the well-known elements. There is reason to believe that this is true. It appears that uranium, 239, forms radium, 226, by the loss of 3 *alpha* particles; and that radium after losing 5 *alpha* particles is changed into lead. (See Fig. 83.) Certainly radium and lead are always found wherever uranium occurs. Whether thorium and actinium are formed during this process or have different radioactive processes of their own is not yet determined.

One question more: What becomes of the *alpha* particles? Do we know anything about them after they have lost their speed and their charges of electricity? The answer to this question comes with no uncertain tone. Whenever a radioactive substance gives the *alpha* rays, **helium** gas is produced. Since helium has an atomic weight of 4,

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* In the figure, large circles have been used to indicate elements wherever the process has been traced with certainty. The squares indicate unknown substances or those about which there may be some question. The small circles indicate *alpha* particles and the dots *electrons*.

there seems to be little reason to doubt that the *alpha* particles become helium atoms when they have lost their charges of electricity.

This disintegration of the atoms of certain of the elements with the formation of others seems to be pretty conclusively indicated by the facts. This explanation of the process was first suggested by Rutherford and is known as the *disintegration theory.*

Radium is in all respects just like other metals of the calcium group except that it is radioactive. There is no question that it is an element. But it differs in no significant way from radium emanation, radium A, B, C, D, E, or F. If one is an element, so are they all. Hence we see that in the disintegration series we have discovered several new substances, all of which should be considered as elements.

The alchemists of old endeavored to make gold out of mercury, lead, and other elements, but after a thousand years of trial the world recognized that they had failed completely. To-day, when we see some elements spontaneously changing into others, the old question once again arises. Is there any likelihood of being able to manufacture gold out of any other substance? We have no evidence to indicate that elements of low atomic weights change into elements of higher atomic weights. Of the elements whose atomic weights are greater than gold, only thorium and uranium are radioactive, and they do not seem to be disintegrating into gold. Moreover, the disintegration process is very slow. Nothing that man can do seems to hasten or to hinder the reaction in the slightest degree. Twentieth century science therefore makes the same answer to this question that the age of alchemy gave.

SUMMARY

THE CHROMIUM GROUP is the second type of the sulfur group. The elements are much more metallic than sulfur, but in the compounds formed the resemblances are close.

CHROMIUM metal is little used except in making hard steel. It is difficult to obtain from its compounds, hence is not commonly met with. Its compounds are more important. Four types are known, depending on the valence with which chromium is acting.

Trivalent chromium (3) is a weak base-former like aluminum, giving rise to green compounds like chromium oxid, Cr_2O_3, and chromium chlorid, $CrCl_3$.

Hexavalent chromium (6) is an acid-former, producing yellow or red salts such as potassium chromate, K_2CrO_4, and lead chromate, $PbCrO_4$. Chromium trioxid, CrO_3, is the anhydrid of *chromic acid*, H_2CrO_4, which resembles sulfuric acid but is more unstable. It readily loses water and forms *dichromic acid*, $H_2Cr_2O_7$.

Chromium compounds showing valences of 2 and 7 are unstable and rare.

MANGANESE is the only known element belonging to the second type of the chlorin group, and the resemblance to chlorin is not strong. It occurs in nature chiefly as the dioxid. Manganese is obtained from its compounds with difficulty and finds but little use except in hardening steel. Five types of manganese compounds are known, depending on the valence shown by manganese.

Divalent manganese (2) is a base-former resembling ferrous iron.

Trivalent manganese (3) is a weak base-former resembling ferric iron.

Tetravalent manganese (4) acts either as a weak base-former or as a weak acid-former, like stannic tin. *Manganese dioxid* is the most important compound, being used chiefly in oxidizing hydrochloric acid into chlorin in the manufacture of "bleaching salt."

Hexavalent manganese (6) is an acid-former, giving rise to *manganic acid*, H_2MnO_4, like chromic acid but more unstable. All its salts are green.

Heptavalent manganese (7) acts as a strong acid-former. *Permanganic acid*, $HMnO_4$, is like perchloric acid, $HClO_4$. It is a strong oxidizing agent. All of its salts are purple. *Potassium permanganate*, $KMnO_4$, is most important, and finds use as a disinfectant, germicide, and deodorizer.

