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# MANUAL

OF

# CHEMISTRY

A GUIDE TO LECTURES AND LABORATORY WORK FOR BEGINNERS IN CHEMISTRY, A TEXT-BOOK SPECIALLY ADAPTED FOR STUDENTS OF MEDICINE, PHARMACY AND DENTISTRY


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ELEVENTH EDITION, THOROUGHLY REVISED


WITH FIFTY-FIVE ILLUSTRATIONS, ONE COLORED SPECTRA PLATE AND SIX COLORED PLATES REPRESENTING FORTY-EIGHT CHEMICAL REACTIONS





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# PREFACE TO THE ELEVENTH EDITION.

In this new edition a number of changes involving rearrangement, addition and deletion have been made. In Section I on Physics, the chapters on light and electricity have been omitted, because it seemed to the reviser that the physics of light has little bearing on a course in elementary chemistry and that, while electricity is of greater importance than light in the study of chemistry, it can be studied to better advantage in a separate treatise on physics. However, the articles on the spectroscope and the polariscope have been retained, but have been placed in the Appendix. Former Sections II, III and IV are consolidated as Section II under the title General Chemistry, which falls into two subdivisions, the first of which treats of the non-metals. the second of the metals. While this classification of the elements is not in strict adherence to the periodic law, it nevertheless seems well adapted for the instruction of beginners as shown by experience, and therefore is retained in this book.

The first subdivision of Section II, dealing with the non-metal has been entirely rearranged so as to give a logical sequence in tl presentation of laws, theories, and facts of observation. Much new matter has been added, some portions have been partly, and the chapter on the determination of atomic and molecular weights entirely, rewritten.

The second subdivision of Section II deals with the metals and their compounds. The classification adopted is that of the analytical groups, but at the same time the position of each metal in the periodic system and the resemblance it bears to the other members of the family to which it belongs are pointed out, thus keeping before the student the periodic system of classification.

Section III is devoted to analytical chemistry and will serve the student as a guide in his laboratory work. Qualitative methods are chiefly considered, but a chapter on quantitative determinations by volumetric methods is also included.

Section IV treats of organic chemistry. Though it is impossible to include within the limits of this text-book an extended consideration of a branch of chemistry so highly developed, yet it is believed that an intelligent study of this part will familiarize the student with carbon compounds sufficiently to give him a clear understanding of their character, and a knowledge of the substances which are most important in medical and pharmaceutical science. Many new compounds and much new matter in the nature of discussion have been added to this section.

With the exception of the chapter on proteins, the section on Physiological Chemistry has been dropped from the Manual, because it is believed that teachers of this subject prefer a separate text in which a more extended treatment can be given the subject than is possible in the limits of this book.

This edition incorporates the additions to, and changes in, official titles of the U. S. P. IX. The international system of atomic weights on the oxygen (16) basis is used.

The U. S. Bureau of Standards, the U. S. P. and Br. P., U. S. government publications, and a number of authors, have adopted the term milliliter (abbreviated mil. or ml.) in place of cubic centimeter (c.c.), inasmuch as the liter, as now fixed, is 0.027 c.c. larger than one thousand cubic centimeters. In this Manual the term cubic centimeter (c.c.) has been retained to avoid confusion and for the reason stated in the article on weights and measures in Section I.

It is hoped that this new edition of the Manual will more than ever before accomplish its object, namely, *to furnish to the student in concise form a clear presentation of the science, an intelligent discussion of those substances which are of interest to him, and a trustworthy guide to his work in the laboratory.*

Owing to the illness and death of Dr. Simon, the revision of this edition has fallen entirely upon the surviving author, who wishes to record here his deep regret at the loss of this highly esteemed friend and associate.

D. B.

BALTIMORE, 1916.

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## ABBREVIATIONS.

c.c. = Cubic centimeter.

B. P. = Boiling-point.

F. P. = Fusing-point.

Sp. gr. = Specific gravity.

U. S. P. = United States Pharmacopœia.

# PRACTICAL CHEMISTRY, MEDICAL AND PHARMACEUTICAL.

## I.

## CHEMICAL PHYSICS.

Both sciences, chemistry and physics, have for their object the study of all substances, or of all varieties of matter, and the changes which they undergo. When these alterations affect the composition of matter we have chemical changes, which are considered by chemistry; when the composition is not affected we have physical changes, considered by physics. But whenever chemical changes take place they are accompanied by physical changes. Indeed, there exists such a close relation, such a mutual dependency, between these two series of phenomena that they cannot be studied altogether independently of one another. Moreover, the chemist uses constantly in his operations instruments or appliances the construction of which is based on physical principles. A knowledge of certain parts of physics is therefore essential for the proper understanding of chemistry. It is for this reason that a few chapters dealing with certain physical conditions of matter precede the parts on chemistry.

Physics is defined above as the study of those changes in matter which do not involve an alteration of the composition or constitution of the matter. The phenomena of light, heat, electricity, magnetism, sound, motion, attraction, etc., fall within its province. A few examples of physical changes may help to make the subject clearer. A piece of iron heated sufficiently becomes luminous, radiates heat, and increases in size. All these are physical changes, because if the iron be cooled it will be found to be the same in character as before it was heated. There has been no change in the substance iron. A body in rapid motion is quite different from the same body at rest, as is evident if the body hit an individual, yet the nature or composition of the body is not altered. A wire through which an electric current is passing is different from one in which there is no current, although the substance of both wires is the same. Many other examples of physical change might be cited.

Chemistry is the study of those changes in bodies which affect their composition, and in this respect chemical changes differ from all other kinds of changes. Another good and broad definition given by the great Russian chemist, Mendelejeff, is the following: Chemistry is concerned with the study of the homogeneous substances or materials of which all objects of the universe are made up, with the transformations of these substances into one another, and with the phenomena which accompany such transformations. When a piece of paper burns, an ash is left, which is altogether different from the original paper. Moreover, if proper care be taken to catch the products escaping during the burning, water vapor and gases will be found, which are also unlike the paper. These are new substances and the change is, therefore, a chemical one. But at the same time several physical changes will be observed, namely, heat and light.

When a piece of the metal magnesium is ignited, it burns and leaves an ash entirely different from the metal, being white and brittle. This is a chemical change, but heat and intense light are observed at the same time, which are physical changes.

When a piece of marble is heated to redness for some time, a substance remains on cooling which, although having the same form as the piece of marble, is nevertheless entirely different in its composition and properties, and is known as quick-lime. When water is poured upon the latter, great heat is produced and the solid lump falls down to a white powder, known as slaked-lime, whereas marble is not affected by water. By a suitably arranged apparatus it could also be shown that an invisible gas is given off when the marble is heated.

These illustrations will be sufficient to point out the nature of physical and chemical changes, and we may proceed now to the discussion of some elementary subjects of physics.

## 1. FUNDAMENTAL PROPERTIES OF MATTER.

**Matter.**—Matter is anything that occupies space and may be apprehended by the aid of our senses. While there are many thousands of various kinds of matter, possessing widely different properties, yet there are properties in common which belong to every kind of matter, and these are known as *essential* or *fundamental properties*. The fundamental properties of matter having a special interest for those studying chemistry are: *Extension*, *Divisibility*, *Gravitation*, *Porosity*, and *Indestructibility*.

**Extension.**—The common property of matter to occupy space is known as extension. All bodies, without exception, fill a certain quantity of space; they all have length, breadth, and thickness. That portion of matter lying within the surrounding surface of a body is called its *mass;* or we may define mass as the quantity of matter which a body possesses. A *body* is a definite portion of matter, such as a knife, a piece of chalk, or a lump of coal. The term *substance* is used to designate some particular kind of matter, possessed of definite qualities, such as gold; water, glass, etc. We distinguish three different conditions of matter, namely: *Solids*,

*Liquids*, and *Gases*. These conditions of matter are known as the three states of aggregation, and we will now consider the peculiarities of matter when existing in either of these states.

**Solid State.**—Solids are distinguished by a self-subsistent figure—*i. e.*, they have a definite size and shape. A solid substance forms for itself, as it were, a casing in which its smallest particles[1] are enclosed. The questions arise, By what means are these particles connected? How are they kept together? No answer can be given other than that the particles themselves attract each other to such an extent that force is necessary to make them alter their relative positions. We see, consequently, that some form of attraction or attractive power is acting between the particles of a solid mass, and we call this kind of attraction *cohesion*, to distinguish it from other forms of attraction.

**Force.**—Force may be defined as the action of one body upon another body, or as the action of particles of matter upon other particles either of the same or of another body. Strictly speaking, we may say that force is the cause tending to produce, change, or arrest motion; or it is any action upon matter changing or tending to change its form or position. Force is a manifestation of energy, and may be originated in a variety of ways.

**Energy.**—Energy is a universal property of matter; it is its capacity for doing work, and is measured by the work it can do. Doing work consists in a transfer of motion, or energy, from the body doing work to the body on which work is done. Wherever we find matter in motion we have a certain quantity of energy which may be made to do work.

As examples of different forms of energy we have motion of masses, heat, light, electricity, chemical changes, etc. Under the influence of the different forms of energy matter is constantly undergoing change. There are changes in position, in temperature, in appearance, in the composition of substances, and in many other directions.

Energy may be potential (*i. e.*, stored up) or kinetic (*i. e.*, actual). For instance, potential energy is the energy which we have in a mass held by the hand, or by a support; as soon as the support is withdrawn the mass falls, and in this instance we witness kinetic or actual energy.

Other instances of potential energy are a drawn bow, a wound-up watch-spring, an elevated tank of water, etc. This potential energy may manifest itself as kinetic energy by sending an arrow through space, by keeping the watch in motion, or by rotating a water-wheel. During the conversion of potential into kinetic energy there is neither gain nor loss; both are absolutely alike in quantity.

**Crystallization.**—The external appearance or the figure of solid bodies is various. It may be an irregular or a *natural regular figure*.

[1] It will be shown later that all matter is supposed to consist of smallest particles, which we call molecules.

Of these two forms, only the latter is here of interest, as it includes all the different crystallized substances.

**Crystals.**—Crystals are solid substances bounded by plane surfaces symmetrically arranged according to fixed laws. In explaining the formation of crystals we have to assume that the particles are endowed with the power of attracting one another in certain directions, thereby building themselves up into geometrical forms.

The external form of a crystal is only an outward expression of a regular internal structure. This is shown by the fact that in non-crystalline homogeneous bodies such properties as elasticity, hardness, cohesion, transmission of light, etc., are the same in all directions, while crystallized bodies show differences along different directions. A model of glass would not be a crystal, since the necessary internal structure is absent.

The first condition essential to the formation of crystals is the possibility of free motion of the smallest particles of the matter to be crystallized; in that case only will they be able to attract each other in such a way as to assume a regular shape, or form crystals. Particles of a solid mass can move freely only after they have been transferred to the liquid or gaseous state. There are two different methods of liquefaction, viz., by means of heat (melting), or solution in some suitable agent (dissolving). In the liquid condition thus produced, the smallest particles can follow their own attraction, and unite to form crystals on removal of the cause of liquefaction (heat or solvent).

In the great majority of cases the method employed for obtaining crystals is to dissolve the substance in a liquid, usually water, taking advantage of the fact that, with very few exceptions, substances are more soluble in hot than in cold liquids. When such a concentrated hot solution, filtered if necessary to remove solid matter, is allowed to cool, the particles of the excess of the substance, beyond what is soluble at the lower temperature, gradually arrange themselves around certain points as nuclei according to the directions of greatest cohesion, and thus crystals with regular faces and angles and definite internal arrangement are built up. The size of the crystals obtained will depend on several factors, but whatever the size may be, the angles between the faces and the position of the faces will be the same for every individual substance. Hence the shape of crystals is a valuable means of identifying substances. If a concentrated hot solution of a substance be cooled quickly, and especially if the liquid be disturbed, as by stirring, the crystals will be small, sometimes almost microscopic in size. But this is often an advantage, because large crystals are apt to enclose some of the liquid containing the impurities between the layers. On the large scale, as in industries, enormous crystals are obtained by the slow cooling of a great volume of solution, for example, in the case of alum, potassium dichromate, etc. When a substance is not much more soluble in a hot than in a cold liquid, for example, common salt in water, the liquid must be removed by allowing it to evaporate, either at ordinary or at elevated temperature, to obtain a good yield of the substance in crystal form.

Sometimes sticks, strings, wires, strips of lead, etc., are suspended in the

solutions, to offer starting-points for the formation of crystals and a ready means for removing the crystals from the liquor. A familiar example is the string in the center of a stick of rock-candy.

A relatively few substances when heated pass from the solid to the gaseous state, without undergoing intermediate liquefaction. When the vapor of such substances comes in contact with cool surfaces, it is deposited in crystals which sometimes attain to remarkable size and beauty. This process is known as *sublimation* and is used in the case of several medicinal agents on the market, for example, iodine, benzoic acid, ammonium chloride, etc. The words *iodine resublimed*, found on labels, and the popular name for mercuric chloride, namely, *corrosive sublimate*, refer to the process of sublimation employed in obtaining these substances.

If two or more (non-isomorphous) substances—for instance, common salt and Glauber's salt—be dissolved together in water, and the solution be allowed to crystallize, the attraction of like particles for one another will be readily noticed by the formation of distinct crystals of common salt alongside of crystals of Glauber's salt; neither do the particles of common salt help to build up a crystal of Glauber's salt, nor the particles of the latter a crystal of common salt. Advantage is taken of this property in separating (by crystallization) solids from each other, when they are contained in the same solution.

Not all matter can form crystals; some substances never have been obtained in a crystallized state, such as starch, gum, glue, etc. A solid substance showing no crystalline structure whatever is called *amorphous*.

Some substances capable of crystallization may be obtained also in an amorphous state (carbon, sulphur). Other substances are capable of assuming different crystalline shapes under different conditions. Thus sulphur, when liquefied by heat, assumes, on cooling, a shape different from the sulphur crystallized from a solution. One and the same substance under the same conditions always assumes the same shape. Substances capable of assuming in solidifying two or more different shapes or conditions, are said to be *dimorphous* and *polymorphous*, respectively. When substances of different kinds crystallize in exactly the same form we call them *isomorphous* (magnesium sulphate and zinc sulphate). Also, a crystal of one kind of matter must have the power of growing in the solution of another kind before the two kinds of matter are considered isomorphous. If two isomorphous substances be contained in one solution, they will crystallize together, and the crystals will be made up of particles of both substances.

For some reason or other crystals sometimes grow mainly in one or two directions and then show forms that are distorted and have little or no resemblance to the normal forms of the system to which they belong. Examples of such forms are the following:

*Tabular* crystals or flat plates, as potassium chlorate, iodine, etc.

*Laminar* crystals, thin plates or leaflets, as acetanilide, naphthol, calcium hypophosphite, etc.

*Acicular* crystals or needles, as aloin, cinchonidine sulphate, quinine salts, etc.

*Prismatic* crystals or prisms, extended chiefly in the direction of the longest axis, as salicylic acid, santonin, cinchonine sulphate, etc.

The shapes of gems must not be confused with crystal forms. They are the result of cutting and polishing for the purpose of causing the gem to reflect more light.

**Characteristic Properties of Solids.**—Solid substances show a great variety of properties caused by the differences in the cohesion of the particles (molecules) composing the substances, and accordingly we distinguish between hard and soft, brittle, tenacious, malleable, and ductile substances.

*Hardness* is that property in virtue of which some bodies resist attempts to force passage between their particles, or which enables solids to resist the displacement of their particles. Diamond and quartz are extremely hard, while wax and lead are comparatively soft.

*Brittleness* is that property of solids which causes them to be broken easily when external force is applied to them. Glass, suphur, coal, etc., are brittle.

*Tenacity* is that property in virtue of which solids resist attempts to pull their particles asunder. Steel is one of the most tenacious substances.

*Malleability*, possessed by some solids, is the property in virtue of which they may be hammered or rolled into sheets. Gold is so malleable that it may be beaten into sheets so thin that it would require about 300,000 laid upon one another to measure one inch.

*Ductility* is the property in virtue of which some solids may be drawn into wire or thin sheets—as, for instance, copper, iron, and platinum.

**Liquid State.**—The characteristic features of liquids are, that they have no self-subsistent figure; that they consequently require some vessel to hold them; and that they present a horizontal surface. While in a solid substance the smallest particles are held together by cohesion to such an extent that they cannot change their relative position without force, in a liquid this cohesion acts with much less energy and permits of a comparatively free motion of the particles; the repellant and attractive forces nearly balance each other in a liquid. That cohesion is not altogether suspended in a liquid is shown by the formation of drops or round globules, which, of course, consist of a large number of smallest particles. If there were no cohesion at all between these particles of a liquid, drops could not be formed.

The term semi-solid and semi-liquid substances are used for bodies occupying a position intermediate between true solids and fluids; butter, asphalt, amorphous sulphur, are instances of this kind.

**Gaseous State.**—Matter in the gaseous state has absolutely no self-subsistent figure. Any quantity of gas in a closed vessel will fill it completely; the smallest particles show the highest degree of mobility and move freely in every direction. Cohesion is entirely suspended in gases; indeed, there is no attraction between the particles,

but they are in rapid motion and tend to spread out in all directions; hence must be retained in a closed vessel. The motion of the particles causes bombardment on the sides of the vessel, and thus produces pressure. This characteristic property, possessed by all gases, is known as *elasticity*, or, better, as *tension*, and is so unvarying that a law[1] has been established in relation to it. This law is known as the *Law of Boyle*, who discovered it in 1661; sometimes it is referred to as the *Law of Mariotte*. It may be expressed thus: The volume of a gas is inversely as the pressure; the density and elastic force are directly as the pressure and inversely as the volume.

The subject will be clearer from the following considerations: A gas behaves much like a spring. If we put weights (force) on the spring it will be compressed—that is, its volume will become less, and if the weights be gradually removed, the spring will expand. Similarly, if we take a metallic tube closed at one end, and fitted with a piston and handle and containing a certain volume of air, for example, a bicycle pump, and then press down upon the handle, the volume of air will become smaller and smaller as the pressure on the handle is increased. It will be observed also that as the volume becomes smaller it offers more and more resistance to compression, that is, its tension or elastic force becomes greater. Also, since the amount of material in the original volume of air remains the same during the experiment, it is plain that when the air is compressed to a small volume, the amount of material in a unit volume, say 1 cubic inch, is very much increased; in other words, the density of the gas is increased as the pressure is increased. If accurate measurements be made of the different pressures applied and the corresponding volumes assumed by the air, a constant relationship will be discovered, such as is expressed in Boyle's Law, stated above. The meaning of the phrase in the law, *the volume of a gas is inversely as the pressure*, is that as the one quantity is increased the other is decreased in just the same proportion. To illustrate, if a volume of a gas measures 1 cubic foot under a pressure of 10 pounds, and the pressure be increased to 15 pounds, in other words, $\frac{15}{10}$ or $\frac{3}{2}$ times, then the volume will change from 1 cubic foot to $1 \div \frac{3}{2} = \frac{2}{3}$ cubic foot. If the pressure be decreased to say 6 pounds, or $\frac{6}{10} = \frac{3}{5}$ of its original value, then the volume will become $1 \div \frac{3}{5} = \frac{5}{3}$ cubic foot, that is, it will expand.

Such a relation as is expressed in Boyle's Law is known in algebra as inverse proportion. Since one of the quantities is always decreased in the same ratio as the other is increased, it follows that the product of the two quantities thus related must always be the same, that is, a constant. Hence, another way of expressing Boyle's Law is to say that the product of the pressure and the corresponding volume of a definite quantity of a gas is always the same. If V and $V^1$ repre-

[1] In science, a *law* or *generalization* is a brief statement which describes some constant mode of behavior, or sums up the constant features of a set of phenomena of a like kind.

sent the volumes of a certain amount of gas, at the corresponding pressures, P and $P^1$, then $V \times P = V^1 \times P^1$. In the example given above, V = 1 cubic foot, P = 10 pounds, and $P^1$ = 15 pounds, hence, $1 \times 10 = V^1 \times 15$, or $V^1 = \frac{10}{15} = \frac{2}{3}$ cubic foot.

As will be seen later, this law is of great value in all experiments where results are calculated from measurements of gas volumes. Vapors from liquids and solids at sufficient temperatures above their points of condensation behave just like gases.

**Divisibility.**—All matter admits of being subdivided into smaller particles, and this property is called divisibility. The processes by which we accomplish the comminution of a solid substance may be of a mechanical nature, such as cutting, crushing, grinding; but beside these modes of subdivision we have other agents or causes by which matter may be divided into smaller particles, and one of these agents is heat.

**Action of Heat on Matter.**—Let us take a piece of ice and convert it, by means of mortar and pestle, into a very fine powder. When the smallest particle of this finely powdered ice is placed under the microscope and heat applied, we shall observe that it becomes liquid, thus proving that it was capable of further subdivision, that it consisted of smaller particles, which have now by the action of heat become movable. By further applying heat to the liquid particle of water we may convert it into a gas or vapor, which will escape into the air, or which we may collect in an empty flask. The flask will be filled completely by this water-gas (or steam) obtained by vaporizing that minute particle of ice-dust. This fact demonstrates that mechanical comminution does not carry us beyond a certain degree of subdivision of matter. That is to say, the smallest fragment of the finest powder still consists of a very large number of much smaller particles. To the smallest particles which compose matter the name molecules has been given.