RADIOACTIVITY is believed to be due to the decomposition of the atoms of the radioactive substances into elements with smaller atoms. The *disintegration theory* supposes that radioactive atoms are breaking down into *alpha* particles which weigh 4 times the weight of the hydrogen atom, and into *electrons* which appear to be about 2000 times as small as a hydrogen atom. The *alpha* particles and the electrons are charged with electricity, the former positively and the latter negatively, and traveling with enormous velocities, give rise to what we call *radioactivity.* When the *alpha* particles lose their charge of electricity, they become atoms of helium. By giving off 3 *alpha* particles and a number of electrons, it is believed that uranium changes into radium. By giving off 5 *alpha* particles, it is thought that radium changes into lead which is not radioactive; *i.e.* it is not disintegrating. Radioactivity differs from all other kinds of chemical reactions, in that it is not hastened at a white heat and is not retarded at the temperature of liquid hydrogen. Nothing that man can do seems to hasten or hinder it in the least.

QUESTIONS

1. Write equations for the action of sulfuric acid on potassium chromate, showing all the possible steps.

2. What would be the reaction of concentrated hydrochloric acid heated with potassium chromate? What noticeable changes would take place?

3. What evidence do you get from a study of chromium and its compounds that oxygen is correctly named — "acid-former?"

4. "The satisfaction that we get from snow-white linen, cotton, and other goods is due to manganese dioxid." Explain.

5. If hydrogen sulfid is passed into a mixture of manganese dioxid and hydrochloric acid, what will happen?

6. How many standard liters of sulfur dioxid gas would be required to bleach a solution containing 31.6 grams of potassium permanganate?

7. In testing drinking water, if a dilute permanganate solution is bleached, it is said that organic matter is present in the water. Explain. Suggest some inorganic substances commonly found in mineral springs which might have the same action. Would soda water bleach permanganate?

8. Show how the character of the compounds varies with the state of oxidation.

9. What do you mean by radioactivity? What are *alpha* particles; *beta* particles; electrons?

10. Is the atomic weight of an element a constant or variable property? If a radioactive element gives off *alpha* particles, can it remain the same element?

11. In what significant respects does radioactivity differ from all other chemical reactions?

12. Have we any ideas about how any of the elements are formed or where they have come from? If so, state them.

13. What evidence have we that one element can change into another?

14. Have we any reason for believing that gold could be made from any of the more common metals? Would the attempt to make gold be a task to which a man of good judgment would devote his efforts? Why?

CHAPTER XXXI

CLASSIFICATION OF THE ELEMENTS

THE detailed study of the elements and of the principal compounds formed by each which we have made, has revealed the fact that, while any given element is very unlike most others in nature and properties, it does show very close and striking similarity to a few of them. If a systematic consideration of the elements is taken up in the order of their increasing atomic weights, hydrogen being excluded since it does not resemble any other elementary substance, we begin with the rare element, helium, At. Wt. 4. This is chiefly remarkable for its inertness. No compounds of it are known. Since it does not seem to have the power to unite with other elements, its valence may be said to be zero. The second element is lithium, At. Wt. 7, a typical metal, forming many compounds, in which it shows a valence of one. Its hydroxid acts as a very strong base. The third element is beryllium, At. Wt. 9, a divalent metal, uniting readily with other elements. Its hydroxid acts as a base, but it is not as strong as lithium hydroxid. Trivalent boron, with At. Wt. 11, is the fourth element. Here metallic properties have fallen off very materially, while the characteristics of non-metallic, acid-forming elements begin to appear. Tetravalent carbon, At. Wt. 12, is the next element, showing acid-forming rather than base-forming properties. Next in order comes nitrogen, At. Wt. 14. It is a typical non-metallic element, forming compounds in which valences of three or five are shown. Oxygen, At. Wt. 16, next in order, possesses strong non-metallic properties and exhibits a valence of two (possibly four or six) in its compounds. Fluorin, At. Wt. 19, is the most non-metallic of all elements, forming compounds in which a valence of one is characteristic.

Although the atomic weights of these substances are not widely different, no one of the elements can be considered as resembling any of the others ; and while the properties of fluorin and lithium seem to be as different as is possible, yet, considering the whole series just mentioned, only a gradual change from the one to the other is to be noted.

Continuing the list, the next element is neon, At. Wt. 20, remarkably inert, forming no compounds and resembling helium so closely as to make a separation of them exceedingly difficult. The next member, sodium, At. Wt. 23, is a typical univalent metal. Its hydroxid is one of the strongest bases, and in every way it resembles lithium very closely. Magnesium, At. Wt. 24, is a divalent metal resembling beryllium. Aluminum, At. Wt. 27, is trivalent and analogous to boron, while silicon, At. Wt. 28, is tetravalent and like carbon. Phosphorus, At. Wt. 31, duplicates most of the compounds of nitrogen. Sulfur, At. Wt. 32, resembles oxygen and shows generally a valence of two or six. Chlorin, At. Wt. 35, possesses non-metallic properties in a very high degree, forms several of the strongest acids, and shows, among others, characteristic valences of one and seven.

Considering the members of what may be termed this second series, we note a similarity so close as to seem almost a duplication of the properties of the first series. The same change from strongly metallic to decidedly non-metallic properties, accomplished by a gradation through intervening elements, is observed. No member of this series can be said to be like any other member, yet each is very like the corresponding member of the first series.

Series.	Group 0.	Group 1. RH R_2O	Group 2. RH_2 RO	Group 3. RH_3 R_2O_3	Group 4. RH_4 RO_2
1	He 4	Li 7	Be 9	B 11	C 12
2	Ne 20	Na 23	Mg 24	Al 27	Si 28
3	Ar 40*	K 39	Ca 40	Sc 44	Ti 48
4		64 Cu	65 Zn	70 Ga	72 Ge
5	Kr 83	Rb 85	Sr 88	Yt 89	Zr 91
6		108 Ag	112 Cd	115 In	119 Sn
7	Xe 131	Cs 133	Ba 137	La 139	Ce 140
8		——	——	——	——
9	——	——	——	——	——
10		197 Au	201 Hg	204 Tl	207 Pb
11	——	——	Ra 226	——	Th 232

Certain very rare substances, at present thought to be elementary in names and atomic weights, approximately determined, are : Praseo Gadolinium — 157 ; Terbium — 159 ; Dysprosium — 162 ; Erbium — 167 ;

Continuing the consideration of the elements, the same variation and similarities are observed; for argon is like neon and helium, potassium like sodium and lithium, calcium like magnesium and beryllium, etc. In short, if the elements are arranged in series according to their increasing atomic weights, spaces being left in some instances for hypothetical elements as yet undiscovered, the elements will be found to arrange themselves in groups, each group containing elements which possess similar properties. From this it would seem that the properties of the elements depend in some way upon their atomic weights. An increase in atomic weight at first produces entirely different properties; but, after a period, it gives rise to properties closely resembling those previously noted.

This relation between the elements was first set forth by Mendeleeff (a likeness of whom is shown in Fig. 84), and is known as the **Periodic Law.** It states that *the properties of the elements are periodic functions of their atomic weights.*

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* Probably incorrectly determined.

Group 5. RH_3 R_2O_5	Group 6. RH_2 RO_3	Group 7. RH R_2O_7	Group 8.			Series.
N 14	O 16	F 19				1
P 31	S 32	Cl 35				2
51 Va	52 Cr	55 Mn	Fe 56	Co 59	Ni 59	3
As 75	Se 79	Br 80				4
93 Nb	96 Mo	——	Ru 102	Rh 103	Pd 107	5
Sb 120	Te 127	I 127				6
——	——	——	——	——	——	7
——	——	——				8
181 Ta	184 Wo	——	Os 191	Ir 193	Pt 195	9
Bi 208	——	——				10
——	238 U	——				11

character, are not placed in the table because of insufficient data. Their dymium — 141; Neodymium — 144; Samarium — 150; Europium — 152; Thulium — 168; Ytterbium — 172; Lutecium — 174; Niton — 222.

That is, that the properties of the elements depend primarily on their atomic weights, and that, when arranged in the order of their increasing atomic weights, elements of a certain type occur periodically.

The **Periodic System** is a method of classification arranging the elements into groups such that the members of each group show great chemical similarity to each other. At the top of each group, as given in the chart, the principal valences of the elements in the group are shown by typical formulas, R standing for any element belonging to the group. The increase in valence from zero to four, and the subsequent decrease in valence toward hydrogen, is shown by the formulas for hydrogen compounds, while the steady increase in valence toward oxygen is indicated by the formulas for oxids.