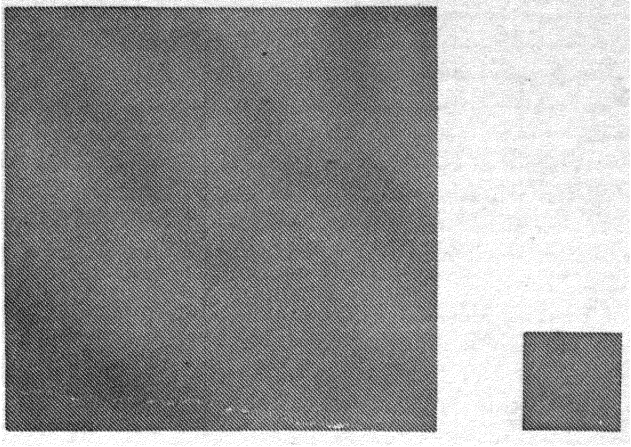
**Molecular Theory.**—The expression molecule is derived from the Latin word *molecula*—a little mass, and means the smallest particle of matter that can exist by itself, or into which matter is capable of being subdivided by physical actions. To explain more fully what is meant by the expression molecule, we will return to the conversion of water into steam.

When water boils at the ordinary atmospheric pressure it expands about 1800 times, or one cubic inch of water yields about 1800 cubic inches, equal to about one cubic foot of steam. In explaining this fact we have either to assume that the water, as well as the steam, is *continuous matter* (Fig. 1), or that the water consisted of small particles of a given size, which now exist in the steam again as such, with the only difference that they are more widely separated from each other (Fig. 2.)

Of the many proofs which we have of the fact that the latter assumption is correct, one may be sufficient, viz., that the quantities

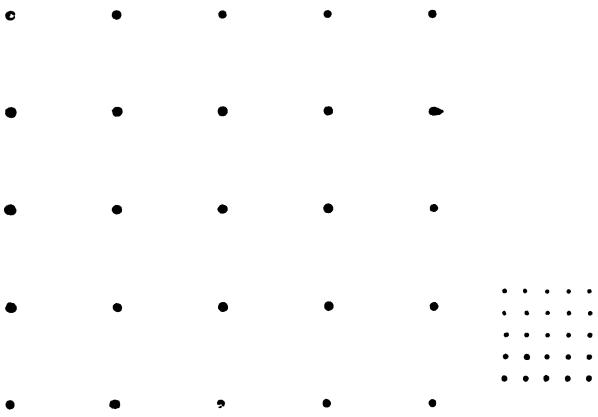
of vapor formed by volatile liquids at any certain temperature above the boiling-point, in close vessels of the same size, are the same, no matter whether the vessel was entirely empty or contains the vapors

FIG. 1



of one, two, or more other substances. For instance: If we place one cubic inch of water in a flask holding one cubic foot, from which flask the air has been previously removed, and then heat the flask to

FIG. 2



the boiling-point, the cubic inch of water will evaporate, filling the vessel with steam. Upon now introducing into the flask a second and a third liquid—for instance, alcohol and ether—we find that of each of these liquids exactly the same quantity will evaporate which would have evaporated if these liquids had been introduced into the empty

flask.[1] This fact is evidence that there must be small particles of steam which are not in close contact, that there are spaces between these particles which may be occupied by the particles of a second, third, or more substances. To these particles of matter we give the name molecules, and the spaces between them we call intermolecular spaces.

We have thus demonstrated the correctness, or, at least, the likelihood, of the so-called molecular theory, but the proof given is but one of many. Other facts which lead us to accept the theory of the molecular condition of matter are: The passage of gases through solids: for example, of carbon dioxide gas through red-hot iron; of water under pressure through gold; the decrease in a volume of water when a salt is dissolved in it; the extreme divisibility of matter as shown by solution, etc.

Our conception of molecules (though individually by far too small to make any impression whatever upon our senses) is so perfect that we have formed an idea of the actual size of these minute particles of matter. Very good reasons lead us to believe that the diameter of a molecule is equal to about $\frac{1}{500000000}$ of one inch, and that one cubic inch of a gas under ordinary conditions contains about one hundred thousand million million millions of molecules.

These figures at first glance appear to be beyond the limit of human conception, but in order to give some idea of the size of these molecules it may be mentioned that if a mass of water as large as a pea were to be magnified to the size of our earth, each molecule being magnified in the same proportion, these molecules would represent balls of about two inches in diameter.

While molecules consequently are exceedingly small particles, yet they are not entirely immeasurable; they are, as Sir W. Thomson says, pieces of matter of measurable dimensions, with shape, motion, and laws of action, intelligible subjects of scientific investigation.

Intimately connected with the molecular theory is the *Law* (more correctly, the hypothesis) *of Avogadro*, which may be stated as follows: *All gases or vapors, without exception, contain, in the same volume, the same number of molecules*, provided temperature and pressure are the same. Or, in other words: *Equal volumes of different gases contain, under equal circumstances, the same number of molecules.* The correctness of this law has good mathematical support deduced from the law of Boyle, many other facts and considerations leading to the same assumption. We shall learn, hereafter, that the law of Avogadro is one of the greatest importance to the science of chemistry.

**Gravitation.**—Every particle of matter in the universe attracts every other particle; consequently, all masses attract each other, and this attraction is known as *gravitation.* The action of gravitation between the thousands of heavenly bodies moving in the universe is to be considered by astronomy, but some of the phenomena caused

[1] As each gas, in consequence of its tension, exerts a certain pressure, the pressure in the flask rises with the introduction of every additional gas.

by the mutual attraction of the substances composing the earth are of importance for our present consideration.

Such phenomena caused by gravitation are the falling of substances, the flowing of rivers, the resistance which a substance offers on being lifted or carried. A body thrown up into the air or deprived of its support will fall back upon the earth. In this case the mutual attraction between the earth and the substance has caused its fall. It might appear that in this case the attraction was not mutual, but exerted by the earth only; it has been proved, however, by most exact experiments, that there is also an attraction of the falling substance for the earth, but the amount of the force of this attraction is directly porportional to the mass of the bodies, and consequently too insignificant in the above case to be noticed.

The law of gravitation, known as *Newton's Law*, may thus be stated: All bodies attract each other with a force directly proportional to their masses and inversely proportional to the squares of their distance apart. With regard to the earth and bodies upon it at a given place, the mass of the earth and the distance between the earth and the bodies remain the same, so that the only thing that varies is the mass of the bodies. Hence, according to Newton's Law, the force with which such bodies are attracted to the earth varies directly as their masses. In other words, if a body A has twice the mass or quantity of matter as a body B, it will be attracted with twice as much force to the earth as the body B.

**Weight.**—Weight is an expression used to denote the quantity of mutual attraction between the earth and the body weighed. When we weigh bodies on a balance, we primarily compare two forces, namely, the pull of the earth on each of the bodies on the pans of the balance, nevertheless, we can use the balance to measure mass or quantity of matter. For if two bodies are exactly balanced, that is, "weigh" the same, we know that the pull of the earth is the same on each, and since this attraction, as was shown above, is directly proportional to the masses or quantity of matter in the two bodies, the masses must be equal. That weight and mass are different ideas is evident from the fact that the force with which a given body is attracted by the earth varies according to latitude and elevation above the earth, while the quantity of matter remains the same. But if two bodies weigh the same in one place, they will do so in any other place. All our weighing is a comparison with, or measurement by, some standard weight, such as pound, ounce, gram, etc.

For scientific purposes the weight of bodies is sometimes determined *in vacuo*, because it eliminates an error due to the buoyant effect of atmospheric air. Weight thus determined is called *absolute weight*, while by ordinary methods we obtain *apparent weight*.

**Weights and Measures.**—For scientific purposes *the metric or decimal system of weights and measures* is used the world over. This system is used also for general purposes by practically all except the English-speaking nations. While

metric weights and measures were legalized in the United States and Great Britain in 1866, unfortunately neither country has as yet enforced their general adoption. The U. S. Pharmacopœia, however, uses the metric system exclusively, and it finds application in all departments of the U. S. government, as also for many other purposes. The basis of the metric system is a quadrant (one-fourth) of the earth's circumference. This divided into ten million parts gives a measure of length termed *meter* (39.37 inches), and this unit of linear measure is the basis for the measures of extension and of weight.

Subdivisions of all units of metric measure are denoted by prefixes of Latin numerals—*i. e.*, $\frac{1}{10}$ by *deci*, $\frac{1}{100}$ by *centi*, $\frac{1}{1000}$ by *milli;* while multiples are denoted by prefixes of the Greek numerals—*i. e.*, 10 by *deka*, 100 by *hecto*, 1000 by *kilo.*

The unit of measure of weight is the *kilogram*, generally abbreviated to *kilo.* (2.2046 pounds avoirdupois). This was originally intended to be the weight in a vacuum of a cubic decimeter (1000 cubic centimeters) of pure water (free from gases) at 4° C. The unit of measure of volume is the *liter* (1.0567 U. S. quart), which, as now determined, is the volume occupied by a quantity of pure water weighing 1 kilogram at 4° C. in a vacuum. Owing to a small error in the original measurement by which the standard kilogram weight was established, the liter as defined above, instead of being a cubic decimeter (1000 cubic centimeters) as originally intended, is equal to 1000.027 cubic centimeters. This value has been established by the International Bureau of Weights and Measures. The Bureau of Standards of the United States Government, the United States Pharmacopœia IX, United States Government Publications, the British Pharmacopœia, and a number of authors have decided to call the one-thousandth part of a liter a *millliliter* (abbreviated to mil. or ml.) instead of 1 cubic centimeter as formerly. One milliliter is equal to 1.000027 cubic centimeters. The difference between a liter and 1000 cubic centimeters is only 0.027 cubic centimeter or 27 milligrams of pure water at 4° C. (less than ½ minim), which difference would require pretty refined apparatus to measure. In the case of small volumes the difference between milliliters and cubic centimeters would be so exceedingly small that it could not be measured by the regular laboratory apparatus, so that practically milliliters can be measured in apparatus graduated in cubic centimeters and fractions without in any way affecting results. In principle it is correct to call the thousandth part of a liter a milliliter, but in practice it is immaterial if we call it a cubic centimeter and measure it as such.

The *gram* is a small unit of measure of weight, and is the thousandth part of a kilogram. One milliliter (1.000027 cubic centimeters) of pure water at 4° C. in a vacuum weighs 1 gram (15.43+ grains).

While in our country for commercial purposes the avoirdupois weight is chiefly used, the apothecaries' weight is employed in this country and Great Britain in prescription-writing by all who do not use the metric system. The common link connecting avoirdupois, troy, apothecaries', and Imperial weights is the grain, which is the same in the four systems. (For table of weights and measures, see Appendix.)

**Specific Weight or Specific Gravity.**—Specific weight or specific gravity denotes the weight of a body, as compared with the weight of an equal bulk or equal volume of another substance, which is taken as a standard or unit. This standard adopted for all solids and liquids, if not otherwise stated, is water at a temperature of 25° C.

(77° F.); that for gases is either atmospheric air or, more generally, hydrogen at a temperature of 0° C. (32° F.).

Specific weight is generally expressed in numbers which denote how many times the weight of an equal bulk of water is contained in the weight of the substance in question. If we say that mercury has a specific gravity or density of 13.6, or that alcohol has a specific gravity of 0.79, we mean that equal volumes of water, mercury, and alcohol represent weights in the proportion of 1, 13.6, and 0.79, or 100, 1360, and 79.

Since all liquids and solids expand or contract with change of temperature, it is very important to note the temperature in taking the specific gravity of substances. For example, the specific gravity of alcohol is less at 25° C. than that at 15° C., because alcohol expands with rise of temperature. Likewise, at a given temperature, say 25° C., it is greater when compared with water at 25° C. than when compared with water at 4° C. or 15° C., because a volume of water weighs less at 25° C. than it does at 15° C. or 4° C. Since the change in volume of solids with change in temperature is much less than in the case of liquids, the difference in specific gravity at different temperatures is much less noticeable for solids than for liquids.

**Density.**—Density, in physics, is defined as the mass or quantity of matter in a unit volume of the substance. In the metric system the mass of 1 c.c. of water at 4° C. (39.2° F.) is practically 1 gram, that is, the density of water at 4° C. is unity. At any other temperature the density of water is less than one. It can be seen that when the specific gravity of a substance is determined by comparison with water at 4° C., the number expressing this specific gravity is identical with the number expressing the density of the substance.

When the comparison is made with water at any other temperature than 4° C., the figures for the specific gravity and the density of a substance are not identical, although the difference between them is usually very small.

The specific gravity of solids heavier than water is generally determined by first weighing the substance in air and then while suspended in water. The body will be found to weigh less in water because it displaces a volume of water equal to its own, and loses a weight equal to that of the water displaced. Consequently the relation between the loss in weight and the weight in air is also the relation between the weights of equal volumes of water and the substance examined. If, for instance, a body is found to weigh 6 grams in air and 2 grams in water, the loss being 4 grams, then the relation between the weights of equal volumes of water and the substance is as 4 to 6, or 1 to 1.5; the latter being the specific gravity of the substance examined.

The specific gravity of a solid soluble in water is determined by weighing it first in air, then in a liquid of known specific gravity, but having no solvent action on the substance. The weight of the solid in air divided by the weight of the liquid displaced and the quotient then multiplied by the specific gravity of the liquid employed, gives the specific weight of the substance examined.

The specific gravity of a solid lighter than water is determined by weighing

it first in air, then in water attached to some heavy substance, the weight of which in water has been ascertained. The two substances combined will weigh less in water than the heavy solid alone. The difference in weight between the two weighings in water added to the weight of the light substance in air gives the weight of water displaced, and this sum, divided into the weight of the solid in air, gives its specific gravity.

The method of finding the specific gravity of a solid by weighing in a liquid depends on the *Principle of Archimedes*, which says: *A body immersed in a liquid loses a part of its weight equal to the weight of the displaced liquid.*

The specific gravity of liquids or gases is determined by weighing in suitable glass flasks equal volumes of the standard substance and the body to be examined. The weight of the latter divided by the weight of the standard substance gives the specific gravity.

Small glass flasks suitably arranged for taking the specific gravity of liquids are known as *pycnometers.*

A second method by which the specific gravity of liquids may be determined is by means of the instruments known as hydrometers, or, if made for some special purposes, as alcoholometers, urinometers, alkalimeters, lactometers, etc.

**Hydrometers.**—Hydrometers are instruments generally made of glass tubes, having a weight at the lower end to maintain them in an upright position in the fluid to be tested as to specific gravity, and a stem above, bearing a scale. The principle upon which their construction depends is the fact that a solid substance when placed in a liquid heavier than itself displaces a volume of this liquid equal to the whole weight of the displacing substance. The hydrometer will consequently sink lower in liquids of lower specific gravity than in heavier ones, as the instrument has to displace a larger bulk of liquid in the lighter than in the heavier liquid in order to displace its own weight.

**Weight of Gases.**—The fact that a gas, when generated or liberated, expands in every direction, might indicate that the molecules of a gas have no weight, are not attracted by the earth. A few simple experiments will, however, show that gases, like all other substances, have weight. Thus a flask from which the atmospheric air has been removed will weigh less than the same flask when filled with atmospheric air or any other gas.

**Barometer.**—A second method by which may be demonstrated the fact that atmospheric air possesses weight, is by means of the barometer. The atmosphere is that ocean of gas which encircles the earth with a layer some 50 or 100 miles in thickness, exerting a considerable pressure upon all substances by its weight. The instruments used for measuring that pressure are known as barometers, and the most common form of these is the mercury barometer. It may be constructed by filling with mercury a glass tube closed at one end (and about three feet long) and then inverting it in a vessel containing mercury, when it will be found that the mercury no longer fills the tube to the top, but only to a height of about 30 inches, leaving

a vacuum above. The column of mercury is maintained at this height by the pressure of the atmosphere upon the surface of the mercury in the vessel; a column of mercury about 30 inches high must consequently exert a pressure equal to the pressure of a column of the atmosphere of the same diameter as that of the mercury column.

As the weight of a column of mercury, having a base of one square inch and a height of about 30 inches, is equal to about 15 pounds, a column of atmosphere having also a base of one square inch must also weigh 15 pounds. In other words, the atmospheric pressure is equal to about 15 pounds to the square inch, or about one ton to the square foot. This enormous pressure is borne without inconvenience by the animal frame in consequence of the perfect uniformity of the pressure in every direction.

A barometer may be constructed of other liquids than mercury, but as the height of the column must always bear an inverse proportion to the density of the liquid used, the length of the tube required must be greater for lighter liquids. As water is 13.6 times lighter than mercury, the height of a water column to balance the atmospheric pressure is 13.6 times 30 inches, or about 34 feet.

It is evident that the pressure of the atmosphere is equal to the weight of a column of mercury, and also that this weight is directly proportional to the length of the mercury column. Hence, different atmospheric pressures can be compared in terms of the length of the mercury column of the barometer, instead of in terms of pounds per square inch. For example, at a pressure of 15 pounds per square inch, the mercury column is about 30 inches, while at a pressure of 10 pounds per square inch, it is 20 inches. The ratio of the pressures in pounds is 10 : 15 or 2 : 3, and the ratio of the mercury columns is 20 : 30 or 2 : 3, which is the same. This fact is of interest in experiments in which gas volumes are dealt with, because calculations have to be made involving a ratio of pressures, and since this ratio is the same as that of the lengths of the mercury column corresponding to the pressures, it simplifies matters greatly to express pressures in terms of the length of a column of mercury.

**Changes in the Atmospheric Pressure.**—The height of the mercury column in a barometer is not the same at all times, but varies within certain limits. These variations are due to a number of causes disturbing the density of the atmosphere, and are chiefly atmospheric currents, temperature, and the amount of moisture contained in the atmosphere.

As the height and with it the density of the atmosphere diminishes gradually from the level of the sea upward, the height of the mercury column will be lower in localities situated at an elevation. This diminution of pressure is so constant that the barometer is used for estimating elevations.

**Porosity.**—We have seen that the molecules of any substance are not in absolute contact, but that there are spaces between them which we call intermolecular spaces; the property of matter to have spaces between the particles composing it is known as *porosity*.

In the case of solids, these spaces or pores are sometimes of considerable size, visible even to the naked eye, as, for instance, in charcoal, while in most cases they cannot be discovered, even by the microscope. That even apparently very dense substances are porous, can be demonstrated by the fact that liquids may be pressed through metallic disks of considerable thickness, that gases may be caused to pass through plates of metal or stone, that solids dissolve in liquids without showing a corresponding increase in volume of the solution thus obtained, and, finally, also by the fact that substances suffer expansion or contraction in consequence of increased or diminished heat, or in consequence of mechanical pressure.

**Surface.**—In every-day life the expression "surface" refers to that part of a substance which is open to our senses, visible and measurable; but from a more scientific point of view, we have also to take into consideration those surfaces which, in consequence of porosity, extend to the interior of matter and are invisible to our eyes and absolutely immeasurable by instruments.

**Surface-action.**—Attraction acts differently under different conditions, and, accordingly, we assign different names to it. We call it cohesion when it acts between molecules, gravitation when acting between masses, and surface-action or surface-attraction when the attraction is exerted either by the visible surface or by that surface which pervades the whole interior of matter. The phenomena caused by this surface-action are extremely manifold, and some are of sufficient interest to be taken into consideration.

**Adhesion.**—Most solid substances, when immersed in water, alcohol, or many other liquids, become moist; immersed in mercury, they remain dry. We explain this fact by saying that the surfaces of most solid substances exert an attraction for the particles of such liquids as water and alcohol to such an extent that these particles adhere to the surface of the solids. Such an attraction, however, does not manifest itself for the particles of mercury. This form of surface-attraction by which liquids are caused to adhere to solids is called *adhesion*.

This adhesion may be noticed also between two plates having plane surfaces. A drop of water pressed between these plates will cause them to adhere to each other. The application and use of glue and mucilage, our methods of writing and painting, the welding together of pieces of metal, etc., depend on this kind of surface action.

**Capillary Attraction.**—While it is the general rule that liquids in vessels present a horizontal surface, this rule does not hold good near the sides of the vessel. When the liquids wet the vessel, as in the case of water in a glass vessel, the surface is somewhat concave in consequence of the attraction of the glass surface for the particles of water; on the contrary, when the liquids do not wet the vessel, as in the case of mercury in a glass vessel, the surface is somewhat convex. The smaller the diameter of the vessel holding the liquids,

the more concave or convex will the surface be. If a narrow tube is placed in a liquid, this surface-action will be more striking, and it will be found that a liquid wetting the tube will not only have a completely concave surface, but the level of the liquid stands perceptibly higher in the tube than the level of the liquid outside. Substances not wetting the tube will show the reverse action, namely, the surface inside of the tube will be convex, and will be below the level of the liquid outside.

The attraction of the surface of tubes for liquids, manifesting itself in the concave shape of the surface and in the elevation of the liquid near the tube, is known as *capillary attraction.* Capillary elevations and depressions depend upon the diameter of the tube, temperature, and the nature of the liquid. The narrower the tube, the higher the elevation or the lower the depression; both are diminished by increased temperature. Capillary elevations and depressions, all other circumstances being equal, are inversely proportional to the diameters of the tubes.

Defining the phenomena of capillary attraction more scientifically, we may say that the adhesive force of glass, wood, etc., for water and most other liquids exceeds the cohesive force acting between the molecules of these liquids, while in mercury the cohesive force predominates over the adhesive.