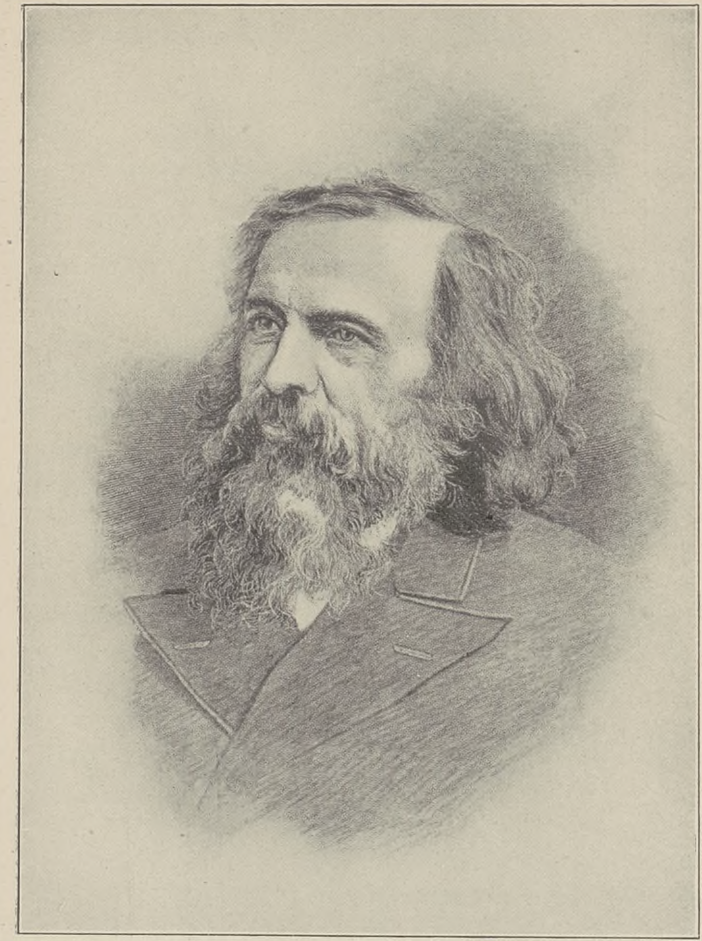
In a general way, each one of the groups of the periodic system may be said to possess certain group properties which are characteristic of each member in the group. Chief among these are the valence and the general character of the elements; *i.e.* do the elements in any particular group act normally as strong acid-formers or strong base-formers, or are they of an intermediate nature?

Within each group, however, certain gradations are to be noted. The most important of these is the fact that as the atomic weight of the elements in any particular group increases, non-metallic properties grow less, while metallic properties increase. This holds true for all groups, whether they be of a general acid-forming, base-forming, or neutral character. Thus, in the strong base-forming group, Cæsium, At. Wt. 133, is more metallic than lithium, At. Wt. 7. In the decidedly non-metallic halogen group, fluorin, At. Wt. 19, shows this non-metallic character in a much greater degree than does iodin, At. Wt. 127. In the intermediate fifth group, nitrogen, At. Wt. 14, is a typical acid-forming element, while bismuth, At. Wt. 208, is typically metallic and a weak base-forming element.

As the atomic weights rise above fifty, in each group the elements separate into two types; and while both types generally possess the group characteristics, they clearly differ from each other in many ways. Thus, in the sixth group, chromium, molybdenum, tungsten, and uranium are quite different from oxygen, sulfur, selenium, and tellurium, although all these elements may with propriety be classed in one group. This separation into two types within each group is indicated in the chart.

The groups of elements, as they have been arranged in the text, are simply the different parts, or groups, of the periodic system.

From the chart it will be seen that the three elements — iron, cobalt, and nickel — could be placed in Group 0 between argon and krypton. In a similar way, ruthenium, rhodium, and palladium, would fit in between krypton and xenon, while osmium, iridium, and platinum would



From Bradbury's "Elementary Chemistry." Copyright, 1903, by D. Appleton & Co.

FIG. 84. — DIMITRI IVANOVITCH MENDELEEFF (1834–1907)

Born in Siberia. He studied the elements and pondered over the relationships between them until in 1869 he worked out the great Periodic Law which has made his name immortal.

come in Series 10 in the same group. This arrangement makes Group 8 the second type of Group 0, and seems to be a wise modification of Mendeleeff's original scheme.

Obvious as is the possibility of classifying the elements into natural families or groups because of their properties, certain irregularities become apparent on further consideration. To begin with, hydrogen has no place in the scheme, and is quite unlike every other element. Its valence would classify it with the halogen or alkali groups. Solid hydrogen does not show any metallic properties, however. This seems to exclude it from Group 1. Hydrogen forms with the halogens some of the stablest compounds known; viz. hydrofluoric acid. Since elements which are chemically similar do not generally unite to form very stable compounds, this would appear to exclude hydrogen from the halogen group also. In two instances the grouping of the elements according to their properties does not preserve the order of increasing atomic weights. Tellurium, 127.5, is higher than iodin, 126.9. Cobalt, 59, seems to be a trifle higher than nickel, 58.7. In none of these instances is there any doubt about the natural relationships of these elements and possibly there is some error in the atomic weight determinations in these cases. Within the last few years it was reported that a new element with very high atomic weight had been separated from tellurium, thus correcting the order of tellurium and iodin. Recent investigations have not confirmed this report, however.

The large number of spaces which it is necessary to leave vacant for elements as yet undiscovered seems unfortunate to some chemists. The rare elements mentioned in the note under the periodic system chart furnish some material, and the disintegration products of uranium, thorium, radium, and actinium seem to afford enough possibilities to fill all the remaining spaces. That these disintegration products should be regarded as elements has already been shown. Most of the spaces left vacant are for elements with high atomic weights. This, taken into consideration with the fact that the elements with high atomic weights are markedly radioactive, *i.e.*, are unstable and disintegrating, suggests an explanation as to why many elements with high atomic weights have not yet been discovered.

Despite these irregularities, the truth of the periodic law is so obvious that any justification of the system of classification based upon it is entirely unnecessary. It is interesting to note that when Mendeleeff first enunciated the law that bears his name, scandium, gallium, and germanium were unknown. From a consideration of the properties of the nearest neighbors of each of these elements (for which spaces had been left), Mendeleeff proceeded to predict their properties, giving to them the names "eka-boron," "eka-aluminum," and "eka-silicon." How well he succeeded may be shown by one comparison of predicted and actual properties.

EKA-BORON	SCANDIUM
Atomic weight 44.	Atomic weight 44.
Oxid, Eb_2O_3.	Oxid, Sc_2O_3.
Sulfate less soluble than aluminum sulfate.	Sulfate less soluble than aluminum sulfate.
Salts colorless.	Salts colorless.
Carbonate insol. in water.	Carbonate insol. in water.
Hydroxid insol. and gelatinous.	Hydroxid insol. and gelatinous.

Other elements, then unknown, have since been discovered and find their places in the periodic system. Furthermore, the recently discovered argon group fits into the scheme in a way previously undreamed of. Scarcely a year passes without bringing to light some new point of evidence indicating the truth of the conception. The Periodic Law is to be regarded as the broadest and most far-reaching generalization of the scientific world, one of the grandest contributions to the world's store of knowledge that man has ever made.

The Periodic Law indicates clearly that the weight of the atom has much influence in determining the properties of the element. Since there are only eight different types of elements, the question at once arises whether the hundred elements known to chemistry are to be considered as essentially different kinds of matter.

The fact that some elements spontaneously disintegrate into others by shooting off *alpha* particles and electrons adds force to the question.

Experiments with X-ray tubes indicate that all metals (probably all elements) can be converted into electrons; for they all give rise to cathode rays, which have been proved identical with the *beta* rays given by radioactive substances. It seems that under the condition of great electrical strain inside these tubes these elements are knocked all to pieces; disintegrated most completely into electrons which are the same regardless of the substance from which they are produced. This seems to indicate that there is really only one form of matter and that the elements are composite things made out of this one fundamental material, arranged according to eight different patterns, just as garments are often made of one material according to several different patterns, with many different sizes in each pattern.

What we call a hydrogen atom appears to be made up of about 2000 electrons; 32,000 are needed for an oxygen atom, and 64,000, arranged according to the same pattern, produce a sulfur atom; 452,000, grouped according to a different pattern, makes an unstable combination known as radium, which continuously shoots off some of its electrons and is said to be radioactive.