The rise or fall of liquids in capillary tubes is explained thus: There is an attraction between the particles in the surface of a liquid which causes the surface to act like a stretched membrane. It requires force to separate the particles in the surface and this force is spoken of as the surface tension of the liquid. Proof of this tension is seen in the fact that insects can stand on water without breaking through, and that an oily needle can float on water although it is heavier than it. Another principle in physics is that a stretched surface of a spherical form exerts a force toward the center of curvature of the surface, and tends to contract toward the center. Illustrations of this are seen in the fact that drops of liquids assume a spherical form, and that soap bubbles contract when the air in the interior of them is allowed to escape. Now, when a fine tube is dipped into a liquid that wets it, particles of the liquid are drawn up by adhesion of the glass, thus causing a curved surface, which, acting like a membrane, draws up the particles below it by cohesion. The liquid rises until the weight of the column counterbalances the cohesion between the particles in the curved surface, that is, the surface tension. Thus we see also why liquids rise higher in fine tubes than wider ones, since it requires a shorter column of liquid of greater diameter to equal in weight a longer column of smaller diameter. Moreover, since surface tension of liquids diminishes as temperature rises, we see why capillary elevation diminishes as temperature increases. The same kind of argument will explain why liquids which do not wet a tube, for example, mercury, will sink in the tube below the level of the liquid outside.

Familiar examples of capillary phenomena are the action of lamp-wicks, the rise of water in wood, sponges, bibulous paper, sand, sugar, and the rise of sap in the vessels of plants.

**Surface-attraction of Solids for Gases.**—Any dry solid substance, carefully weighed, will, after having been exposed to a higher temperature, show a decrease in weight while yet warm. Upon cooling, the original weight will be restored. This fact cannot be explained otherwise than that some substance or substances must have been expelled by heat, and that this substance or these substances are reabsorbed on cooling.

This is actually the case, and the substances expelled and reabsorbed are the gaseous constituents of the atmospheric air, chiefly the aqueous vapor.

Every solid substance upon our earth condenses upon its surface more or less of the gaseous constituents of the atmosphere. This condensation takes place upon the outer as well as upon the inner surface. The amount of gas absorbed depends upon the nature of the gas as well as upon the nature of the absorbing solid. Some of the so-called porous substances, such as charcoal, generally condense or absorb larger quantities than solids of a more dense and compact structure. Heat, as stated above, counteracts this absorbing power.

The absorptive power of charcoal for gases varies with the nature of the charcoal and the gas absorbed, as will be seen from the following table:

Unit volume of charcoal absorbs—

| | Boxwood. | Cocoanut. |
|---|---|---|
| Ammonia gas | 90 vols. | 172 vols. |
| Hydrochloric acid gas | 85 " | |
| Sulphur dioxide | 65 " | |
| Hydrogen sulphide | 55 " | |
| Nitrogen monoxide | 40 " | 86 vols. |
| Carbon dioxide | 35 " | 68 " |
| Ethylene gas | 35 " | 75 " |
| Carbon monoxide | 9.42 " | 21 " |
| Oxygen | 9.25 " | 18 " |
| Nitrogen | 7.5 " | 15 " |
| Hydrogen | 1.75 " | 4 " |

Pine charcoal has about one-half the absorptive power of boxwood charcoal. Platinum sponge absorbs about 250 times its volume of oxygen. Other porous substances, as meerschaum, gypsum, silk, etc., are also very absorbent.

**Surface-attraction of Solids for Liquids or for Solids Held in Solution.**—When a mixture of different liquids, or a mixture of different solids dissolved in a liquid, is brought in contact with or filtered through a porous solid substance, such a charcoal or bone-black, it will be found that the surface of the solid substance retains a certain amount of the liquids or of the solids held in solution, and that it retains more of one kind than of another.

It is this peculiarity of surface-attraction which is made use of in purifying drinking water by allowing it to pass through charcoal. Bone-black is similarly used for decolorizing sugar-syrup and other liquids.

**Absorbing Power of Liquids.**—In a similar manner as in the case of solids, liquids also exert an attraction for gases. When a gas is condensed within the pores or upon the surface of a solid, or when it is taken up and condensed by a liquid, we call the process *absorption.* This absorbing power of different liquids for different gases varies greatly; it is facilitated by low temperature and high pressure, and counteracted by high temperature and removal of pressure. Thus: One volume of water absorbs at ordinary temperature and pressure about 0.03 volume of oxygen, 1 volume of carbon dioxide, 30 volumes of sulphur dioxide, and 800 volumes of ammonia.

**Diffusion.**—When a cylindrical glass vessel has been partially filled with water, and alcohol, which is specifically lighter than water, is poured upon it, care being taken to prevent a mixing of the two liquids, so as to form two distinct layers, it will be found that after a certain lapse of time the two liquids have mixed with each other, particles of water having entered the alcohol and particles of alcohol the water, until a uniform mixture of the two liquids has taken place. Upon repeating the experiment with a layer of water over a column of solution of common salt, it will again be found that the two liquids gradually enter one into the other until a uniform salt solution has been formed.

In a similar manner, two or more gases introduced into a vessel or a room will readily mix with each other. This gradual passage of one liquid into another, of a dissolved substance into another liquid, or of one gas into another gas, is called *diffusion.*

The rate of diffusion is different for different substances. Saline substances may be divided into a number of equidiffusive groups. The quantity of a substance diffused varies also with the temperature. Thus, the rate of diffusion of hydrochloric acid at 49° C. is 2.18 times that at 15° C. The following table gives the approximate times of equal diffusion for the substances named:

| | | | |
|---|---|---|---|
| Hydrochloric acid | 1.0 | Magnesium sulphate | 7.0 |
| Sodium chloride | 2.3 | Albumin | 49.0 |
| Sugar | 7.0 | Caramel | 98.0 |

Magnesium sulphate is one of the least diffusible saline substances, yet it diffuses 7 times faster than albumin and 14 times faster than caramel.

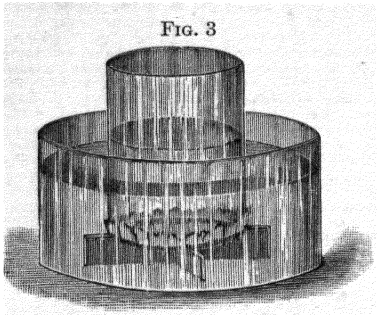
Diffusion is exhibited also by solids, even at ordinary temperature. Sir W. Roberts-Austen placed gold and lead in contact four years at 18° C., and found the surfaces united. Gold had penetrated the lead to more than 5 millimeters from the surface, while within 0.75 millimeter from the surface gold was found at the rate of 1 oz. 6 pwt. per ton, which would be profitable to extract.

The phenomena of diffusion can be explained only on the theory that matter is made up of particles or molecules in motion. They are one of the strong links in the chain of evidence upon which the molecular theory of matter is founded.

**Osmose. Dialysis.**—This diffusion takes place also when two liquids are separated by a porous diaphragm, such as bladder or parchment paper, and it is then called *osmose*, *endosmosis*, or *dialysis*.

The apparatus used for dialysis is called a *dialyzer* (Fig. 3), and consists usually of a glass cylinder, open at one end and closed at the other by the membrane to be used as the separating medium. This vessel is placed into another, and the two liquids are introduced into the two vessels. If the inner vessel be filled with a salt solution and the outer one with pure water, it will be found that part of the salt solution passes through the membrane into the water, while at the same time water passes over to the salt solution.

FIG. 3



Dialyzer.

On subjecting different substances to this process of dialysis, it has been found that some substances pass through the membrane with much greater facility or in larger quantities than others, and that some do not pass through at all. As a general rule, crystallizable substances pass through more freely than amorphous substances. Those substances which do not pass through membranes in the process of dialysis are known as *colloids*, those which diffuse rapidly, *crystalloids*.

Capillary attraction, or, more generally speaking, surface-attraction, is undoubtedly to some extent the cause of the phenomenon of osmose, the surface of the diaphragm exercising an attraction upon the liquids.

Diffusion through the membrane will not take place unless the membrane is in contact with water, and, moreover, its limit will be reached when the concentration outside is the same as that inside the dialyzer. Hence, a large quantity of water should be on the outside and often renewed. Generally, water flows through the membrane toward the denser liquid, which increases in volume, but alcohol and ether are exceptions. They act like liquids which are denser than water. In the case of acids, water flows either into the acids or from the acids, according as they are more or less dilute. When a dilute alcohol is kept for a time in a bladder the volume diminishes, but the alcoholic strength increases. The reason for this is, no doubt, that the bladder permits the water to pass rather than the alcohol.

An interesting effect of osmosis is seen in the purgative action of magnesium sulphate. A solution of this salt is not readily absorbed and causes a flow of water from the intestinal bloodvessels by osmosis, which, together with the direct stimulating action of the

salt to peristalsis, causes purging action. All strong saline solutions, above 0.7 per cent., abstract liquids from animal tissues when in contact with them.

**Diffusion of Gases.**—A diffusion similar to that of liquids takes place also when two different gases are separated from each other by some porous substance, such as burned clay, gypsum, and others.

It has been found that specifically lighter gases diffuse with greater rapidity than the heavier ones. The quantities of two different gases which diffuse into one another in a given time are, as a general rule, inversely as the square roots of their specific gravities. Oxygen is sixteen times as heavy as hydrogen; when the two gases diffuse, it will be found that four times as much hydrogen has penetrated into the oxygen as of the latter gas into the hydrogen. This regularity in the diffusion of gases is expressed in the *Law of Graham*, thus: The velocity of the diffusion of any gas is inversely proportional to the square root of its density.

**Indestructibility.**—All matter is indestructible—*i. e.*, cannot possibly be destroyed by any means whatever, and this property is known as *indestructibility*. Form, shape, appearance, properties, etc., of matter may be changed in many different ways, but the matter itself can never be annihilated. Apparently, matter often disappears, as, for instance, when water evaporates or oil burns; but these apparent destructions indicate simply a change in the form of matter; in both cases gases are formed, which become invisible constituents of the atmospheric air, and can, therefore, not be seen for the time being, but may be recondensed or rendered visible in various ways.

Not only is matter indestructible, energy also partakes of this property. This is expressed in the *law of the conservation of energy*, which says that in a limited system of bodies no gain or loss of energy is ever observed. But energy may be converted from one form into some other form. Motion may be converted into heat, and heat into motion, or this motion into electrical energy and chemical energy. In fact, all the different forms of energy are convertible one into the other, theoretically, without loss. This fact is spoken of as the *law of the correlation of energies*.

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QUESTIONS.—Define matter, force, and energy. Describe the characteristic properties of matter in the solid, liquid, and gaseous states. State the difference between amorphous, crystalline, polymorphous, and isomorphous substances. State the laws of Boyle and Avogadro. Explain the terms mass and molecule. What are cohesion, adhesion, and gravitation? Mention instances of their action. Give a definition of weight and of specific weight. Explain construction and use of mercury barometer. Define capillary attraction, absorption, diffusion, and osmose; give instances illustrating their action. What is meant by saying that matter and energy are indestructible?

## 2. HEAT.

**Motion of Molecules.**—If we place over a gas-flame a vessel containing a lump of ice of the temperature of 0° C., or 32° F., the ice melts and becomes converted into water; but if we measure with a thermometer the temperature of the water at the moment when the last particle of ice is melted, we still find it at the freezing-point, 0° C. or 32° F. From the position of the vessel over the flame, as well as from the fact that the ice has been liquefied, we know that the vessel and its contents have absorbed heat. Yet vessel and water show the same temperature as before. If the heat of the flame is allowed to continue its action on the ice-cold water, the thermometer will soon indicate a rapid absorption of heat until the temperature reaches 100° C. or 212° F. Then the water begins to boil and escapes in the form of steam, but the temperature remains stationary until the last particle of water has disappeared.

There must be, consequently, some relation between the state of aggregation of a substance and that agent which we call heat. It was the heat which liquefied the ice, it was the heat which converted the liquid water into steam or gaseous water. Yet the water, having absorbed considerable heat during the process of melting, shows a temperature of 0° C. (32° F.), and the steam also having absorbed large quantities of heat, shows 100° C. (212° F.), the temperature of boiling water. A certain amount of heat has consequently been lost or at least hidden. What has become of it?

To answer this we must first examine a little further into the nature of heat. It is a well-known fact that when two solid bodies are rubbed together heat is produced. Ice may be melted and water boiled by friction; wood may be made to ignite by rubbing it suitably. It is found by accurate experiments that there is an intimate relation between the amount of heat generated and the amount of work done to generate it. The amount of heat is always equivalent to the amount of work expended. This fact is one of the manifestations of the law known as the law of the correlation of energy.

Many other illustrations of production of heat by the expenditure of work could be given, and all would point to the conclusion that heat is associated in some way with the condition of the small particles of which substances are made up—*i. e.*, the molecules.

It is believed that the molecules of all bodies are in motion. Those of gases are perfectly free to move in any direction, while in liquids and solids they are restricted in their motion. In solids the molecules are held rigidly in a fixed position and can vibrate only back and forth. The molecules thus have a certain energy of motion which is called kinetic energy, and in liquids and solids an energy of position also, known as potential energy. This potential energy is due to the position or molecular arrangement of the particles, and to make a change in this necessitates the overcoming of the forces which hold

the molecules in place by an expenditure of energy from some outside source.

Thus it is believed that whenever heat energy is added to a body it either goes to increasing the motion of molecules—*i. e.*, the kinetic energy, or to making a change in the relative positions of the molecules—*i. e.*, in their potential energy, or to both.

When the motion of the molecules is increased—*i. e.*, when the kinetic energy is increased—there is a rise in temperature, which we can measure by a thermometer. What we call *temperature* is the degree or intensity of the sensible heat of a body.

On the other hand, heat is absorbed whenever solids pass into the liquid state; or liquids into the gaseous state. This fact is often made use of in producing artificial cold. Thus, liquefied ammonia is employed in the manufacture of ice, the required low temperature being produced by evaporation of the ammonia. Similarly, the heat absorbed during the liquefaction of snow or powdered ice by an admixture of common salt and the liquefaction of the latter through solution serve for generating a low temperature. The action of the various *freezing mixtures* depends on this principle.

**Latent Heat.**—Sometimes heat may be added to a body without any change of temperature, as above in the case of the melting of ice and the boiling of water. In such cases it is believed that the heat added is absorbed in changing the relative arrangement of the molecules, which change must evidently take place in passing from solid to liquid water and from liquid to gaseous water. This will account for the apparent loss of heat in melting ice or in boiling water. It is lost only to our senses, and exists in another form as potential energy of the molecules; hence it is called *latent heat.*

This latent heat is given out again when the molecules return to their former arrangement. Hence steam in condensing to water, and water in assuming the solid state, give off large quantities of heat.

**Sources of Heat.**—Our principal source of heat is the sun. Other sources are: The interior of the earth, the high temperature of which is made manifest by the existence of volcanoes and by the increase of temperature noted in boreholes sunk into the earth's crust; mechanical actions, as friction and compression; electric currents; and, finally, chemical action, as witnessed in the ordinary processes of combustion and of animal life.

Up to within a few years ago the principal method for generating heat depended on combustion. Heat generated by electricity is now at our command. The introduction of the electric furnace has provided means for obtaining much higher temperature than formerly. It is through these modern means that temperatures are produced sufficiently high for the liquefaction or volatilization of all substances.

On the other hand, during the last few years methods have been invented for producing very much lower temperatures than formerly. Several gases which were believed to be permanent can now be liquefied, and even solidified.

**Heat Effects.**—The most familiar changes resulting from the application of heat, that is, from the absorption of heat energy, are those affecting the volume, the temperature, and the molecular arrangement or physical state of matter. These changes do not take place independently, but accompany one another. Chemical changes are also often produced by application of heat, but these are considered in chemistry.

**Increase of Volume by Heat.**—As a general rule, the volume of any mass increases with increase in its temperature, but this increase is not alike for all matter. Gases expand more than liquids, liquids more than solids, and of the latter the metals more than most other solid substances. While the expansion of any two or more different solids or liquids is not alike, gases show a fixed regularity in this respect, namely, all gases without exception expand or contract alike when the temperature is raised or lowered an equal number of degrees.

This expansion or contraction of gases is 0.3665 per cent., or $\frac{1}{273}$ of their volume at 0° C. for every degree centigrade; thus 100 volumes of air become 100.3665 volumes when heated from 0° to 1° C., or 136.65 when heated from 0° to 100° C. This regularity in the expansion and contraction of gases is expressed in the *Law of Charles*, which says: *If the pressure remain constant, the volume of a gas increases regularly as the temperature increases, and decreases as the temperature decreases.* If heat be applied to a gas confined in a closed vessel and be thus prevented from expanding, the increase of heat will manifest itself as pressure, which rises with the same regularity as shown for expansion, viz., 0.3665 per cent. for every degree centigrade.

It often becomes necessary to reduce the volume of a gas measured at any temperature and at any pressure to the volume it would occupy at 0° C. and 760 mm. pressure, which have been adopted as normal temperature and pressure. The method for making this calculation is given in the paragraph on gas-analysis, for which see Index.

In expansion of solids and liquids the heat energy applied is utilized partly in forcing the molecules farther apart or overcoming cohesion, partly in raising the temperature or giving the molecules greater motion, and partly in doing external work, that is, work that the expanding body does in raising a load that may be resting upon it, or overcoming any force exerted against it. In the expansion of gases, there being no cohesion between the molecules, the heat energy is utilized in raising the temperature and in doing work by the gas against external force.

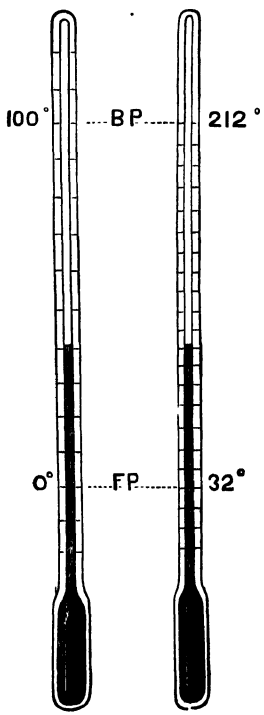
Expansion is a very important thing which must be taken into account by constructors, for example, of bridges, railroad beds, etc. Also in very careful physical measurements, expansion of glass apparatus, solutions, barometers, etc., must be carefully noted.

**Increase in Temperature by Heat.**—As was said above, the present molecular theory of matter regards the molecules as in motion, and the result of this energy of motion is what we call temperature, or intensity or degree of heat. Anything that increases this motion of

the molecules, causes a rise of temperature. Our skin is possessed of nerve structures by which we can judge whether a body is hot or cold or whether one body is hotter than another, but these are not delicate enough to make quantitative distinctions between temperatures. For this purpose we make use of instruments called

**Thermometers.**—In these, use is made of the fact that bodies expand while the temperature rises, and that the expansion is proportional to rise of temperature. Thermometers, therefore, measure directly only expansion, and indirectly degrees of heat, but the expansion is used as a measure of the degree of heat. The most common thermometer is the mercury thermometer. This instrument may be easily constructed by filling a glass tube, having a bulb at the lower end, with mercury, and heating the tube until the mercury boils and all air has been expelled, when the tube is sealed. It is then placed in steam arising from water boiling actively under normal barometric pressure of 760 millimeters of mercury, and the point to which the mercury rises is marked B. P. (boiling-point); after which it is placed in melting ice, and the point to which the mercury sinks is marked F. P. (freezing-point). The distance between the boiling- and freezing-points is then divided into 100 degrees in the so-called centigrade or Celsius thermometer, into 80 degrees in the Réaumur thermometer, and into 180 degrees in the Fahrenheit thermometer. The inventor of the latter instrument, Fahrenheit, commenced counting, not from the freezing-point, but 32 degrees below it, which causes the freezing-point to be at 32°, and the boiling-point at 180 degrees above it, or at 212° (Fig. 4). Degrees of temperature below the zero point of either instrument are designated by −, *i. e.*, minus.

FIG. 4




Centigrade. Fahrenheit. Thermometric scales.

As 100 degrees centigrade are equivalent to 180 degrees Fahrenheit, it follows that 1 degree C. = 1.8 degree F., or 1 degree F. = $\frac{1}{1.8}$ degree C. In converting the degrees from one scale to the other it must be remembered that the zero point of Fahrenheit is 32 degrees below the zero on the centigrade scale. Consequently, in converting the reading on a Fahrenheit scale into centigrade degrees, 32 degrees must be deducted, or, *vice versa*, be added, before the calculation can be made. In other words, to convert Fahrenheit into centigrade: Subtract 32 and divide by 1.8; to convert centigrade into Fahrenheit: Multiply by 1.8 and add 32.

**Recording or Self-registering Thermometers.**—One kind of these instruments is so constructed

as to show the highest, the other the lowest temperature to which the thermometer had been exposed from the time it was last adjusted. The physician's fever thermometer is a maximum recording thermometer with a scale ranging usually from 94° to 112° F. These thermometers have near the bulb a constriction in the tube which breaks the column of mercury when it contracts. Consequently the thin column of mercury retains its position on cooling, but may be forced back through the constriction into the bulb by shaking the instrument.

**Absolute Temperature.**—If differences of temperature are due to faster or slower motion of molecules, we can well imagine that there is a limit in both directions. Where the limit is to be found for rapidity of motion is unknown, but good reasons lead us to believe that we know the point at which molecular motion ceases.

One of the reasons which lead us to believe in the correctness of this statement is the Law of Charles, above mentioned. In accordance with this law, it follows that if a mass of air at 0° C. is heated, its volume is increased $\frac{1}{273}$ of the original volume for every degree its temperature is raised. At 273° C. its volume is consequently doubled, and at 546° C. tripled. If a mass of air is cooled below 0° C., its volume is diminished $\frac{1}{273}$ of its volume for every degree its temperature is lowered. Consequently, if its volume were to continue to decrease at that rate until it reached —273° C., mathematically speaking its volume would become nothing. In fact, the air long before this low temperature had been reached would cease to be a gas—would first liquefy, then solidify, and at the temperature of —273° C. would become a compact mass in which the molecules were at absolute rest. This point of no heat is called the *absolute zero*, and temperature reckoned from this point is called *absolute temperature*.

The fraction $\frac{1}{273}$ is called the *coefficient of expansion* for centigrade degrees, while $\frac{1}{491}$ is the coefficient of expansion for degrees of Fahrenheit. The absolute temperature may be found by adding 273 to the reading on a centigrade thermometer, or 459 to the reading on a Fahrenheit thermometer.

While the temperature of absolute zero may never be obtainable by man, so much successful work in the field of low temperatures has been done lately that temperatures within 9 degrees of absolute zero have been observed.

In chemistry and other fields, temperature is often indicated by such phrases as red heat, white heat, etc. The following table gives approximately the degrees corresponding to such expressions:

| | |
|---|---|
| Incipient red heat | 525° C. (977° F.). |
| Dark red heat | 700° C. (1292° F.). |
| Bright red heat | 950° C. (1742° F.). |
| Yellow heat | 1100° C. (2012° F.). |
| Incipient white heat | 1300° C. (2372° F.). |
| White heat | 1500° C. (2732° F.). |

**Mechanical Equivalent of Heat.**—While thermometers indicate the *intensity of heat,* it is often desirable to measure *heat quantities.* These determinations are based on the intimate relationship existing between heat and mechanical or molecular motion, which are capable of being converted one into the other. Thus, friction produces heat and heat produces motion in the steam engine. Heat, through its power to produce motion, can do work, and the amount of work it can do depends on the quantity of heat.

The unit of heat quantity now universally used in chemical and physiological work is the *calorie.* It is the amount of heat consumed in raising 1 kilogram of water from 0° C. to 1° C. (or, approximately, 1 pound of water 4 degrees of Fahrenheit). If this amount of heat could all be made to do mechanical work, it would be sufficient to raise 420 kilograms 1 meter high, or 3000 pounds 1 foot high—*i. e.,* the calorie is equivalent to 420 kilogram-meters, or 3000 foot-pounds. The heat generated by combustion is determined in the laboratory by means of an apparatus known as the *calorimeter.* This is generally so constructed that a definite weight of substance may be burned in a chamber surrounded by cold water. The rise in temperature of this known quantity of water serves as the basis for calculation.

**Specific Heat.**—Equal weights of different substances require different quantities of heat to raise them to the same temperature. For instance: The same quantity of heat which is sufficient to raise 1 pound of water from 60° to 70° will raise the temperature of 1 pound of olive oil from 60° to 80°, or that of 2 pounds of olive oil from 60° to 70°. Olive oil consequently requires only one-half the heat necessary to raise an equal weight of water the same number of degrees. As water has been selected as the standard for comparison, we may say that specific heat is the heat required to raise a certain weight of a substance a certain number of degrees, compared with the heat required to raise an equal weight of water the same number of degrees.

The heat required to raise 1 gram of water 1 degree centigrade is usually taken as the unit of comparison. On thus comparing olive oil, we find its specific heat to be $\frac{1}{2}$. If we say the specific heat of mercury is $\frac{1}{32}$, we indicate that equal quantities of heat will be required to raise 1 pound of water or 32 pounds of mercury 1 degree, or that the heat which raises 1 pound of water 1 degree will raise 1 pound of mercury 32 degrees.

**Conduction of Heat.**—When the end of a metallic bar is heated, a rise in its temperature is soon noticed at a distance from the heated part. This transfer of heat from some source, for instance from a flame to a cold substance, is practically a transfer of motion from more rapidly moving molecules to those moving more slowly. It may be compared to the motion imparted to a billiard ball at rest or moving slowly by another ball propelled with greater velocity. The more rapidly moving ball will lose part of its velocity in imparting

motion to the other ball. Similarly, the rapidly moving molecules of the hot body in transferring motion to molecules moving slowly in the cold body lose some of their velocity—*i. e.*, the hot body itself becomes cooler. The expression "cooling off" must never be understood to imply a transfer of cold, but always a removal of heat. In taking a cold bath, or in applying an ice-bag to a fever patient, we bring about a slower molecular motion in the tissues exposed to the cold material.

The direct transfer of molecular motion is called *conduction of heat*, but in examining various materials we find that they show a great difference in their power to conduct heat. For instance, if we hold in a flame the end of a glass rod, it may be made red-hot, while but little increase of heat will be perceived at the other end. We accordingly distinguish between good and bad conductors of heat. Gases and liquids (mercury excepted) are bad conductors, and of the solids the metals are the best. The following table gives the comparative heat-conducting power of a number of substances, that of silver being taken as the standard, and represented by 1:

| | | | |
|---|---|---|---|
| Copper . | 0 96 | Glass . . . . | 0 0005 |
| Iron . . | 0 20 | Wool . . . | 0 00012 |
| Stone . . | 0 006 | Paper . . . . | 0 000094 |
| Water . | 0 002 | Air . . | 0 000049 |

**Convection.**—On fastening a piece of ice to the bottom of a test-tube, and filling this with water and holding it over a flame in such a manner that only the upper portion of the tube is heated, the water may be made to boil before the ice has been melted. The reason is that water is a bad conductor of heat. If the flame be applied to the lower part of the test-tube, the whole mass of water will remain cold until the ice has melted, and the temperature will then rise evenly through the mass of water, because the heated lighter particles will move upward while the colder ones move downward. Thus ascending and descending currents are produced, equalizing the temperature. The term *convection* is applied to this method of conveying and distributing heat. Air or gases behave similarly, and this fact is of practical interest in the construction of chimneys and in heating and ventilating buildings.

**Radiation of Heat.**—A heated body, for instance a ball of red-hot iron, suspended in the air or in a vacuum will heat objects near by. If a screen is placed between these objects and the heated body, no rise in temperature is noticed. Heat is here propagated through space in straight lines, commonly spoken of as heat rays.

In order to explain these phemonena, as also others closely related to them, such as those of light and electricity, it has been necessary to assume the existence of some agent that serves as a means for this propagation. This hypothetical agent, called *ether*, is a medium of

extreme tenuity and elasticity supposed to be diffused throughout the universe, and indeed permeating all matter.

Similarly, as waves of water are generated by dropping a stone into it, and as sound waves are produced in air by causing it to vibrate, so heat waves are produced in the ether whenever it is disturbed by the rapid molecular motion of a heated body.

While our views regarding the nature of ether are of a hypothetical character, there can be no doubt of the existence of these heat waves. Indeed, their length, their velocity, and many other features have been fully determined; they obey largely the same laws which have been established for light waves—*i. e.*, when striking against a body they are generally reflected, transmitted, diffused, or absorbed, It is this absorption of heat, as we call it, which causes the heating effects through space. It may be compared to the motion that can be imparted to an object floating on still water. By disturbing the water, as by dropping a stone into it at a distance from the floating object, concentric ripples or waves pass from the point where the water was disturbed, and in striking the floating object cause it to move. Similarly, waves of heat pass from a heated body through the ether in every direction, and in striking against a body cause its molecules to move faster—*i. e.*, render it warmer. It is by this process that heat is transmitted from the sun to the earth.

**Change in Molecular State.**—As was pointed out above in the discussion of the nature of heat, it requires energy to bring about a change in the relative position of the molecules of a substance, which is called internal work. This is true for solids and liquids, but not for gases, since there is practically no cohesion between the particles of a gas, and so no work is required to change the position of the particles. Several familiar phenomena involve change in the molecular state.

**Fusion or Melting.**—This name is applied to the process by which a solid passes into the liquid state. When a liquid passes into the solid state, the process is known as solidification. As a rule, when solids are heated, they begin to melt at a definite temperature, which is known as the *fusion-point* or *melting-point*. Conversely, when liquids are cooled, they begin to solidify at a definite temperature, which is identical with the melting-point of the solid. Moreover, the temperature remains constant as long as fusion or solidification continues.

Solids that are individuals (not mixtures) and are perfectly pure as far as they melt without decomposition, have definite or sharp melting-points, which fact is utilized in chemistry extensively for determining the identity of substances and their purity. A small amount of impurity in a substance often causes a notable change in its melting-point and the temperature rises between the beginning and the end of melting, instead of remaining constant.

Some solids, like wax and paraffin, which are mixtures, do not remain at the same temperature during fusion, and in such cases the melting-point is taken as the average of the temperatures at which fusion and solidification begin.

The *determination of the melting-point* is carried out by introducing a column about $\frac{1}{4}$ inch long of the finely powdered substance into a capillary glass tube sealed at one end, and attaching this to the bulb of a thermometer. The latter is then dipped into a liquid of high boiling-point and the temperature is slowly raised. The instant the substance melts, the temperature is noted, which is the melting-point, often abbreviated M. P.

**Latent Heat of Fusion.**—This is the number of heat units (calories) required to make 1 gram of a substance fuse. Different substances have different latent heats of fusion, but water (ice) has the greatest. To melt 1 gram of ice at 0° C. to water at 0° C. requires 80 calories, or as much heat becomes latent as will raise 1 gram of water from 0° C. to 80° C.

**Change of Volume by Fusion.**—When any solid fuses, a change in volume always occurs. Some substances expand during fusion, for example, bismuth, wax; others contract, for example, brass, cast-iron, ice. When a solid floats in its own liquid, this is evidence that it contracts on fusion, because the density of the solid is less than that of its liquid. When a solid sinks in its own liquid, there is expansion on fusion.

**Evaporation and Boiling.**—Many liquids, even some solids, evaporate or assume the gaseous state at nearly all temperatures. Water and ice, mercury, camphor, and many other substances vaporize at temperatures which are far below their regular boiling-points. This fact is to be explained by the assumption that during the rapid vibratory motion of the particles of these masses, some particles are driven from the surface beyond the sphere to which the surrounding molecules exert an attraction, and thus intermingle with the molecules of the surrounding air.

This evaporation, which takes place at various temperatures and at the surface only, is not to be confounded with boiling, which is the rapid conversion of a liquid into a gas at a fixed temperature with the phenomena of ebullition, due to the formation of gas in the mass of liquid. Boiling-point may therefore be defined as the highest point to which any liquid can be heated under the normal pressure of one atmosphere.

A liquid in a closed space evaporates until a definite pressure is attained by the vapor at a fixed temperature, when the liquid and vapor remain in equilibrium. When this limit is reached the vapor is said to be "saturated." If the temperature is increased, more liquid evaporates and the pressure increases. If the temperature of a saturated vapor falls, some vapor is condensed to liquid, or if the pressure is increased, some vapor will also condense to liquid. At a given temperature a saturated vapor exerts a definite pressure, which is different for different vapors. Thus, in terms of a column of mercury, at 20° C. (68° F.), water vapor exerts a pressure of 17 mm., alcohol vapor, 60 mm., and ether vapor, 450 mm.

As a rule, in experiments where gas volumes are measured, the gas is saturated with aqueous vapor, which has to be taken into account in making calculations. If a volume of gas saturated with water-vapor is measured at atmospheric pressure, the tension of the gas alone is the difference between the barometric pressure and the tension of the saturated water-vapor at the given temperature.

*Tension of Saturated Water-vapor* (Regnault).

| Temperature, Centigrade. | Tension in mm. | Temperature, Centigrade. | Tension in mm. |
|---|---|---|---|
| 0° | 4.6 | 16° | 13.5 |
| 1° | 4.9 | 17° | 14.4 |
| 2° | 5.3 | 18° | 15.4 |
| 3° | 5.7 | 19° | 16.3 |
| 4° | 6 1 | 20° | 17.4 |
| 5° | 6.5 | 21° | 18.5 |
| 6° | 7.0 | 22° | 19.7 |
| 7° | 7.5 | 23° | 20.9 |
| 8° | 8.0 | 24° | 22.2 |
| 9° | 8 5 | 25° | 23.6 |
| 10° | 9.1 | 26° | 25 0 |
| 11° | 9.8 | 27° | 26.5 |
| 12° | 10.4 | 28° | 28 1 |
| 13° | 11.1 | 29° | 29.8 |
| 14° | 11.9 | 30° | 31.6 |
| 15° | 12.7 | | |

*Distillation* is the conversion of a liquid into a gas, and the condensation of the gas into a liquid, by causing the gas to pass through a cooling device or *condenser*, whereby the heat that was made latent and is necessary for maintaining the gaseous state, is extracted. Distillation is usually carried on by boiling the liquid under atmospheric pressure, but sometimes it is done under reduced pressure by exhausting the air from the apparatus, and then the liquid boils at a much lower temperature. Distillation is a very useful process for purifying liquids, as, thereby, non-volatile impurities may be easily removed from liquids. Moreover, mixtures of liquids having different boiling-points may be separated approximately into the constituents by distillation (see Fractional Distillation in Index).

The process of vaporization, known as *sublimation*, has been mentioned under Crystals, page 21.

The *determination of the boiling-point* is best done in a flask, as shown in Fig. 42. If inflammable or noxious vapors are likely to be evolved, they may be condensed to the liquid state by connecting the exit tube of the flask with a condenser. It is important that the thermometer should not be immersed in the liquid, but should be surrounded only by the vapor of the liquid. Heat is applied to the flask until the liquid assumes a state of active ebullition, and when vapor is escaping freely and the temperature ceases to rise, the latter

is noted. This is the boiling-point of the liquid at the atmospheric pressure prevailing at the time.

Pure liquids, under the same pressure, always have the same boiling-points, and this property is very important in chemistry in judging of the purity of liquids. Impure liquids not only have different boiling-points from the pure substances, but also the temperature rises during boiling instead of remaining constant.

The boiling-points of different liquids vary widely. Thus, mercury boils at 357° C., water at 100° C., alcohol at 78° C., chloroform at 61° C., ether at 35° C., oxygen at —182.5° C., hydrogen at —252.5° C., under standard atmospheric pressure.

**Latent Heat of Vaporization.**—When a liquid passes to the gaseous state, heat energy is absorbed or becomes latent, and, conversely, when a vapor is condensed to a liquid, the same heat energy is given out. If the heat is not added to the liquid from the outside, the heat is absorbed from the liquid itself during vaporization and its temperature falls. The sensation of cold produced by the evaporation of water, alcohol, ether, chloroform, etc., from the skin is familiar to everyone. It is by evaporation of moisture from the skin that the temperature of our body is kept normal in heated weather. A thin glass beaker containing ether and resting on some water on a glass plate may quickly be frozen to the plate by passing a rapid current of air through the ether.

The number of calories of heat required to vaporize 1 gram of any liquid at a given temperature is called its *latent heat of vaporization*. The latent heat of steam at 100° C. is 535.9 calories, that is, it requires as much heat to convert 1 gram of water at 100° C. into steam at 100° C., as would raise 535.9 grams of water 1° C. in temperature. Steam has the largest latent heat of all known substances, hence, its value in warming houses, etc., by the steam-heating process.

**Influence of Pressure on State of Aggregation.**—We have seen that the volume of a substance, and, more especially, of a gas, depends upon pressure and temperature, an increase of pressure or decrease of temperature causing the volume to become smaller. We learned also that liquids may be converted into gases, and that this conversion takes place at a certain fixed temperature, called the boiling-point. This point, however, changes with the pressure. An increased pressure will raise, a decreased pressure will lower, the boiling-point. This is due to the fact that bubbles of vapor can form in the body of a liquid only when the tension of the vapor is equal to the pressure exerted on the surface of the liquid. If that be increased, the tension of the vapor must also be increased, which can only be done by raising the temperature.

Thus, water boils at the normal pressure of one atmosphere at 100° C. (212° F.), but it will boil at a lower temperature on mountains in consequence of the diminished atmospheric pressure. If the pressure be increased, as, for instance, in steam-boilers, the boiling-point will be raised. Thus, the boiling-point of water under a pressure of two atmospheres is at 122° C. (251° F.), of five atmo-

spheres at 153° C. (307° F.), of ten atmospheres at 180° C. (356° F.). A difference of pressure of 10 millimeters from the normal atmospheric pressure (760 mm.) produces a difference of 0.36° C. in the boiling-point of water, 100° C.

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QUESTIONS.—What is the view in regard to the nature of heat? What is meant by sensible heat and latent heat? What is the law in regard to expansion of gases when heated? Explain the construction of a thermometer and the principle on which it depends. What Fahrenheit temperature corresponds to 50° C., to 130° C., to —40° C.? What Centigrade temperature corresponds to 167° F., to 311° F., to 14° F.? What is meant by absolute temperature? Give a definition of the following: Calorie, specific heat, conduction, convection, and radiation of heat. Define melting and state how the melting-point is determined; define latent heat of fusion. State the difference between evaporation and boiling. What is distillation and sublimation? What is meant by latent heat of vaporization? What is the influence of pressure on the boiling-point of liquids?

# II.

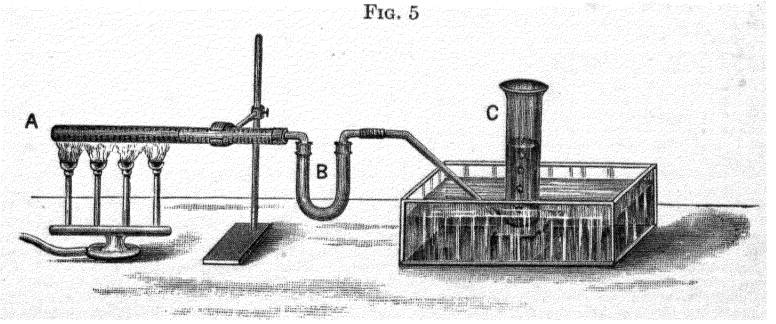
# GENERAL CHEMISTRY.

## 3. ELEMENT, COMPOUND, CHEMICAL AFFINITY, MODES OF EFFECTING CHEMICAL CHANGE.

HAVING considered some of the subjects of physics, we may now pass to the field of chemistry. The nature of a chemical change and the scope of chemistry have already been discussed on page 18. One of the simplest means of bringing about a change in the composition of matter is by applying heat. Let us see what may be learned from the following experiment.

**Decomposition by Heat.**—The results of the action of heat upon matter have been stated to be: Increased velocity of the motion of molecules, increase in volume of the substance heated, and in many cases a conversion of solids into liquids and of these into gases. Besides these results there frequently may be noticed another.

FIG. 5




Decomposition of mercuric oxide in *A*, collection of mercury in *B*, and of oxygen in *C*

To illustrate this action of heat, we will select the red oxide of mercury, a solid substance which is insoluble in water, almost tasteless, and of a brick-red color. When this oxide of mercury is placed in a glass tube and heated, it will be found to disappear gradually, and we might assume that it has been converted into a gas from which, upon cooling, the red oxide of mercury would be re-obtained.

If the apparatus for heating the oxide of mercury be so constructed that the escaping gases may be collected and cooled, we shall not find the red oxide in our receiver, but in its place a colorless gas, while at the same time globules of metallic mercury will be found deposited in the cooler parts of the apparatus (Fig. 5).

The action of heat consequently has in this case produced an effect entirely different from the effects spoken of heretofore. There is no doubt that the first action of the heat upon the oxide of mercury is an increased velocity of the motion of its molecules and simultaneously an increase of its volume, but afterward a decomposition of the oxide takes place, and two substances are liberated, each different from the oxide.

One of these substances is a silvery-white, heavy, liquid metal, the mercury; the other substance is a colorless, odorless gas, which supports combustion much more freely than does atmospheric air, and is known as oxygen.

**Elements.**—We have thus succeeded in proving that red oxide of mercury may be converted or decomposed by the mere action of heat into mercury and oxygen. It is but natural to inquire whether it would be possible further to subdivide the mercury or the oxygen into two or more new substances of different properties. To this question, which has been experimentally propounded to Nature over and over again, we have but one answer, viz.: Oxygen and mercury are substances incapable of decomposition by any method or means as yet known to us. They resist the powerful influences of electricity and heat, even when raised to the highest attainable degrees of intensity, and they issue unchanged from every variety of reaction hitherto devised with the view of resolving them into simpler forms of matter.

Therefore we are justified in regarding oxygen and mercury as non-decomposable or simple substances, in contradistinction to compound or decomposable substances, such as the red oxide of mercury.

All substances which cannot by any known means be resolved into simpler forms of matter, are called *elements;* all substances which may, by one process or another, be resolved or decomposed in such a manner that new substances with new properties are formed, are called *compound substances* or *compounds.*

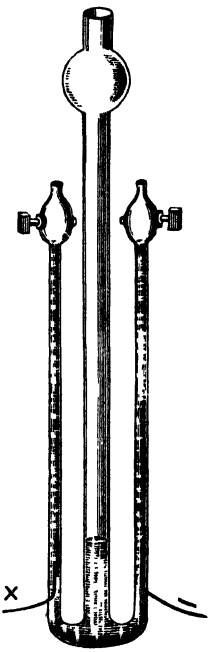
While the number of known compounds exceeds many thousands, the number of elements is comparatively small, about eighty of these simple substances being known to exist on our earth. And yet this small number of elements, by combining with each other in many different proportions, form all that boundless variety of matter which we see in nature.