Whether this be true or not, we cannot as yet state definitely, but certain facts point in this direction. Surely there can be no harm in realizing that the myriads of different things which appeal to us in such varied ways and make the world so interesting and beautiful may possibly be due to an ever-increasing complexity in the number and arrangement of one primordial form of matter, the electron.

SUMMARY

THE PERIODIC LAW. If the elements are arranged in order according to their increasing atomic weights, the first eight elements are all distinctly different and may be said to constitute eight different types of elements. The second series of eight elements, however, closely resemble the preceding eight. No new types are found, but each element duplicates approximately the properties of an element in the first series. Continuing the consideration, we find the same repetition of types and the elements continue to arrange themselves into natural groups. From this it is evident that the properties of the elements depend in some way on their atomic weights. An increase in atomic weight at first produces different properties, but after a period it gives rise to properties closely resembling those previously noted. Mendeleeff first worked out the relations between the elements and stated the *Periodic Law; i.e. the properties of the elements are periodic functions of their atomic weights.*

THE PERIODIC SYSTEM is a method of classification based on the Periodic Law. It arranges the elements into groups such that the members of each group show great chemical similarity to each other. Each group possesses certain group properties, such as the general character of the element, its valence, etc. In each group the element with highest atomic weight possesses greater metallic properties than the others; and *vice versa*, the element with smallest atomic weight is more non-metallic than the others. Within each group forking into two branches occurs.

The facts that matter can be disintegrated into electrons and that some elements are spontaneously decomposing into others by shooting off electrons or *alpha* particles, give rise to the possibility that there may be only one form of matter, the electrons, out of which all substances are made.

QUESTIONS

1. Using words of your own choosing, state the Periodic Law. (Do not give the statement printed in italics on page 398.)

2. What is the difference between the Periodic Law and the Periodic System?

3. In the Periodic System as given on pages 398 and 399, what is the meaning of the dashes? What possibilities are there of filling these places?

4. State the characteristics of the alkali group (excluding the copper branch); of the halogen group (excluding manganese); of the carbon group; of the argon group.

5. If hydrogen belongs to the alkali group, state some properties which you would expect solid hydrogen to possess.

6. If hydrogen belongs to the halogen group, state all the properties which you would expect it to possess.

7. Is lead an element? Is radium an element? What is the most significant difference between them?

8. Within a few days after they have been formed, uranium X, radium emanation, and radium E change into other substances. Should they be considered as elements? Why? Actinium emanation changes in a few seconds into actinium A. Would this fact prevent it from being an element?

9. If we were to classify the elements as "short-lived" and "long-lived," name some "short-lived" elements. Name several "long-lived" elements.

10. What reasons are there for thinking that there may be only one form of matter?

APPENDIX

LIST OF ELEMENTS.[1] 1916

The more common elements are printed in heavy type.