In the case of oxide of mercury heat has evidently caused a weakening of the attractive force which held the two elements, mercury and oxygen, together, thus permitting them to part company. Such a change is known as *decomposition.* But, in other cases, heat

increases the attraction between elements, so that they unite to form more complex bodies, which would not occur at ordinary temperature. Such a change is known as *combination*. For example, magnesium metal does not unite with the oxygen of the air at ordinary temperature, but when heated sufficiently, it unites with oxygen with great vigor. In fact, mercury unites with oxygen when heated to a temperature a little below its boiling-point, and forms the red oxide, but if the latter is heated to a higher temperature it is decomposed.

The student must not think that elements are obtained in all cases of decomposition by heat. In some instances the new products obtained are themselves compounds, while in others an element and a new compound result. For example, when calcium carbonate is heated (see page 18), calcium oxide, a solid compound, and carbon dioxide, a gaseous compound, are obtained. When potassium chlorate, a compound of potassium, chlorine, and oxygen, is heated, the element oxygen is evolved, while a new compound composed of potassium and chlorine, and known as potassium chloride, remains as a solid in the vessel.

FIG. 6




Electrolysis of water.

The quantity of heat required for decomposition differs widely according to the nature of the substance. Some substances can be produced only at a temperature below the freezing-point of water, a higher temperature causing their decomposition; other substances may be decomposed at temperatures between the freezing- and boiling-points; others again, and to these belong the majority of inorganic compounds, may be raised to red or white heat before decomposition sets in; and still another number of compounds have never yet been decomposed by heat. Theoretically, however, we assume that all compounds may be decomposed by heat, should it be possible to raise it to a sufficiently high degree.

**Decomposition by the Electric Current.**—A highly important effect of electric currents is their power to cause chemical decomposition—*i. e.*, the splitting up of matter into two of its component parts. Thus, if the terminals of a battery are placed in a vessel with acidified water, gas-bubbles rise from both terminals, and on examination the gases are found to be hydrogen and oxygen, which are the constituents of water. In order to collect the gases and measure their volume, the apparatus shown in Fig. 6 may be used. It consists of three connected

glass tubes, which are filled with water acidified with sulphuric acid. The electric current is made to pass through the liquid from the poles, in this case preferably pieces of platinum foil fastened to platinum wire fused in the glass tubes. On passing a current through the liquid, oxygen rises from the positive, and hydrogen from the negative pole. The process of splitting up a compound body by electricity is called *electrolysis;* the bodies undergoing decomposition are termed *electrolytes.* The metallic conductors by which the current enters and leaves a liquid or gaseous electrolyte are called *poles* or *electrodes,* and are designated by the same names given to the plates in the generating cell—*i. e.,* they are called positive (+) pole or anode, and negative (—) pole or cathode. The decomposition product appearing at the positive pole is said to be electronegative, the one appearing at the negative pole is electropositive. The electrolyte must be a conductor of electricity, and either in the liquid or gaseous state. The electrolyte is brought into the liquid state either by melting it if solid or dissolving it in some other molten medium, or, as is most frequently the case, by dissolving it in water, which in some cases is rendered acid or alkaline, before electrolysis is carried out.

When an electric current passes through a solution of a metallic salt (which consists of a metal united with an acid, such as hydrochloric, sulphuric, or any other acid) the salt undergoes decomposition, the metal passing to the electronegative pole and the acid component to the electropositive pole. Use is made of this property in the different processes of electroplating and electrotyping. Among the metals requiring the weakest current for their electrolytic precipitation are copper, silver, gold, and nickel, and these are often precipitated upon other metals which form the negative pole.

Electricity is widely used at the present day in chemical industries and in quantitative chemical analysis. Some examples of chemicals obtained thus are metallic sodium and potassium, caustic potash, chlorine which is converted into bleaching powder, potassium chlorate, aluminum by electrolysis of a solution of aluminum oxide in molten cryolite, pure copper from the impure product, pure iron, nitric acid by a powerful electric discharge through air.

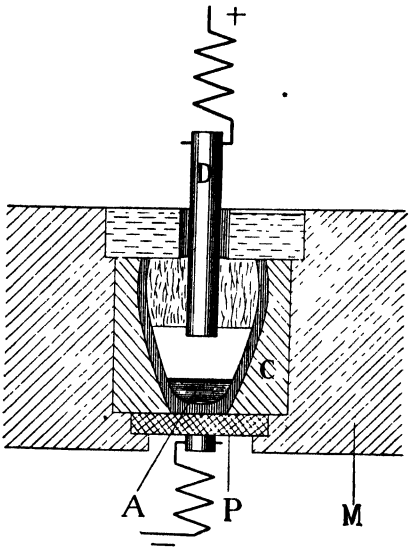
**Electric Furnace.**—There are three modes of utilizing the electric current to bring about chemical transformations, namely: (1) the direct as in plain electrolysis; (2) the indirect, in which the current is used to generate heat, the chemical change being the result of this heat; and (3) a combination of electrolysis and heat, the current being used to generate heat and effect electrolysis at the same time.

Whenever a current passes through a metal or any other material, it meets with more or less resistance, the amount of which depends on the nature and thickness of the material. This resistance gives rise to the conversion of electrical energy into heat. Practical use is now extensively made of these heating effects by passing strong currents through poor conductors, as is done in the heaters used for

heating cars or buildings, in stoves for cooking purposes, in the *vulcanizers* used in dental operations, and in *electric furnaces*. In the latter, powerful currents are employed to produce temperatures unattainable by processes of combustion or by any other means at our disposal. These furnaces have not only revolutionized many processes of manufacture, but have led to the discovery of a number of substances.

The construction of electric furnaces differs widely according to the use made of them. Fig. 7 represents the vertical section of a

FIG. 7




Electric furnace.

furnace used for the manufacture of aluminum-bronze. The material to be acted on is contained in a graphite crucible, *A*, resting on the metallic plate *P*, and surrounded by a mass of carbon, *C*, the whole being enclosed by the furnace wall *M*. *D* is a carbon rod, and acts as the anode, while connection through the metallic plate is made with the cathode from below.

**Chemical Effects of Light.**—The well-known bleaching effect that sunlight has on many dyestuffs shows that light has the power to bring about chemical changes. The art of photography is one of the practical applications of this principle. Plant life is dependent on the light that reaches us from the sun. The storage of many chemicals in the dark, or in colored glass bottles, is often necessary to protect them from the decomposing influence of light.

The phenomena of heat, light, and electricity resemble each other in so far as they are phenomena of motion. Heat is the consequence of the motion of

material particles (molecules); light is the consequence of the vibratory motion of the hypothetical medium, ether; probably the same is true of electricity.

These motions, in being transferred, have, as shown above, frequently the tendency of splitting up the molecules of compound substances.

**Mutual Action of Substances upon Each Other.**—As a general rule, it may be said that no chemical action takes place between two substances both of which are in the solid state, because the molecules do not come in sufficiently close proximity to exchange their parts. The free motion of the molecules in liquid or gaseous substances facilitates such a proximity, and consequently chemical action. It is often sufficient to have but one of the acting substances in the gaseous or liquid state, while the second one is a solid. By converting two solids into extremely fine powder and mixing them together thoroughly, chemical combination may follow, provided the affinity between them be sufficiently strong.

**Physical Phenomena Accompanying Chemical Action.**—By a careful observation of all the details in a great variety of chemical actions, an intimate connection between physics and chemistry becomes apparent. A noteworthy fact that stands out prominently is that in every change in composition, energy in some form is produced or consumed. In the decomposition of red oxide of mercury, heat energy is constantly being absorbed and rendered latent as the oxide separates into the free elements, oxygen and mercury. As soon as the heat supply is withdrawn the decomposition ceases. When magnesium burns, that is, unites with oxygen, a great quantity of heat and intense light is produced, and the action after starting is self-sustaining. We have seen that electric energy is consumed in bringing about chemical change. On the other hand, chemical action under proper control can be made to produce electric energy, that is, an electric current. In some cases the energy of light rays is consumed in producing chemical change, for example, in photography. Decomposition can be accomplished in certain instances by mechanical energy, as violent trituration, while, on the other hand, the production of mechanical energy by chemical action is illustrated by the explosion of gunpowder and movement of muscles.

**Chemical or Internal Energy.—Exothermic and Endothermic Actions.**—From the previous discussion, we learn that there must be another kind of energy stored up in latent form in matter which under proper conditions is converted into forms of energy with which we have already become familiar in Section I on Physics; namely, heat, electricity, light, mechanical energy. This form of energy, which is made manifest during chemical change, is called *chemical* or *internal energy*. Every element and compound should be looked upon not merely as consisting of certain kinds of matter, but also as a storehouse of chemical energy. In many chemical changes part of the internal energy is liberated in forms which can be measured, such as heat, electricity, etc. This portion is known as *free* or *available*

*internal energy*, and is different in amount according to the nature of the substances concerned in the chemical change. For example, the same weight of various articles of food, when undergoing combustion in the animal body, produces very different amounts of heat, and therefore these foods have different values as fuels for keeping up the temperature of the animal body.

Sometimes it is necessary to augment the internal energy of substances from a supply of energy such as heat, electricity, etc., in order to bring about chemical change. Indeed, it has been found that all chemical changes may be divided into two classes: (1) those which take place spontaneously and in which a certain amount of the chemical energy of the substances acting is liberated and converted into some other forms of energy, which thus become available for use; (2) those which do not take place spontaneously, but which must be sustained by the addition of energy from without to the substances acting. The energy set free in spontaneous chemical actions usually appears as heat, and all actions proceeding with liberation of heat are called *exothermic*, while those actions which absorb heat are called *endothermic*. The study of the energy changes in chemical actions is very important for a full understanding of such actions. The study of the heat produced or absorbed in chemical changes constitutes a subdivision known as Thermochemistry.

**Chemical Reaction.**—Chemical reaction in its broadest sense, refers to any chemical change, but is used more especially when the intention is to study the nature of the substances decomposed or formed. The expression *reagent* is applied to those substances used for bringing about such changes.

**Chemical Affinity.**—There must be some cause which enables or even forces the different elements to unite with each other so as to form compound bodies. There must be, for instance, a cause which enables oxygen and mercury to combine and form a red powder.

This cause is to be found in the existence of another form of attraction which causes the smallest particles of different elements to unite to form new substances with new properties. This kind of attractive power is called *chemical force* or *chemical affinity*, and bodies possessing this capacity of uniting with each other are said to have an affinity for each other.

There is a great difference between chemical attraction and the various forms of attraction spoken of heretofore. Cohesion simply holds together the molecules of the same substance, adhesion acts chiefly between the molecules of solid and liquid substances, gravitation acts between masses. But all these forces do not change the nature, the external and internal properties of matter; this is done when chemical force or affinity is operating, when a chemical change takes place.

For instance: In a piece of yellow sulphur the molecules are held together by cohesion, and we can counteract this cohesion by mechanical subdivision, reducing the sulphur to a fine powder; or by the

application of heat we can further subdivide the sulphur, melt, and finally volatilize it; or we can throw a piece of sulphur into the air, when it will fall back upon the earth in consequence of gravitation; or we can dip it into water, when it becomes moist in consequence of surface action. Yet in all these cases sulphur remains sulphur.

It is entirely different when sulphur enters into chemical combination exerting chemical attraction, for instance, when it burns; this means when it combines with the oxygen of the atmospheric air. In this case a new substance, a disagreeably smelling gas, a compound of oxygen and sulphur, is formed.

It is consequently a complete change in the properties of matter which follows the action of true chemical attraction; we might define affinity to be a force by which elements unite and new substances are generated.

It should be noted that *affinity* does not really explain why chemical union takes place, why an attraction between elements exists. It is merely a term that has come into use to express a fact that can be observed; namely, that elements do unite, but why they do so no one knows. Likewise no one knows why the earth attracts bodies, although we say it is due to gravitation. This is simply equivalent to saying that an attractive force exists between the earth and bodies upon it, a fact which anyone can observe. But no one knows why this force exists or its nature.

## 4. FUNDAMENTAL LAWS OF CHEMICAL COMBINATION, SYMBOLS, FORMULAS, CHEMICAL EQUATIONS, CALCULATIONS.

**Law of the Constancy of Composition.**—This law, also known as the law of definite proportions, was the first ever recognized in chemical science; it was discovered toward the close of the 18th century, and may be stated thus: *A definite compound always contains the same elements in the same proportion;* or, in other words, *all chemical compounds are definite in their nature and in their composition.*

To make this law perfectly understood, the difference between a mechanical mixture and a chemical compound must be pointed out. Two powders, for instance sugar and starch, may be mixed together very intimately in a mortar, so that it seems impossible for the eye to discover more than one body. But in looking at this powder with the aid of a microscope, the particles of sugar as well as those of starch may be easily distinguished. The mixture thus produced is a *mechanical mixture of molecule clusters.*

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QUESTIONS.—Define a chemical change and state the various modes of effecting it, with examples. Define element, compound, combination, and decomposition. About how many elements exist? What is chemical energy? Define exothermic and endothermic actions. What is chemical affinity, and how does it differ from other forces?

It is somewhat different when two substances, for instance two metals, are fused together, or when two gases or two liquids (oxygen and nitrogen, water and alcohol) are mixed together, or when finally a solid is dissolved in a liquid (sugar in water). In these instances no separate particles can be discovered even by the microscope. The mixtures thus produced are *mixtures of molecules*. Such mixtures always exhibit properties intermediate between those of their constituents and in regular gradation according to the quantity of each one present. The proportions in which substances may be mixed are variable.

In a true chemical compound the proportions of the constituent elements admit of no variation whatever; it is not formed by the mixing of molecules, but by the *combination of molecules;* the properties of a compound thus formed usually differ very widely from those of the combining elements.

Powdered iron and powdered sulphur may be mixed together in many different proportions. If such a mixture be heated until the sulphur becomes liquid, the two elements, iron and sulphur, combine chemically, but they do so in one proportion only, 56 parts by weight of iron combining with 32 parts by weight of sulphur, to form 88 parts of sulphide of iron. If the two substances are mixed together in any other proportion than the one mentioned, the excess of one will be left uncombined.

**Law of Multiple Proportions.**—While two or more elements may unite in certain definite proportions to give one definite compound, it does not follow that, under other conditions, they may not unite in other proportions to give another entirely different compound, but still perfectly definite in its composition. Many such examples are known in chemistry. Copper unites with oxygen in two proportions, forming two distinct oxides. Tin does the same. There are four different compounds of the elements potassium, chlorine, and oxygen, and nitrogen and oxygen unite in five different ways. In 1804 John Dalton, of England, by a study of such multiple compounds, proposed the law of multiple proportions. He had studied the composition of two gaseous compounds of carbon and hydrogen, and found one (olefiant gas) to contain 6 parts of carbon to 1 part of hydrogen, while the other (marsh gas) contained 6 parts of carbon to 2 parts of hydrogen. Upon what seems now to be a slight basis, Dalton put forth his law, which, however, has been verified by every exact analysis since his time, and which is one of the most important foundation-stones upon which the structure of chemical science is reared. The law of multiple proportions may be stated thus: *If two elements, A and B, are capable of uniting in several proportions, the quantities of B which combine with a fixed quantity of A bear a simple ratio to each other.*

Besides the above illustrations of the law, several other examples may be mentioned. Sulphur and oxygen unite in two proportions to form two distinct compounds, one a gas known as sulphur dioxide,

the other a solid known as sulphur trioxide. In these the quantities of oxygen, united with a fixed weight of sulphur, are in the ratio of $1 : 1\frac{1}{2}$ or $2 : 3$. There are two sulphides of iron, known respectively as ferrous sulphide and pyrite; in these the weights of sulphur united with a fixed weight of iron are in the ratio of $1 : 2$. The phrase *simple ratio*, in the law, means in the ratio of small whole numbers. This feature of the law is strikingly illustrated in the case of the four compounds containing potassium, chlorine, and oxygen, in which the variable weights of oxygen united with fixed weights of potassium and chlorine are in the ratio of $1 : 2 : 3 : 4$; also in the case of the five compounds of nitrogen and oxygen, in which the weights of oxygen united with a fixed weight of nitrogen bear the ratio of $1 : 2 : 3 : 4 : 5$.

**Combining Weights of Elements.**—The proportions in which any two elements unite may be expressed by any two figures which stand in the proper ratio. Thus we may say that water is made up of hydrogen and oxygen in the proportions by weight of 1 to 8, or 2 to 16, or 5 to 40. Similarly we may state the composition of ferrous sulphide as 7 parts of iron to 4 parts of sulphur, or 56 parts of iron to 32 parts of sulphur. Expressing the composition of compounds thus in a random manner, there seems to be no relationship between the relative quantities with which the different elements unite with one another. But upon closer inspection of the proportions by weight in which the elements unite, it is found that they can be reduced to a system of figures which show a remarkable relationship. It is found, purely from the results of analysis and independently of any theory, that a certain figure can be assigned to each element, which has the remarkable property that it or a simple multiple of it expresses the relative proportion by weight in which that element unites with the other elements. Chemists soon became aware of the fact that hydrogen is the lightest of all known matter and also that it enters into union with other elements in the smallest proportions. Hence in establishing the above-mentioned system of numbers, such figures are chosen that the relative proportion by weight of the element hydrogen which enters into union with other elements in the smallest proportion, shall be represented by not less than one. For reasons which will appear later, the figure assigned to oxygen is 16, and on this scale the figure for hydrogen is 1.008. The following few examples will make the above statement clearer to the student:

1.008 parts of hydrogen unite with 35.46 parts of chlorine.
39.1 parts of potassium unite with 35.46 parts of chlorine.
$2 \times 39.1$ parts of potassium unite with 16 parts of oxygen.
$2 \times 1.008$ parts of hydrogen unite with 16 parts of oxygen.
65.37 parts of zinc unite with 16 parts of oxygen.
65.37 parts of zinc unite with $2 \times 35$ 46 parts of chlorine.

This list could be extended to include combinations involving all the elements, but it is sufficient to show that the figures assigned to the respective elements are reciprocally related. This system of figures may be called *combining weights*, and has a deep significance which will appear clearer when the atomic theory is discussed. They are in fact the same figures which later on we shall come to know as atomic weights, but for the present we will call them combining weights or *chemical unit weights*.

**Chemical Symbols.**—For reasons to be better understood hereafter, chemists designate each element by a symbol, and the first or first two letters of the Latin name of the element have generally been selected. Thus, the symbol of hydrogen is H, of oxygen O, of mercury Hg (from hydrargyrum), of sulphur S, etc. These symbols designate, moreover, not only the elements, but also a definite proportion by weight of the elements. For instance, O not only stands for oxygen, but also one chemical unit weight or 16 parts by weight of oxygen; Hg represents mercury and also 200.6 parts by weight. On the page preceding the Index is a table giving the names of the elements, symbols, and chemical unit (atomic) weights.

**Formulas of Compounds.**—By accurate qualitative and quantitative analysis, it is possible for the chemist to determine the kinds of elements united in a given compound and the relative proportions of the elements. From the results of the analysis the proportions are figured on the basis of 100 parts of compound, or, in other words, in percentages. For example, the substance known generally as table salt and called in chemistry sodium chloride, is found to contain two elements, sodium and chlorine, in the proportion of 39.34 per cent. of sodium to 60.66 per cent. of chlorine.

If the nature and composition of all compounds had to be stated in the above manner, the process would be rather cumbersome, and at the same time it would be impossible for one to remember the composition of the vast number of compounds that exist. Fortunately a method of representing the nature and composition of compounds by *formulas* has been devised which saves time and space, gives a better insight into compounds, and makes it possible for one to remember their composition. A formula represents the composition of a compound in terms of the chemical unit weights of the constituent elements. It is formed by writing the symbols of the elements side by side, and when more than one chemical unit weight of any element is involved, the amount is indicated by a figure placed to the right of the symbol of the element. Thus, $H_2O$ stands for the substance water and tells at a glance that it contains the elements hydrogen and oxygen, and in the proportion of 2 chemical unit weights of hydrogen to 1 chemical unit weight of oxygen, that is, $2 \times 1.008$ parts of hydrogen to $1 \times 16$ parts of oxygen. The formula for common salt is NaCl, which shows that it consists of the elements sodium and chlorine united in the proportion of 1 chemical unit weight of

each, or 23 parts of sodium to 35.46 parts of chlorine. $CO_2$ is the formula for carbon dioxide and indicates that 1 chemical unit weight of carbon or 12 parts by weight is united with 2 chemical unit weights of oxygen or $2 \times 16$ parts by weight.

The sum of the parts by weight corresponding to the chemical unit weights of the elements represented by the symbols in the formula of any compound may be designated the *formula weight.* Thus the formula weight of $H_2O$ is 18.016 = (2 × 1.008 parts of hydrogen + 1 × 16 parts of oxygen), meaning that in every 18.016 parts of water, there are 2.016 parts of hydrogen combined with 16 parts of oxygen; the formula weight of NaCl is 58.46, which means that every 58.46 parts of sodium chloride (table salt) contains 23 parts of sodium combined with 35.46 parts of chlorine. A numeral placed before a formula or symbol means so many formula weights of the compound, or so many chemical unit weights of the element. Thus 2NaCl means 2 formula weights or $2 \times 58.46$ parts by weight of sodium chloride; 3O means 3 chemical unit weights or $3 \times 16$ parts by weight of oxygen. The figures placed after the symbols in a formula, as $CO_2$, never vary because they represent the proportions involved in the composition of the compound, which is constant.