Name	Symbol	Valences	At. Wt.	Name	Symbol	Valences	At. Wt.
Aluminum	Al	3	27.1	Neodymium	Nd	3	144.3
Antimony	Sb	3–5	120.2	Neon	Ne	0	20
Argon	A	0	39.9	**Nickel**	Ni	2–3	58.7
Arsenic	As	3–5	75	Niobium[3]	Nb	5–3	93.5
Barium	Ba	2	137.4	Niton	Ni	0	222
Beryllium[2]	Be	2	9.1	**Nitrogen**	N	3–5	14
Bismuth	Bi	3	208	Osmium	Os	8–6–4	190.9
Boron	B	3	11	**Oxygen**	O	2	16
Bromin	Br	1–5	79.9	Palladium	Pd	4–2	106.7
Cadmium	Cd	2	112.4	**Phosphorus**	P	5–3	31
Cæsium	Cs	1	132.8	**Platinum**	Pt	4–2	195
Calcium	Ca	2	40.1	**Potassium**	K	1	39.1
Carbon	C	4–2	12	Praseodymium	Pr	3	140.9
Cerium	Ce	4–3	140.3	Radium	Ra	2	226
Chlorin	Cl	1–5–7–3	35.5	Rhodium	Rh	3	102.9
Chromium	Cr	3–6–7–2	52	Rubidium	Rb	1	85.5
Cobalt	Co	2–3	59	Ruthenium	Ru	4–3–6–8	101.6
Copper	Cu	2–1	63.6	Samarium	Sa	3	150.4
Dysprosium	Dy	3	162.5	Scandium	Sc	3	44.1
Erbium	Er	3	167.4	Selenium	Se	2–6–4	79.2
Europium	Eu	3	152	**Silicon**	Si	4	28.3
Fluorin	F	1	19	**Silver**	Ag	1	107.9
Gadolinium	Gd	3	157.3	**Sodium**	Na	1	23
Gallium	Ga	3	69.9	**Strontium**	Sr	2	87.7
Germanium	Ge	4–2	72.5	**Sulfur**	S	2–4–6	32.1
Gold	Au	1–3	197.2	Tantalum	Ta	5	181.5
Helium	He	0	4	Tellurium	Te	2–4–6	127.5
Hydrogen	H	1	1	Terbium	Tb	3	159.2
Indium	In	3	114.8	Thallium	Tl	1–3	204
Iodin	I	1–5–7	126.9	Thorium	Th	4–3	232.4
Iridium	Ir	3–4–2	193.1	Thullium	Tu	3	168.5
Iron	Fe	3–2	55.9	**Tin**	Sn	2–4	118.7
Krypton	Kr	0	83	Titanium	Ti	4	48.1
Lanthanum	La	3	139	Tungsten	W	6–4–2	184
Lead	Pb	2–4	207.2	Uranium	U	6–4	238.2
Lutecium	Lu	2	175	Vanadium	V	5–3	51
Lithium	Li	1	7	Xenon	Xe	0	130.7
Magnesium	Mg	2	24.3	Ytterbium	Yb	3	173.5
Manganese	Mn	2-7-4-6-3	54.9	Yttrium	Y	3	88.7
Mercury	Hg	2–1	200.6	**Zinc**	Zn	2	65.4
Molybdenum	Mo	6–4–2	96	Zirconium	Zr	4	90.6

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[1] Calculated from the basis, O=16.

[2] Also called Glucinum.

[3] Also called Columbium.

PHYSICAL PROPERTIES OF THE ELEMENTS

Element	Specific Gravity	Melting Point	Boiling Point	Element	Specific Gravity	Melting Point	Boiling Point
Aluminum	2.67	657	1800	Neon			
Antimony	6.72	630	1440	Nickel	8.85	1452	
Argon		−187.9	−186.1	Niobium	7.06	1950	
Arsenic	5.70	500	449.5	Nitrogen		−214	−194
Barium	3.78	850		Osmium	22.48	2500	
Beryllium	1.85	960		Oxygen		−227	−183
Bismuth	9.65	269	1420	Palladium	11.40	1549	
Boron	2.58	3000	3500	Phosphorus	1.82Y	44.2	269
Bromin	3.10	−7.3	59		2.11R		
Cadmium	8.72	321	778	Platinum	21.48	1752	
Cæsium	1.88	26.37	270	Potassium	0.87	62.5	667
Calcium	1.85	760		Praseodymium		940	
Carbon	3.55d	3500		Radium			
	2.25g			Rhodium	11.50	2000	
	1.70a			Rubidium	1.52	38.5	696
Cerium	6.65	623		Ruthenium	11.20	1900	
Chlorin		−102	−33.6	Samarium			
Chromium	6.47	1515	2200	Scandium			
Cobalt	8.55	1530		Selenium	4.48	217	680
Copper	8.93	1083	2310	Silicon	2.49	1200	
Erbium				Silver	10.50	960	1955
Fluorin		−223	−187	Sodium	0.97	95.6	742
Gadolinium				Strontium	2.55	800	
Gallium	5.95	30.15		Sulfur	2.06O	115–119	448.5
Germanium	5.47	900	1350		1.96M		
Gold	19.32	1062		Tantalum	10.70	2250	
Helium		−271	−269.5	Tellurium	6.24	452	1390
Hydrogen		−252.5	−259	Terbium			
Indium	7.40	155	800	Thallium	11.85	302	1600-1800
Iodin	4.95	114	184.4	Thorium	11.00		
Iridium	21.83	1950		Thullium			
Iron	7.84	1800	2450	Tin	7.29	233	2270
Krypton		−169	−151.7	Titanium	4.5	1800	
Lanthanum	6.10	810		Tungsten	17.20	1700	
Lead	11.37	327	1525	Uranium	18.68	800	
Lithium	0.59	186	1400	Vanadium	5.50	1630	
Magnesium	1.75	632.6	1120	Xenon		−140	−109.1
Manganese	7.25	1300	1900	Ytterbium			
Mercury	13.57	−39.4	357	Yttrium			
Molybdenum	8.65			Zinc	7.15	419	918
Neodymium		840		Zirconium	6.4	2350	