The figures placed before the symbol of an element or the formula of a compound vary according to the proportions involved in the various chemical transformations in which the element or compound takes part.

**Formulas Deduced from Results of Analysis.**—As stated above, the chemist is able to determine very accurately the percentage of each element in a compound, and the results are expressed in terms of the ordinary physical unit of weight, the gram. He could indeed construct a symbolic representation of the compound involving the percentage figures directly. Thus, in the case of sodium chloride, he might write the formula $Na_{39.34\%}\ Cl_{60.66\%}$. Such formulas would be of very little value as they are clumsy, lacking in system, and impossible to retain. So the chemist proceeds to express the composition of the compound in terms of another unit of measure that is used in chemistry only, namely, the chemical unit weights or combining weights, a different but definite one for each element. He first finds the relative number of combining weights by dividing the percentage figures of the analysis by the combining weights of the respective elements. Thus in the case of sodium chloride:

| | Percentage | | Combining weight | | Relative number of combining weights |
|---|---|---|---|---|---|
| Sodium | 39.34 | ÷ | 23.0 | = | 1.7104 |
| Chlorine | 60.66 | ÷ | 35.46 | = | 1.7106 |

The figures thus obtained expressing the ratio of the combining weights of the elements, contain decimals; hence the next step is to obtain a new set of figures free from decimals that bear the same

ratio as the previous figures, because the composition of all compounds can be expressed by integral multiples of the combining weights. In the present case, it is easily seen that 1.7104 : 1.7106 is the same as 1 : 1, that is, sodium chloride contains sodium and chlorine in the proportion of 1 combining weight of each. As the symbols stand for 1 combining weight, evidently the composition is expressed by the formula NaCl.

Let us take one more illustration in the case of water:

| | Percentage | | Combining weight | | Relative number of combining weights | |
|---|---|---|---|---|---|---|
| Hydrogen . . . . . | 11.18 | ÷ | 1.008 | = | 11.0912 | 2 |
| | | | | | or | |
| Oxygen . . | 88.81 | ÷ | 16 00 | = | 5.5506 | 1 |

Hence the formula for water is $H_2O$.

**Chemical Equations.**—To tell every time in words what takes place when two substances act on each other chemically would be a long and tedious process. For example, when hydrochloric acid containing hydrogen and chlorine is brought in contact with silver nitrate containing silver, nitrogen and oxygen, there is formed a white, curdy, insoluble substance containing silver and chlorine, which is called silver chloride, and nitric acid containing hydrogen, nitrogen and oxygen, which is soluble. To avoid such lumbering descriptions, the chemist has devised a method in chemical language for representing chemical changes, which is short, concise and tells the whole story at a glance. He uses *chemical equations*, which speak in the language of symbols, formulas and combining weights. Such an equation is formed by writing the formulas of the substances that react on the left of the sign of equality, and connecting them by the sign +, and the formulas of the products of the reaction on the right of the sign of equality, also connected by the + sign. For example, the long description of the mutual decomposition of hydrochloric acid and silver nitrate is concentrated into one line in the following equation:

$$HCl + AgNO_3 = AgCl + HNO_3.$$

The formulas show the composition of the substances before and after the change, and also the relative quantities, namely, one formula weight of each in this instance. We see at once that 36.46 parts of hydrochloric acid react with 169.89 parts of silver nitrate and produce 143.34 parts of silver chloride and 63.02 parts of nitric acid. The + sign should be read *and*, and the = sign should be read *gives*.

A chemical equation has nothing in common with an algebraic one, except in form. It cannot be factored, or in any way be handled as an algebraic equation. It is simply a statement of facts learned by experiment. Until we have learned beforehand the composition of the substances entering into chemical reaction and also of the

products formed, and the proportions involved, we have no basis upon which we can legitimately write an equation.

**Calculations in Chemistry.**—It was stated above that to establish the formula of a compound required a careful quantitative determination of the proportions of the constituents of a compound; conversely, if we know the formula of a compound, we can calculate from it the relative quantities of the elements, or the percentage composition of the compound. Also, if we know the formula, and the weight of one constituent, we can calculate the weight of the other constituents, and the total weight of the compound. Let us consider the red oxide of mercury, which has the formula, HgO. This tells us that every formula weight or (200.6 + 16) parts of mercuric oxide contain 200.6 parts of mercury and 16 parts of oxygen. Hence to calculate the percentage composition, or parts per hundred, we use the proportions:

$$216.6\text{HgO} : 200.6\text{Hg} :: 100\text{HgO} : x \text{ Hg}.$$

$$x = \frac{200.6 \times 100}{216.6} = 92.61 \text{ per cent. of mercury.}$$

and

$$216.6\text{HgO} : 16\text{O} :: 100\text{HgO} : x \text{ O}.$$

$$x = \frac{16 \times 100}{216.6} = 7.38 \text{ per cent. of oxygen.}$$

Of course, in all cases where there are only two constituents, and we find the per cent. of one, the other need not be calculated.

If we had a quantity of oxide of mercury that we knew contained, say 30 parts of mercury, and we wanted to know the weight of the oxygen present or the total weight of oxide, the following proportions would give us the answers:

$$200.6\text{Hg} : 16\text{O} :: 30\text{Hg} : x \text{ O};$$
$$200.6\text{Hg} : 216.6\text{HgO} :: 30\text{Hg} : x \text{ HgO}.$$

When mercuric oxide is decomposed by heat, it is decomposed into the elements mercury and oxygen, as we have already seen. If we wished to know how many grams of oxygen would be given off from 25 grams of the oxide, the following proportion would give us the answer:

$$216.6\text{HgO} : 16\text{O} :: 25\text{HgO} : x \text{ O}.$$

Chemical equations not only are used for representing chemical changes, but also are the starting-point in all the chemical calculations in which the quantities of substances entering into chemical actions, or the quantities of the product formed, are concerned. Every correct chemical equation is correct mathematically also—*i. e.*, the sum of the formula weights of the factors equals the sum of the formula weights of the products. For instance: Sodium carbonate and calcium chloride form calcium carbonate and sodium chloride. expressed in chemical equation we say:

$$Na_2CO_3 + CaCl_2 = CaCO_3 + 2NaCl.$$

Sodium carbonate and calcium chloride are the factors, calcium carbonate and sodium chloride the products. Adding together the formula weights of the factors and those of the products we find equal quantities, as follows:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 2Na = 46 | | Ca = 40.07 | | Ca = 40.07 | | 2Na = 46.0 | |
| C = 12 | | 2Cl = 70.92 | | C = 12.0 | | 2Cl = 70.92 | |
| 3O = 48 | | | | 3O = 48.0 | | | |
| 106 | + | 110.99 | = | 100.07 | + | 116.92 | |

The above calculation teaches, for instance, that 106 parts by weight of sodium carbonate are acted upon by 110.99 parts by weight of calcium chloride, and that 100.07 parts by weight of calcium carbonate and 116.92 parts by weight of sodium chloride are formed by this action. If we wished to know how much calcium carbonate would be produced by the action of 15 pounds of sodium carbonate, we would use the following proportion:

$$106Na_2CO_3 : 100.07CaCO_3 :: 15Na_2CO_3 : x\ CaCO_3.$$

$$x = \frac{100.07 \times 15}{106} = 14.16 \text{ pounds of calcium carbonate.}$$

Calcium carbonate being insoluble in water, while the other substances are soluble, it can be collected by filtration and washing. When dried its weight can be determined, which serves as a check on the correctness of the calculations.

## 5. GENERAL REMARKS REGARDING ELEMENTS.

**Relative Importance of Different Elements.**—Of the total number of about eighty elements, comparatively few (about one-fourth) are of great and general importance for the earth, and the phenomena taking place upon it. These important elements form the greater part of the mass of the solid portion of the earth, and of the water and atmosphere, and of all animal and vegetable matter.

Another number of elements are of less importance, because either they are not found in any large quantity, or do not take any active or essential part in the formation of organic matter; yet they are of

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QUESTIONS.—State the law of constancy of composition. What is the distinction between a mixture and a chemical compound? Give examples of each. State the law of multiple proportions. What is meant by combining weights of the elements? What are symbols and what do they stand for? How is the composition of substances expressed by formulas and upon what basis are they constructed? What is a chemical equation and what does it express? If the formula for water is $H_2O$, how much hydrogen and how much oxygen are required to form 20 parts of water?

interest and importance on account of being used, in their elementary state or in the form of different compounds, in every-day life for various purposes.

A third number of elements are found in such minute quantities in nature that they are almost exclusively of scientific interest. Even the existence of some elements, the discovery of which has been claimed, is doubtful.

The elements enumerated in column I are those of great and general interest; in II those claiming interest on account of the special use made of them; in III those having scientific interest chiefly.

| I. | II. | |
|---|---|---|
| Aluminum | Antimony | Lead |
| Calcium | Arsenic | Lithium |
| Carbon | Barium | Manganese |
| Chlorine | Bismuth | Mercury |
| Hydrogen | Boron | Molybdenum |
| Iron | Bromine | Nickel |
| Magnesium | Cadmium | Platinum |
| Nitrogen | Cerium | Radium |
| Oxygen | Chromium | Silver |
| Phosphorus | Cobalt | Strontium |
| Potassium | Copper | Tin |
| Silicon | Fluorine | Tungsten |
| Sodium | Gold | Uranium |
| Sulphur | Iodine | Vanadium |
| | Iridium | Zinc |

| III. | | |
|---|---|---|
| Argon | Lanthanum | Selenium |
| Beryllium (Glucinum) | Lutecium | Tantalum |
| Cæsium | Neodymium | Tellurium |
| Columbium (Niobium) | Neon | Terbium |
| Dysprosium | Niton | Thallium |
| Erbium | Osmium | Thorium |
| Gadolinium | Palladium | Thulium |
| Gallium | Praseodymium | Titanium |
| Germanium | Rhodium | Xenon |
| Helium | Rubidium | Ytterbium |
| Holmium | Ruthenium | Yttrium |
| Indium | Samarium | Zirconium |
| Krypton | Scandium | |

**Classification of Elements.**—Classification of elements may be based upon either physical or chemical properties, or upon a consideration of both. A natural classification of all elements is the one dividing them into two groups of metals and non-metals.

**Metals.**—Metals are all elements which have that peculiar lustre

known as metallic lustre; which are good conductors of heat and electricity; which, in combination with oxygen, form compounds generally showing basic properties; and which are capable of replacing hydrogen in acids, thus forming salts.

**Non-metals or Metalloids.**—Non-metals or metalloids are all elements not having the above-mentioned properties. Their oxides in combination with water generally have acid properties. In all other respects the chemical and physical properties of non-metals differ widely. Their number amounts to 18, the other elements being metals.

**Natural Groups of Elements.**—Besides classifying all elements into metals and non-metals, certain members of both classes exhibit so much resemblance in their properties that many of them have been arranged into natural groups. The members of such a natural group frequently show some connection between atomic weights and properties.

| | | | |
|---|---|---|---|
| Chlorine, 35.46 | Sulphur, 32.07 | Lithium, 6.94 | Calcium, 40.07 |
| Bromine, 79.92 | Selenium, 79.2 | Sodium, 23.0 | Strontium, 87.63 |
| Iodine, 126.92 | Tellurium, 127.5 | Potassium, 39.1 | Barium, 137.37 |

Each three elements mentioned in the above four columns resemble each other in many respects, forming a natural group. The relation between the atomic weights will hardly be suspected by looking at the figures, but will be noticed at once by adding together the atomic weights of the first and last elements and dividing this sum by 2, when the atomic weights (very nearly, at least) of the middle members of the series are obtained. Thus:

$$\frac{35.46 + 126.92}{2} = 81.19; \qquad \frac{32.07 + 127.5}{2} = 79.78;$$

$$\frac{6.94 + 39.1}{2} = 23.02; \qquad \frac{40.07 + 137.37}{2} = 88.72.$$

**Physical Properties of Elements.**—Most elements are, at the ordinary temperature, solid substances, two are liquids (bromine and mercury), and of the more important elements five are gases (oxygen, hydrogen, nitrogen, chlorine, and fluorine).

Most, if not all, of the solid elements may be obtained in the crystallized state; a few are amorphous and crystallized, or polymorphous. The physical properties of many elements in these different states differ widely. For instance: Carbon is known crystallized as diamond and graphite, or amorphous as charcoal. The property of elements to assume such different conditions is called *allotropy*, and the different forms of an element are termed *allotropic modifications*.

Some of the gaseous elements are also capable of existing in allotropic modifications. For instance: Oxygen is known as such and as ozone, the latter differing from the common oxygen both in its physical and chemical properties.

Most of the elements are tasteless and odorless; a few, however, have a distinct odor and taste, as iodine and bromine.

**Non-metals.**—We shall begin our studies with a consideration of the non-metallic elements and their principal compounds. In this elementary course only the more important elements will be studied at length, while others for one reason or another will receive brief mention. The number of the non-metals is about eighteen and of these, those mentioned below will receive principal attention.

### Symbols, Atomic Weights, and Derivation of Names.

| | | | |
|---|---|---|---|
| Boron, | B | = 11. | From *borax*, the substance from which boron was first obtained. |
| Bromine, | Br | = 79.92. | From the Greek βρῶμος (bromos), stench, in allusion to the intolerable odor. |
| Carbon, | C | = 12.0. | From the Latin *carbo*, coal, which is chiefly carbon. |
| Chlorine, | Cl | = 35.46. | From the Greek χλωρός (chloros), green, in allusion to its green color. |
| Fluorine, | F | = 19.0. | From *fluorspar*, the mineral calcium fluoride, used as flux (*fluo*, to flow). |
| Hydrogen, | H | = 1.008. | From the Greek ὕδωρ (hudor), water, and γεννάω (gennao), to generate. |
| Iodine, | I | = 126.92. | From the Greek ἰον (ion), violet, referring to the color of its vapors. |
| Nitrogen, | N | = 14.01. | From the Greek νίτρον (nitron), nitre, and γεννάω (gennao), to generate. |
| Oxygen, | O | = 16.0. | From the Greek ὀξύς (oxus), acid, and γεννάω (gennao), to generate. |
| Phosphorus, | P | = 31.04. | From the Greek φῶς (phos), light, and φέρειν (pherein), to bear. |
| Silicon, | Si | = 28.3. | From the Latin *silex*, flint, or silica, the oxide of silicon. |
| Sulphur, | S | = 32.07. | From *sal*, salt, and πῦρ (pur), fire, referring to the combustible properties of sulphur. |

### State of Aggregation.

Under ordinary conditions the non-metals show the following states:

| *Gases.* B. P. | *Liquids.* B. P. | *Solids.* F. P. | B. P. |
|---|---|---|---|
| Hydrogen, —253° C. | Bromine, 64° C. | Phosphorus, 44° C. | 280° C. |
| Oxygen, —183 | | Iodine, 114 | 184 |
| Nitrogen, —194 | | Sulphur, 114 | 448 |
| Chlorine, — 33 | | Carbon, Slightly volatile in electric furnace. | |
| Fluorine, —190 | | Boron, | |
| | | Silicon, | |

## Occurrence in nature.

*a. In a free or combined state.*

Carbon in coal, organic matter, carbon dioxide, carbonates.
Nitrogen in air, ammonia, nitrates, organic matter.
Oxygen in air, water, organic matter, most minerals.
Sulphur chiefly as sulphates and sulphides.

*b. In combination only.*

Boron in boric acid and borax.
Bromine in salt wells and sea-water as magnesium bromide, etc.
Chlorine as sodium chloride in sea-water, etc
Fluorine as calcium fluoride, fluorspar.
Hydrogen in water and organic matter.
Iodine as iodides in sea-water.
Phosphorus as phosphate of calcium, iron, etc, in bones and rocks.
Silicon as silicic acid or silica, and in silicates.

## Time of discovery.

Sulphur, Carbon, } Long known in the elementary state; recognized as elements in the latter part of the eighteenth century.
Phosphorus, 1669, by Brandt, of Germany.
Chlorine, 1774, by Scheele, of Sweden.
Nitrogen, 1772, by Rutherford, of England.
Oxygen, 1773, by Scheele, of Sweden; 1774, by Priestley, of England.
Hydrogen, 1766, by Cavendish, of England.
Boron, 1808, by Gay-Lussac, of France.
Fluorine, 1810, by Ampère, of France
Iodine, 1812, by Courtois, of France.
Silicon, 1823, by Berzelius, of Sweden.

Water: 1781 - Cavendish, Priestley

## 6. OXYGEN.

O″=16.

**History.**—Oxygen was discovered in the year 1773 by Scheele, in Sweden, and one year later by Priestley, in England, independently of each other; its true nature was soon afterward recognized by Lavoisier, of France, who gave it the name oxygen, from the two Greek words, ὀξύς (oxus), acid, and γεννάω (gennao), to produce or generate. Oxygen means, consequently, generator of acids.

**Occurrence in Nature.**—There is no other element on our earth present in so large a quantity as oxygen. It has been calculated that not less than about one-third, possibly as much as 45 per cent,, of the

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QUESTIONS.—Why are not all the elements of equal importance? State the physical and chemical properties of metals. How are metals distinguished from non-metals? What relation often exists between the atomic weights of elements belonging to the same group? Explain the term allotropic modification. Mention some elements capable of existing in allotropic modifications.

total weight of our earth is made up of oxygen; it is found in a free or uncombined state in the atmosphere, of which it forms about one-fifth of the weight. Water contains eight-ninths of its weight of oxygen, and most of the rocks and different mineral constituents of our earth contain oxygen in quantities varying from 30 to 50 per cent.; finally, it is found as one of the common constituents of most animal and vegetable matters.

If the unknown interior of our earth should be similar in composition to the solid crust of mineral constituents which have been analyzed, then the subjoined table will give approximately the proportions of those elements present in the largest quantity.

| | | | |
|---|---|---|---|
| Oxygen . | 45 parts | Calcium . . | 4 parts. |
| Silicon . . | 28 " | Magnesium . | 2 " |
| Aluminum . . | 8 " | Sodium . | 2 " |
| Iron . . . . | 6 " | Potassium . | 2 " |

**Preparation.**— The oxides of the so-called noble metals (gold, silver, mercury, platinum) are by heat easily decomposed into the metal and oxygen:

$$HgO = Hg + O;$$
$$Ag_2O = 2Ag + O.$$

A more economical method of obtaining oxygen is the decomposition of potassium chlorate, $KClO_3$, into potassium chloride, KCl, and oxygen by application of heat:

$$KClO_3 = KCl + 3O.$$

While the above formula represents the final result of the decomposition, it takes place actually in two stages. At first potassium chlorate gives up but one-fifth of its total oxygen, forming potassium chloride and perchlorate, $KClO_4$ thus:

$$5KClO_3 = 3KClO_4 + 2KCl + 3O.$$

This part of the decomposition takes place at a comparatively low temperature; after it is complete, the temperature rises considerably and the decomposition of the perchlorate begins:

$$KClO_4 = KCl + 4O.$$

If the potassium chlorate be mixed with 30–50 per cent. of manganese dioxide, and this mixture be heated, the liberation of oxygen takes place with greater facility and at a lower temperature than by heating potassium chlorate alone. Apparently, the manganese dioxide takes no active part in the decomposition, as its total amount is found in an unaltered condition after all potassium chlorate has been decomposed by heat. A satisfactory explanation regarding this action of manganese dioxide is yet wanting.

A third method is to heat to redness, in an iron vessel, manganese dioxide ($MnO_2$), which suffers then a partial decomposition:

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

In this case there is liberated but one-third of the total amount of oxygen present, while two-thirds remain in combination with the manganese.

Other methods of obtaining oxygen are: Decomposition of water by electricity, heating of dichromates, nitrates, barium dioxide, and other substances, which evolve a portion of the oxygen contained in the molecules.

Heating a concentrated solution of bleaching powder with a small quantity of a cobalt salt (cobaltous chloride) furnishes a liberal supply of oxygen, the calcium hypochlorite of the bleaching powder being decomposed into calcium chloride and oxygen:

$$Ca(ClO)_2 = CaCl_2 + 2O.$$

Oxygen may be obtained at the ordinary temperature by adding water to a mixture of powdered potassium ferricyanide and barium dioxide, and also by the decomposition of potassium permanganate and hydrogen dioxide in the presence of dilute sulphuric acid.

A commercial method operated to some extent is Brin's process, which consists in pumping purified air under pressure over barium oxide contained in a tube and heated to about 700° C., whereby barium dioxide is formed. The accumulated nitrogen of the air escapes by a valve from the end of the tube. When formation of barium dioxide is complete, the air supply is cut off and the pump is reversed, thus producing a partial vacuum in the tube. Under this condition, although the same temperature is maintained as before, the barium dioxide decomposes into barium oxide and oxygen, which latter is pumped away and stored in tanks. Oxygen of about 96 per cent. is obtained. The changes taking place in the two stages are represented thus:

$$BaO + O = BaO_2;$$
$$BaO_2 = BaO + O.$$

This process is a good example of the kind of change known as *Reversible Action* (chapter 11). When the dioxide is exhausted the process is repeated. One kilogram of barium oxide yields about 10 liters of oxygen at a single operation.

Another commercial method used extensively is the liquefaction of air (see chapter on Nitrogen) and subsequent fractional distillation of the liquefied air, by which oxygen and nitrogen are separated. By this method, oxygen of 98 per cent. purity can readily be obtained.

Other methods used on a large scale are similar in principle to Brin's process. One devised by Kassner consists in heating a mixture of lead oxide (PbO) and calcium carbonate ($CaCO_3$) in a current of air at 700° C., whereby carbon dioxide ($CO_2$) is given off, oxygen is absorbed and calcium plumbate ($CaPbO_3$) is formed. If now carbon dioxide be passed over the latter, there is a reversal of the chemical change, and oxygen is given off.

The quantity of oxygen liberated from a given quantity of a substance may be easily calculated from the combining and formula weights of the substance or substances suffering decomposition. For instance: 100 pounds of oxygen may be obtained from how many pounds of potassium chlorate, or from how many pounds of manganese dioxide? (See page 64.)

The formula weight of potassium chlorate is found by adding together 1 com-

bining weight each of potassium, 39.1, and chlorine, 35.46, and 3 combining weights of oxygen, $3 \times 16 = 48$, which gives 122.56. Every 122.56 parts by weight of potassium chlorate liberate 48 parts by weight of oxygen. Hence:

$$122.56 : 48 :: x : 100$$
$$x = 255.33 \text{ pounds of potassium chlorate.}$$

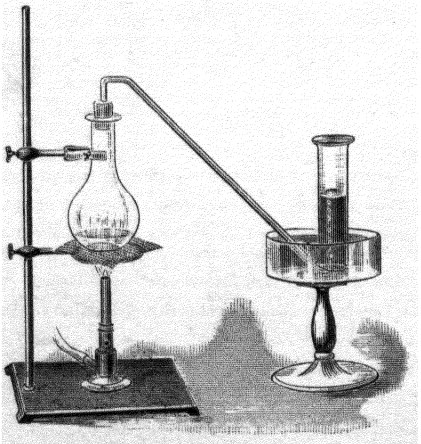
In a similar manner, it will be found that 814.97 pounds of manganese dioxide are necessary to produce 100 pounds of oxygen. $MnO_2 = 54.93 + 32 = 86.93$. $3MnO_2 = 3 \times 86.93 = 260.79$. Every 260.79 parts furnish $2 \times 16 = 32$ parts of oxygen.

$$32 : 260.79 :: 100 : x$$
$$x = 814.97 \text{ pounds of manganese dioxide.}$$

The density of a gas is the weight of 1 liter. To find what volume corresponds to a given weight of a gas, divide the weight by the density. The density of oxygen is 1.429 grams in 1 liter at 0° C. and 760 mm. pressure. Hence, under these conditions, 100 grams of oxygen would measure $100 \div 1.429 = 69.979$ liters. (For method of calculating gas volumes under other than standard conditions of temperature and pressure, see article on Gas Analysis.)

*Experiment* 1.—Generate oxygen by heating a small quantity (about 5 grams) of potassium chlorate in a dry flask of about 100 c.c. capacity, to which, by means of a perforated cork, a bent glass tube has been attached, which leads under the surface of water contained in a dish (Fig. 8). Collect the gas by placing over the delivery-tube large test-tubes (or other suitable ves-

FIG. 8.



Apparatus for generating oxygen.

sels) filled with water. Notice that a strip of wood, a wax candle, or any other substance which burns in air, burns with greater energy in oxygen, and that an extinguished taper, on which a spark yet remains, is rekindled when placed in oxygen gas. Notice, also, the physical properties of the gas. If the decomposition has been too rapid by using too large a flame, the gas will appear cloudy, due to the dragging over of some of the contents of the flask by it. The cloud will disappear upon standing.

CAUTION.—*In all experiments of this kind, where a vessel is filled with a hot gas, the exit tube should be removed from water before removing the flame, to prevent water from being drawn back into the vessel as the gas cools and contracts.*

*Experiment* 2. In a porcelain crucible held in a pipe-stem triangle, place a layer of potassium chlorate about ½ inch deep. Heat moderately at first until frothing ceases, and then gradually to low red heat. Cool and dissolve the residue in a little water in the crucible, warming to hasten solution. Taste the solution. Does it taste like common salt (sodium chloride)? Compare with the taste of potassium chlorate. Pour some of the solution into a test-tube and add a few drops of a solution of silver nitrate. Do the same with a solution of common salt. The white clotted substance, known as a *precipitate*, is silver chloride, and is given by all soluble chlorides. Also add some silver nitrate solution to a solution of a little potassium chlorate. Is any precipitate formed? All chlorates are soluble.

**Physical Properties.**—Oxygen is a colorless, inodorous, tasteless gas, slightly heavier than air. Under a pressure of 50 atmospheres, and at a temperature of —118° C. (—180.4° F.) it condenses to a transparent, pale-bluish liquid, which under ordinary atmospheric pressure boils at —183° C. (—297.4° F.). Its absolute boiling-point, above which it cannot be condensed to a liquid by any pressure no matter how high, is —118° C. (—180.4° F.).

For practical, including medical, purposes oxygen is sold stored in strong steel cylinders, the gas being condensed by a pressure, generally, of 225 pounds to about $\frac{1}{150}$ of its volume. Oxygen is now official in the U. S. P. under the title *oxygenium*, and must contain not less than 95 per cent. of oxygen. It should not contain more than traces of carbon dioxide, halogen elements, acids or bases, tests for which are given in the U. S. P.

The temperature above which a gas cannot be liquefied by pressure is known as its *critical temperature*. The failure of former attempts to liquefy oxygen and a few other gases was due to the fact that, though an enormous pressure was used, the gas was not brought to the critical temperature.

Oxygen is but sparingly soluble in water (about 3 volumes in 100 at common temperature). A liter of oxygen under 760 mm. pressure, and at the temperature of 0° C. (32° F.), weighs 1.429 grams.

**Chemical Properties.**—The principal feature of oxygen is its great affinity for almost all other elements, both metals and non-metals, with nearly all of which it combines in a direct manner. The more important elements with which oxygen does not combine directly are: Cl, Br, I, F, Au, Ag, and Pt; but even with these it combines indirectly, excepting F.

The act of combination between other substances and oxygen is called *oxidation*, and the products formed, *oxides*. The large number of oxides are divided usually into three groups, and distinguished as *basic oxides* (sodium oxide, $Na_2O$, calcium oxide, $CaO$), *neutral oxides* (water, $H_2O$, manganese dioxide, $MnO_2$, lead dioxide, $PbO_2$), and

*acid-forming* or *acidic oxides*, also called *anhydrides* (carbon dioxide, $CO_2$, sulphur trioxide, $SO_3$). Whenever the heat generated by oxidation (or by any other chemical action) is sufficient to cause the emission of light, the process is called *combustion*. Oxygen is the chief supporter of all the ordinary phenomena of combustion. Substances which burn in atmospheric air burn with greater facility in pure oxygen. This property is taken advantage of to recognize and distinguish oxygen from most other gases. Processes of oxidation evolving no light are called *slow combustion*. An instance of slow combustion is the combustion of the different organic substances in the living animal, the oxygen being supplied by respiration.

In some cases the heat generated by the slow combustion of a substance may raise its temperature sufficiently high to cause ignition, which is then called *spontaneous combustion*. Thus, greasy rags or wet hay, when piled in heaps, may ignite spontaneously, because some oils and damp hay undergo slow oxidation, which raises the temperature.

For a process of oxidation it is not absolutely necessary that free oxygen be present. Many substances contain oxygen in such a form of combination that they part with it easily when brought in contact with substances having a greater affinity for it. Such substances are called *oxidizing agents*, as, for instance, nitric acid, potassium chlorate, potassium permanganate, etc.

In all combustions we have at least two substances acting chemically upon one another, which substances are generally spoken of as combustible bodies and supporters of combustion. Illuminating gas is a combustible substance, and oxygen a supporter of combustion; but these terms are only relatively correct, since oxygen may be caused to burn in illuminating gas, whereby it is made to assume the position of a combustible substance, while illuminating gas is the supporter of combustion.

While some substances, such as iron and phosphorus, undergo slow combustion at the ordinary temperature, there is a certain degree of temperature, characteristic of each substance, at which it inflames. This point is known as *kindling temperature*, and varies widely in different substances. Zinc ethyl ignites at the ordinary temperature, phosphorus at 50° C. (122° F.), sulphur at about 450° C. (842° F.), carbon at a red heat, and iron at a white heat. The heat produced by the combustion keeps the temperature of the body above the kindling temperature, and it is for this reason that a substance continues to burn until it is consumed, provided the supply of oxygen be not cut off, and the temperature be not through some cause lowered below the kindling temperature.

The total amount of heat evolved during the combustion of a substance is the same as that generated by the same substance when undergoing slow combustion, but the intensity depends upon the time required for the oxidation. A piece of iron may require years to combine with oxygen, and it may be burned up in a few minutes; yet the total heat generated in both cases is the same, though we can notice and measure it in the first instance by most delicate instruments only, while in the second it is very intense.

Where heat is evolved when two or more elements combine chemically, heat

is absorbed when decomposition takes place. In fact, the quantities of heat evolved and absorbed by combining and decomposing identical quantities of matter are absolutely alike. Thus, heat is evolved when mercury and oxygen combine, but the same quantity of heat is absorbed when the mercuric oxide thus formed is decomposed into its elements by the action of heat.

Whenever a substance has the power to unite with others, it can do *chemical work;* it possesses *chemical energy.* Consequently, all combustible substances can do work; *i. e.*, by combining with oxygen they evolve heat, which in turn may be transformed into motion or into some other form of energy.

The chief supply of chemical energy at our disposal is derived from plant-life. All kinds of wood, and its decomposition-product, coal, possess chemical energy. This energy is stored up in vegetable matter, because the sun's heat caused a decomposition of water and carbon dioxide, which substances are the two chief compounds used in the construction of plant tissue. In burning vegetable matter the oxygen removed from the water and carbon dioxide by the action of the sun's rays is taken up again, and heat is evolved.

**Ozone** is an allotropic modification of oxygen, which is formed when non-luminous electric discharges pass through atmospheric air or through oxygen; when phosphorus, partially covered with water, is exposed to air, and also during a number of chemical decompositions. Ozone differs from ordinary oxygen by possessing a peculiar odor, by being an even stronger oxidizing agent than common oxygen, by liberating iodine from potassium iodide, etc. This latter action may be used for demonstrating the presence of ozone by suspending in the gas a paper moistened with a solution of potassium iodide and starch. The iodine, liberated by the ozone, forms with starch a dark-blue compound. Three volumes of oxygen suffer a condensation to two volumes when converted into ozone, and *vice versa.*

Ozone is obtained in a pure condition by passing the impure gas through a tube cooled by liquid oxygen. It is then a blue liquid which boils at —110° C. (—166° F.), forming a blue gas. Atmospheric air, in which part of the oxygen has been converted into ozone by the electrical method, is used for bleaching purposes, purification of starch, resinifying oils, purifying water of germs and organic matter, etc.

Ozone occurs in small quantities in country air, but is rarely noticed in cities, where it is decomposed too quickly by the impurities of the atmospheric air. It has been assumed that ozone acts advantageously, as it has a tendency to destroy matters which are unwholesome. Too little, however, is known of the subject to justify a positive opinion in regard to it.

**Thermo-chemistry.** It is stated in Chapter 3 that the free or available chemical energy in a chemical change usually appears as heat. This heat can be measured in calories in an apparatus called a calorimeter (see page 43). The equations ordinarily used to represent chemical changes do not express energy changes, but simply what kinds of substances are concerned in the change, and what new substances are formed. For example, the expression, $2H + O = H_2O$, when translated means that when hydrogen and oxygen unite water is formed, but it says nothing about the fact that a great amount of chem-

ical energy is liberated as heat. Likewise the expression, HgO = Hg + O, which means that when mercuric oxide undergoes decomposition (by heat) mercury and oxygen are formed, says nothing about the fact that during the change, heat energy is absorbed and transformed into chemical energy. For the purpose of showing the energy change involved, use is made of *thermal equations*. The amount of heat energy in calories represented in thermal equations as liberated or absorbed refers to certain weights of the substances involved in the chemical change. These weights are the number of grams corresponding to the chemical symbols of the substances. For instance, the thermal equation for the formation of water is written, $2H + O = H_2O + 68{,}400$ cal., which means that when 2.016 grams of hydrogen unite with 16 grams of oxygen to form 18.016 grams of water (corresponding to the symbol $H_2O$), 68,400 calories of heat are liberated, or enough to raise over 68 kilograms of water 1 degree in temperature. The thermal equation,

$$HgO = Hg + O - 30{,}600 \text{ cal.},$$

means that when 216.6 grams of oxide of mercury (corresponding to HgO) are decomposed by heat into mercury and oxygen, 30,600 calories of heat are absorbed and converted into chemical energy which is associated with the elements mercury and oxygen. The plus sign is used when heat is liberated in the formation of a compound, and the latter is termed *exothermic;* while the minus sign indicates absorption of heat, and the compound is termed *endothermic*. Exothermic compounds are relatively stable, while endothermic ones are unstable and often explosive. They decompose easily with liberation of heat.

Ozone is endothermic, as heat is absorbed during its formation from oxygen. When it decomposes heat is liberated. The thermal equation, $2O_3 = 3O_2 + 64{,}800$ cal., states that when 96 grams of ozone (corresponding to $2O_3$) decomposes into ordinary oxygen, 64,800 calories of heat are liberated. The greater chemical energy of ozone over that of oxygen accounts for its greater chemical activity as compared with oxygen.

Thermo-chemical measurements are of great importance in several practical directions; for example, for determining the fuel values of samples of coal, coke, wood, fuel values of articles of food in the field of physiology, etc.

## 7. HYDROGEN. WATER. HYDROGEN DIOXIDE.

$H = 1.008$ $H_2O = 18.016$ $H_2O_2 = 34.016$.

**History.**—Hydrogen was obtained by Paracelsus in the 16th century; its elementary nature was recognized by Cavendish, in 1766. The name is derived from ὕδωρ (hudor), water, and γεννάω (gennao), to generate, in allusion to the formation of water by the combustion of hydrogen.

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QUESTIONS.—By whom and at what time was oxygen discovered? How is oxygen found in nature? Mention three processes by which oxygen may be obtained. How much oxygen may be obtained from 490 grams of potassium chlorate? State the physical and chemical properties of oxygen. Explain the terms combustion, slow combustion, combustible substance, and supporter of combustion. Mention some oxidizing agents. What is ozone, and how does it differ from common oxygen? Under what circumstances is ozone formed? What is thermochemistry? What is a thermal reaction?

**Occurrence in Nature.**—Hydrogen is found chiefly as a component element of water; it enters into the composition of most animal and vegetable substances, and is a constituent of all acids. Small quantities of free hydrogen are found in the gases produced by the decomposition of organic matters (as, for instance, in the intestinal gases), and also in the natural gas escaping from the interior of the earth.

**Preparation.**—Hydrogen may be obtained by passing an electric current through water previously acidified with sulphuric acid, by which it is decomposed into its elements:

$$H_2O = 2H + O.$$

A second process is the decomposition of water by metals. Some metals, such as potassium and sodium, decompose water at the ordinary temperature; while others, iron, for instance, decompose it at a red heat:

$$2K + 2H_2O = 2KOH + H_2$$
$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

The experiment with potassium or sodium must be done carefully because the action is very energetic. When a small piece of sodium is placed on water, there is a hissing sound, the metal melts to a globule by the heat produced, and if the motion of the globule be impeded as by placing it on filter paper floating on the water, a flame will be produced, which will be colored intensely yellow by the vapor of sodium. To get evidence of the liberation of hydrogen, a brass or lead tube about one inch long, closed at one end, is plugged with sodium, dropped into water, and a test-tube or cylinder filled with water and inverted is brought quickly over the tube. When the collected gas is tested, it shows the properties stated below.

The reaction between sodium and water is more interesting from the point of view of the other product formed than as a method of obtaining hydrogen. After the sodium has disappeared, the water turns a piece of red litmus paper blue, has a soapy feel between the fingers and a peculiar taste. When evaporated it leaves a white solid, which has been shown to contain the elements sodium, hydrogen and oxygen in the proportion of one chemical unit weight of each as represented in the formula, NaOH. It evidently is closely related to water in composition, one of the components of water having been in part displaced by the metal sodium. A part of the composition of water is still present in the new compound, namely, hydrogen and oxygen in the proportion of a chemical unit weight of each, represented by the expression (OH). For this reason, the new substance is called sodium *hydroxide*. It is also called an *alkali*, and is a member of a large class of compounds called in chemistry *metallic hydroxides* or *bases*, which will be discussed more fully later. Any substance which acts on litmus as sodium hydroxide does, is said to have an alkaline reaction. A property possessed by all the members of the class of compounds called metallic hydroxides which might be stated here

incidentally, is that of nullifying (neutralizing) such properties of acids, as sour taste, action on litmus paper, corrosive action on tissues, etc. This is the result of chemical union between the acid and the hydroxides.

The most convenient and cheapest method of generating hydrogen is by the action of an acid on some cheap metal, such as iron. On the small scale in the laboratory zinc is often used, although zinc is more expensive than iron. A few general remarks on acids before discussing the generation of hydrogen will be in order.

All *acids* contain hydrogen in combination with one or more elements. They usually have a sour taste, turn blue litmus paper red, act readily on carbonates of metals, such as sodium carbonate or calcium carbonate, and attack certain metals and combine with them, with evolution of hydrogen. The displacement of the hydrogen of acids by metals takes place more or less easily, and the resulting product is a member of a very large group of compounds called salts. The most frequently employed acids are hydrochloric, sulphuric and nitric. *Hydrochloric acid* is a gaseous colorless compound of hydrogen and chlorine, represented by the formula HCl, and very soluble in water. The aqueous solution is also known as hydrochloric acid, and it is an aqueous solution that is almost always employed. The acid is very sour, has a strong action on litmus, and is very active in general. The concentrated acid of commerce contains about 39 per cent. *Sulphuric acid* is a compound containing hydrogen, sulphur and oxygen in proportions represented by the formula $H_2SO_4$. It is a thick liquid, the concentrated acid of commerce containing about 94 per cent. of acid, the rest being water. When pure it is colorless, odorless, very corrosive. When mixed with water a great quantity of heat is produced, hence care must be exercised when diluting the acid with water. *Nitric acid* is a liquid composed of hydrogen, nitrogen and oxygen in the proportions represented by the formula $HNO_3$. When pure it is a colorless, extremely corrosive liquid, the concentrated acid of commerce containing about 70 per cent. of actual acid, the rest being water. In addition to its acid properties, it is, in contrast to the other two acids, an active oxidizer, for which reason it cannot be employed to generate hydrogen, as will be explained when nitric acid is studied in detail.

When either *diluted* hydrochloric or sulphuric acid is poured upon granules of zinc or iron in a beaker or flask, a brisk effervescence soon begins, which may be hastened by heating gently. The changes taking place are represented by the following equations:

$$Zn + 2HCl = \underset{\text{Zinc chloride}}{ZnCl_2} + 2H.$$

$$Zn + H_2SO_4 = \underset{\text{Zinc sulphate}}{ZnSO_4} + 2H.$$

$$Fe + H_2SO_4 = \underset{\text{Ferrous sulphate.}}{FeSO_4} + 2H.$$

The metals disappear and by proper experiments may be shown to be in combination with the other constituents of the acids, having displaced the hydrogen of the acids. The products, zinc chloride and sulphate, and iron sulphate, are crystalline well-known and useful salts. It will be noted that in them, as in salts in general, most of the properties that the metals and the acids possess in the uncombined state, have disappeared.

Hydrogen may also be obtained by heating granulated zinc or aluminum with strong solutions of potassium or sodium hydroxide, in which case the decomposition is explained thus:

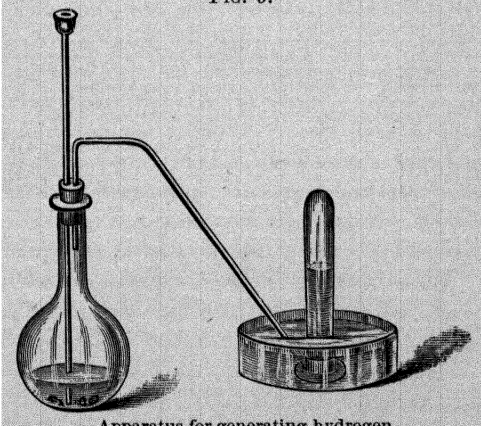
$$Zn + 2KOH = \underset{\text{Potassium zincate.}}{K_2ZnO_2} + 2H.$$

$$Al + 3NaOH = \underset{\text{Sodium aluminate.}}{Na_3AlO_3} + 3H.$$

Whenever hydrogen is generated, care should be taken to expel all atmospheric air from the vessel in which the generation takes place, before the hydrogen is ignited, as otherwise an explosion may result.

*Experiment* 3.—Place a few pieces of granulated zinc (about 10 grams) in a flask of about 200 c.c. capacity, which is arranged as shown in Fig. 9. Cover

FIG. 9.