WEIGHTS AND MEASURES

THE METRIC SYSTEM WITH ENGLISH EQUIVALENTS

Measures of Length

1 millimeter, mm. = 0.03937 inch
1 centimeter, cm. = 10 mm. = 0.3937 inch
1 decimeter, dm. = 10 cm. = 3.937 inches
1 meter, m. = 10 dm. = 39.37 inches
1 kilometer, km. = 1000 m. = 0.6214 mile

Measures of Volume

1 cubic centimeter, ccm. = 0.06103 cu. inch
1 cubic decimeter or 1 liter, l. = 1000 ccm. = 61.03 cu. inches, or 1.057 quarts
1 cubic meter = 1000 l. = 35.32 cu. feet

Measures of Weight

1 milligram, mg. = 0.0154 grain
1 gram, g. = 1000 mg. = 15.432 grains
1 kilogram (kilo) K. = 1000 g. ≐ 2.2046 pounds av.

Troy or Apothecaries' Weight

POUND	OUNCES	DRAMS	SCRUPLES	GRAINS	GRAMS
1	12	96	288	5760	373.268
	1	8	24	480	31.103
		1	3	60	3.888
			1	20	1.296
				1	0.0648

Avoirdupois Weight

POUND	OUNCES	DRAMS	GRAINS	GRAMS
1	16	256	7000	453.60
	1	16	437.5	28.35
		1	27.343	1.77

Liquid Measure

GALLON	QUARTS	PINTS	FLUID OUNCES	FLUID DRAMS	MINIMS
1	4	8	128	1024	61440
	1	2	32	256	15360
		1	16	128	7680
			1	8	480
				1	60

CONVERSION FACTORS

To Change	To	Multiply by
Inches	Centimeters	2.54
Feet	Meters	.305
Miles	Kilometers	1.609
Meters	Inches	39.37
Kilometers	Miles	.621
Square inches	Square centimeters	6.452
Square yards	Square meters	.836
Square centimeters	Square inches	.155
Square meters	Square yards	1.196
Cubic inches	Cubic centimeters	16.386
Cubic yards	Cubic meters	.765
Cubic centimeters	Cubic inches	.061
Cubic meters	Cubic yards	1.308
Minims	Grains	.95
Minims	Cubic centimeters	.0617
Fluid ounces	Cubic centimeters	29.57
Quarts	Liters	.946
Cubic centimeters	Fluid ounces	.034
Liters	Quarts	1.057
Grains	Milligrams	64.799
Ounces (av.)	Grams	28.35
Pounds (av.)	Kilograms	.454
Ounces (troy)	Grams	31.103
Pounds (troy)	Kilograms	.373
Grams	Grains	15.432
Kilograms	Pounds	2.205

CENTIGRADE AND FAHRENHEIT SCALES

To reduce a Fahrenheit temperature to its equivalent in Centigrade degrees: Subtract 32° algebraically and multiply the remainder by $\frac{5}{9}$.

To reduce a Centigrade temperature to its Fahrenheit equivalent: Multiply by $\frac{9}{5}$, and add 32° to the product algebraically.

VAPOR PRESSURE OF WATER IN MM. OF MERCURY

Temp.	Pressure	Temp.	Pressure	Temp.	Pressure
−10	2.09	12	10.46	26	24.99
− 5	3.11	13	11.16	27	26.51
0	4.60	14	11.91	28	28.10
+ 1	4.94	15	12.70	29	29.78
2	5.30	16	13.54	30	31.55
3	5.69	17	14.42	35	41.83
4	6.10	18	15.36	40	54.91
5	6.53	19	16.35	50	91.98
6	7.00	20	17.39	60	148.79
7	7.49	21	18.50	70	233.09
8	8.02	22	19.66	80	354.64
9	8.57	23	20.89	90	525.45
10	9.17	24	22.18	100	760.00
11	9.79	25	23.55		

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