Apparatus for generating hydrogen.

the zinc with water, and pour upon it through the funnel tube a little sulphuric acid, adding more when gas ceases to be evolved. Notice the effervescence around the zinc. Collect the gas in test-tubes over water and ignite it by taking the test-tube (with mouth downward) to a flame near by. Notice that the first portions of gas collected, which are a mixture of hydrogen and atmospheric air, explode when ignited in the test-tube, while the subsequent portions burn quietly. Pour the contents of one test-tube into another one by allowing the light hydrogen gas to rise into and replace the air in a test-tube held over the one filled with hydrogen. Take two test-tubes completely filled with the gas; hold one mouth upward, the other one mouth downward: notice that from the

first one the gas escapes after a few seconds, while it remains in the second tube a few minutes, as may be shown by holding the tubes near a flame to cause ignition.

After having ascertained that all atmospheric air has been expelled from the flask, the gas may be ignited directly at the mouth of the delivery tube, after moving it out of the water.

Continue to add acid until the zinc is nearly all dissolved, remembering that the action is not instantaneous and some time should be allowed before the next addition of acid. Warming the flask will hasten the action, and as long as small gas-bubbles arise from the zinc, action is not over. Avoid adding too much acid, but if there is an excess, it may be removed by adding more zinc. Note the dark particles floating in the liquid and the bad odor of the hydrogen, which are due to the impurities in the zinc. Finally, filter the solution (by folding a circle of filter-paper twice at right angles through the center, opening it into a cone, placing in a funnel, wetting with water, and pouring the solution into it), and evaporate it to about one-third its volume at a temperature a little below boiling. Set aside a day to cool and crystallize. If no crystals appear, evaporate further. The crystals are zinc sulphate, the same as is used in medicine. They are an illustration of the *formation of a salt by the action of an acid on a metal.* Filter the crystals and examine them carefully. Expose some to the air for several days. Does any change take place? Save the crystals for Experiment 37.

*Experiment* 4. Pour into a test-tube of not less than 50 c c. capacity, 5 c.c. of hydrochloric acid, fill up with water, close the tube with the thumb and set it inverted into a porcelain dish partly filled with water. Weigh of metallic zinc 0.04 gram, and bring it quickly under the mouth of the test-tube, so that the generated hydrogen rises in the tube. Prepare a second tube in the same manner, and introduce 0.04 gram of metallic magnesium. In case the decomposition of the acids by the metals should proceed too slowly, a little more acid may be poured into the dishes.

When the metals are completely dissolved it will be seen that the volumes of hydrogen in the two tubes bear a relation to each other of about 10 to 27.

In order to measure the gas volumes as correctly as the simple apparatus permits, the tubes should be transferred to a large beaker filled with cold water, bringing the surfaces of the liquids in the test-tube and beaker on a level, and marking on the outside of the test-tubes (with a file or paper strip) the exact height of the gas.

After having emptied the test-tubes, they may be filled with water from a pipette or from a burette to the point which has been marked, and thus the exact volume of gas generated is ascertained.

Repeat the operation, using 0 065 gram of zinc and 0.024 gram of magnesium. Notice that in this case equal volumes of hydrogen are obtained. Calculate the weight of hydrogen from the cubic centimeters liberated, and compare this weight with the weights of zinc and magnesium used. What relation is there between the weights of the liberated hydrogen and the metals used, and the combining weights of these three elements?

**Properties.**—Hydrogen is a colorless, inodorous, tasteless gas; it is the lightest of all known substances, having a specific gravity of 0.0695 as compared with atmospheric air ( = 1). One liter of hydrogen at 0° C. (32° F.), and a barometric pressure of 760 mm., weighs

0.08987 gram, or 1 gram occupies a space of 11.127 liters; 100 cubic inches weigh about 2.265 grains.

Hydrogen and helium resist liquefaction more than other gases. Hydrogen has been liquefied by causing the gas, cooled to a temperature of −205° C. (−337° F.), to escape under certain conditions from a vessel in which it was stored at a pressure of 180 atmospheres. Liquid hydrogen is clear and colorless; it has a sp. gr. of 0.07, and boils at —253° C. (—423° F.), under normal atmospheric pressure; it also has been solidified, and the temperature reached is thought to be about −256° C. (−428° F.).

In its chemical properties, hydrogen resembles the metals more than the non-metals; it burns easily in atmospheric air, or in pure oxygen, with a non-luminous, colorless, or slightly bluish flame producing during this process of combustion a higher temperature than can be obtained by the combustion of an equal weight of any other substance.

Two volumes of hydrogen combine with one volume of oxygen, forming two volumes of gaseous water, and the formation of water by the combustion of hydrogen distinguishes it from other gases.

The chemical affinity which hydrogen possesses for oxygen is so great that it abstracts the oxygen from many oxides. Thus, if hydrogen at a red heat be passed over the oxides of copper or iron the metals are set free, while water is formed:

$$CuO + 2H = H_2O + Cu.$$

This process of abstracting oxygen from an oxide is called *reduction* or *deoxidation*, and substances having the power of accomplishing this result are called *reducing* or *deoxidizing agents*. Hydrogen, consequently, is a reducing agent.

We thus see that, while in physical properties O and H resemble one another closely, their chemical properties are practically the reverse of each other. Elements which, like the metals, combine readily with oxygen, do not combine with hydrogen; and, *vice versa*, elements which, like chlorine, combine most readily with hydrogen, will scarcely combine with oxygen. It will be shown later that, as a general rule, elements which resemble one another in chemical properties are not apt to combine with one another, while those differing widely have great affinity for one another.

**Nascent hydrogen.** It was stated above that hydrogen is a good reducing agent, but as far as hydrogen in the free state is concerned reduction takes place, as a rule, only when heat is employed. There is a condition of hydrogen, however, in which it is able to reduce many compounds at ordinary temperature, while free hydrogen has no measurable action on the same. For example, the hydrogen liberated during electrolysis of a dilute acid is able to reduce many compounds present in solution immediately around the pole (cathode) at which the hydrogen is produced. It also shows different degrees of activity according to the material of which the pole is made. Similarly, hydrogen generated by the action of dilute acids on metals has reducing power on substances immediately surrounding the metals during action, whereas free

hydrogen gas passed through a solution of the same substances or in contact with them in the dry state has no action. To illustrate: hydrogen gas passed through a solution of arsenous oxide, $As_2O_3$, has no effect, but if the oxide is present in a mixture of dilute hydrochloric acid and zinc the hydrogen formed quickly reduces it to arsine gas, $AsH_3$. This is one of the most delicate tests for arsenic. The more active condition of hydrogen at the time of its liberation is spoken of as the *nascent state.* It seems that this increased activity of hydrogen in contact with the substances that liberate it is an example of contact or catalytic action (see page 87). Good support to this view is the fact that the efficiency of the nascent hydrogen varies according to the nature of the material in association with which the hydrogen is produced.

**Water, $H_2O$ = 18.016. Hydrogen Monoxide.**—Water exists on our globe in the three states of aggregation. Air at all temperatures contains water in the gaseous form. Liquid water occurs plentifully in the oceans, rivers, etc., and also in plants and animals. Seven-tenths of the human body is water; potatoes contain of it 75 per cent., and watermelons as much as 94 per cent. Solid water exists not only as ice and snow, but it also enters into the composition of many rocks, and is a constituent of many crystals containing water of crystallization.

Absolutely pure water is not found in nature. The purest natural water is rain-water collected after the air has been purified from dust, etc., by previous rain. Comparatively pure water may be obtained by melting ice, since, when water containing impurities is frozen partially, these are mostly left in the uncongealed water.

The waters of springs, wells, rivers, etc., differ widely from each other; they all contain more or less of substances dissolved by the water in its course through the atmosphere or through the soil and rocks. The constituents thus absorbed by the water are either solids or gases.

Solids generally found in natural waters are common salt (sodium chloride), gypsum (calcium sulphate), and carbonate of lime (calcium carbonate); frequently found are chlorides and sulphates of potassium and magnesium, traces of silica and salts of iron. Gases absorbed by water are constituents of the atmospheric air, chiefly oxygen, nitrogen, and carbon dioxide. One hundred volumes of water contain about two volumes of nitrogen, one volume of oxygen, and one volume of carbon dioxide.

Water is said to be *hard* when it contains so much of salts of calcium and magnesium that the formation of lather by soap is delayed because these salts form insoluble compounds with the soap. Water containing but little of inorganic matter is said to be *soft.*

When the hardness is caused by metallic sulphates or chlorides the water is called *permanently hard,* while it is termed *temporarily hard* when the metals are present as carbonates, dissolved by carbonic acid. On boiling such water carbon dioxide escapes, the carbonates of the metals are precipitated, and the water is rendered soft.

**Mineral Waters.**—Mineral waters are spring waters containing one or more substances in such quantities that they impart to the water a peculiar taste and generally a decided medicinal action. According to the predominating constituents we distinguish *bitter* waters, containing larger quantities of magnesium salts; *iron* or *chalybeate* waters, containing carbonate or sulphate of iron; *sulphur* or *hepatic* waters, containing hydrogen sulphide; *effervescent* waters, strongly charged with carbonic acid; *cathartic* waters, generally containing sodium or magnesium sulphate, etc.

**Drinking-water.**—A good drinking-water should be free from color, odor, and taste; it should neither be an absolutely pure water, nor a water containing too much of foreign matter. Water containing from 2 to 4 parts of total inorganic solids (chiefly carbonate of lime and common salt) in 10,000 parts of water and about 1 volume of carbon dioxide in 100 volumes of water, may be said to be a good drinking-water. There are, however, good drinking-waters which contain more of total solids than the amount mentioned above.

Most objectionable in drinking-water are *organic substances*, especially when derived from animal matter, and more especially when in a state of decomposition, because such decomposing organic matter is frequently accompanied by living organisms (germs) which may cause disease. Boiling of water destroys these germs, and by subsequent filtering of the boiled water through sand, charcoal, spongy iron, etc., an otherwise unwholesome water may be rendered fit for drinking.

In nature water is rendered free from organic impurities by the oxidizing power of atmospheric oxygen, which is taken up by the water and is readily transferred upon organic matter present.

It should be remembered that no filter can remain efficient for any length of time, as the impurities of the water are retained by the materials used as a filter, and this may become, therefore, a source of pollution instead of a purifier. By heating to a low red heat the materials used for filtering, these are cleaned and may be used again. The methods applied to the analysis of drinking-water will be mentioned later. (See Index.)

**Distilled Water** (*Aqua Destillata*).—The process for obtaining pure water is distillation in a suitable apparatus. From 1000 parts of water used for distillation, the first 100 parts distilled over should not be used, as they contain the gaseous constituents. The solids contained in the water are left in the undistilled portion, which should not be less than 100 parts.

**Composition of Water.**—Until the discovery of oxygen, water was thought to be a simple substance. In 1781 Cavendish, of England, discovered the qualitative composition of water when he obtained it by causing hydrogen and oxygen to unite. Water was thus produced *synthetically*.

The proportion of hydrogen and oxygen in water has been determined accurately by weighing the oxygen and the water formed by union with hydro-

gen, also by weighing both constituents and the water after union. The results of the most accurate experiments showed that water contains 11.185 per cent. of hydrogen and 88.815 per cent. of oxygen, or 2.016 parts by weight of hydrogen to 16 parts, by weight, of oxygen. By volume, hydrogen and oxygen unite in the proportion of 2 : 1 to form water.

**Analysis and Synthesis.**—These terms refer to two methods of research in chemistry, accomplished by two kinds of reaction, analytical and synthetical.

Analysis is that mode of research by which compound substances are broken up into their elements or into simpler forms of combination, and analytical reactions are all chemical processes by which the nature of an element, or of a group of elements, may be recognized.

Synthesis is that method of research by which bodies are made to unite to produce substances more complex.

Analytical and synthetical methods, or reactions, frequently blend into one another. This means: A reaction made with the intention of recognizing a substance may at the same time produce some compound of interest from a synthetical point of view.

**Properties of Water.**—Water is an inodorous, tasteless, and, in small quantities, colorless liquid. Thick layers of water show a blue color. On cooling, water contracts until it reaches the temperature of 4° C. (39.2° F.), at which point it has its greatest density. If cooled below this temperature it expands and the specific gravity of ice is somewhat less than that of water. Water is perfectly neutral, yet it has a tendency to combine with both acid and basic substances. These compounds are usually called *hydroxides* (formerly *hydrates*), such as NaOH, $Ca(OH)_2$, etc. These compounds are often formed by direct union of an oxide with water, thus:

$$CaO + H_2O = Ca(OH)_2.$$
$$SO_3 + H_2O = SO_2(OH)_2.$$

Water is the most common solvent, both in nature and in artificial processes. As a general rule, solids are dissolved more quickly and in larger quantities by hot water than by cold, but to this there are many exceptions. For instance: Common salt is nearly as soluble in cold as in hot water; sodium sulphate is most soluble in water of 33° C. (91° F.), and some calcium salts are less soluble in hot than in cold water.

The term *solution* is applied to any clear and homogeneous liquid obtained by causing the transformation of matter from a solid or gaseous state to the liquid state by means of a liquid called a solvent or menstruum; solutions may also be obtained from two liquids, as when we dissolve oil in ether. A solution is said to be *saturated* when the solvent will not take up any more of the substance being dissolved.

Two kinds of solutions are distinguished—viz., *simple* solutions and *complex* or *chemical* solutions. In the former we have a mere physical change, the molecules of the dissolved body being present with all their characteristic proper-

ties, and on evaporation the dissolved solid will be reobtained unchanged. Instances of this kind are solutions of sugar or table salt in water.

In chemical solutions there takes place a rearrangement of the constituent elements, both of the solvent and of the substance dissolved. Moreover, on evaporation of the solution a substance is obtained entirely different from the one which has been dissolved. Instances of this kind are the dissolving of sodium in water, when sodium hydroxide is formed; or the dissolving of zinc in sulphuric acid, when zinc sulphate is formed. The term *emulsion* is used to designate a more or less homogeneous liquid rendered opaque or milky by the suspension in it of finely divided particles of fat, oil, or resin. The milk of mammalia and the milk-like juice of certain plants are instances of true emulsions.

Many salts combine with water in crystallizing; crystallized sodium sulphate, for instance, contains more than half its weight of water. This water is called *water of crystallization*, and is expelled generally at a temperature of 100° C. (212° F.). Some crystallized substances lose water of crystallization when exposed to the air; this property is known as *efflorescence*. Crystals of sodium carbonate, ferrous sulphate etc., effloresce, as is shown by the formation of powder upon the crystalline surface. Substances are said to be *anhydrous* when they are destitute of water, for instance, when crystals have lost their water of crystallization or when ether or alcohol has been freed from dissolved water. The term *anhydride* is sometimes used for oxyacids which have been deprived of all water, so that they are no longer acids, but oxides. Thus, by removing water from sulphuric acid, $H_2SO_4$, there is left sulphur trioxide, or sulphuric acid anhydride, $SO_3$. The term *deliquescence* is applied to the power of certain solid substances to absorb moisture from the air, thereby becoming damp or even liquid, as, for instance, potassium hydroxide, calcium chloride, etc. Such substances are spoken of also as being *hygroscopic*, and are used for drying gases.

The term *effervescence* refers to the escape of a gas from water or from any other liquid in which the gas was held under pressure or in which it may be generated; as, for instance, when an acid is added to a carbonate, whereupon carbon dioxide escapes with energetic bubbling.

The explanation of efflorescence and deliquescence is found in a well-known principle of physics. It is well known that liquids will evaporate in a closed space until the pressure of the vapor is equal to the vapor tension of the liquid, when equilibrium is established and evaporation of the liquid apparently ceases. This means that vapor particles fly back into the liquid at the same rate that liquid particles leave the surface of the liquid to become vapor. If the vapor pressure in any way becomes greater than the vapor tension of the liquid, some vapor will be condensed to liquid. On the other hand, if the vapor pressure is constantly lower than the vapor tension of the liquid, evaporation will go on until no more liquid is left. One way of accomplishing this is by free exposure of liquids to the atmosphere. Of course the amount of the vapor pressure varies with the temperature. Now it is found that substances

containing water of crystallization have a vapor tension just as water has. For example, when a crystal of sodium sulphate ($Na_2SO_4.10H_2O$) is allowed to rise to the top of a barometer tube at 9° C., it exerts a vapor tension of 5.5 mm.—that is, the pressure of the water vapor given off by the crystal is enough to depress the mercury column 5.5 mm. Those substances crystallizing with water which at ordinary temperature exert a vapor tension greater than the pressure of the water vapor in the atmosphere, are efflorescent and must be kept in closed containers, just as water must be to prevent loss of water. When the vapor tension of the substances is about the same or less than the atmospheric vapor pressure, the substances are stable and need not be carefully bottled, except to keep them clean. The average pressure of the water vapor in the atmosphere at 9° C. is about 5 mm. At this temperature crystals of sodium sulphate have a vapor tension of 5.5 mm. and are efflorescent, while those of copper sulphate have a vapor tension of 2 mm. and are stable in the air.

Deliquescent substances are always very soluble in water. A layer of moisture condenses on these just as it does on all bodies exposed to the atmosphere. In the case of extremely soluble substances, the condensed moisture forms a thin layer of very concentrated solution upon their surfaces. Concentrated solutions have a vapor tension less than that of water, and much less than the atmospheric vapor pressure. The result is that water vapor continues to condense from the atmosphere upon the substances until they dissolve and form solutions so dilute that their correspondingly increased vapor tension balances the vapor pressure of the moisture in the atmosphere.

**Hydrogen Dioxide, Hydrogen Peroxide, $H_2O_2$ = 34.016.**—This compound may be obtained in aqueous solution from several metallic dioxides which, when treated with an acid, yield the corresponding hydrogen dioxide.

Sodium dioxide and barium dioxide are the compounds chiefly employed in its manufacture, the acid used being either carbonic, hydrochloric, hydrofluoric, sulphuric, or phosphoric acid. The decomposition, when sulphuric acid and barium dioxide are used, is this:

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

In no case is it possible to obtain, as might appear from the above equation, pure hydrogen dioxide directly, as a considerable quantity of water has to be present in order to effect the decomposition. The aqueous solution, if quite pure, can be concentrated by evaporation at a temperature not exceeding 60° C. (140° F.) until it has a strength of 50 per cent. If this be further heated *in vacuo* at a gradually increased temperature, a nearly pure hydrogen dioxide distils over at a temperature of 85° C. (185° F.).

Pure hydrogen dioxide is a colorless oily liquid, of a specific gravity 1.45. It is soluble in water, alcohol, and ether, which latter extracts it from its aqueous solutions.

Hydrogen dioxide decomposes slowly at ordinary temperature, more rapidly on exposure to light and at higher temperatures; at

100° C. the decomposition is often explosively rapid. Many inert substances, in powder, cause its decomposition, and it is for this reason that even dust particles from the air act decomposingly, especially during evaporation. The presence of very small quantities of certain substances retards the decomposition. Traces of free acids, as also boro-glycerin, have been used for this purpose. It has been found that a very small quantity of acetanilide is an excellent preservative and it is now added to commercial hydrogen dioxide solution.

Hydrogen dioxide possesses bleaching, caustic, and antiseptic properties. It is used as a bleaching agent for hair, wool, teeth, and other articles, and as an antiseptic in surgical and in dental operations. It effervesces with pus, as also with saliva, in consequence of the liberation of oxygen.

**Catalytic Action.**—There are a number of instances in chemistry where a substance, which apparently undergoes no change itself, causes by its presence an increase in chemical change in other substances, or induces a change where, without it, there would be no chemical action. This is known as *catalytic* or *contact action* and the process is called *catalysis*. Examples of this action are seen in the decomposition of hydrogen dioxide by dust particles, or finely divided platinum, the influence of manganese dioxide on potassium chlorate in the preparation of oxygen, and the explosion of a mixture of hydrogen and oxygen when platinum black is introduced into it.

**Solution of Hydrogen Dioxide** (*Liquor Hydrogenii Dioxidi*).—Solution of hydrogen dioxide should contain about 3 per cent., by weight, of pure dioxide, corresponding to about 10 volumes of available oxygen in 1 volume of the solution.

The solution is colorless and without odor, and has a slightly acidulous taste, producing a peculiar sensation and soapy froth in the mouth. It is liable to deteriorate by age, especially on exposure to heat and light.

*Pyrozone* is the trade name under which a 50 per cent. hydrogen peroxide is sold, but diluted pyrozone also is found in the market.

*Glycozone* is hydrogen dioxide dissolved in glycerin instead of in water.

Hydrogen dioxide, owing to its instability and tendency to decompose into water and oxygen, is an excellent oxidizing agent. It is frequently used in preference to other such agents, because by its use no other products are introduced into solutions than water and oxygen. Toward a few substances, which themselves are unstable and easily give up oxygen, it also acts as a reducing agent. For example, silver oxide is reduced to metallic silver thus:

$$Ag_2O + H_2O_2 = 2Ag + O_2 + H_2O.$$

When hydrogen dioxide decomposes into water and oxygen, heat is liberated. The thermal equation is—

$$H_2O_2 = H_2O + O + 23{,}100 \text{ cal.},$$

that is, when 34.016 grams of hydrogen dioxide corresponding to the formula, $H_2O_2$, decompose, 23,100 calories of heat energy are liberated. This is in addition to the heat that is produced when the liberated oxygen unites with other substances. In this way the great activity of hydrogen dioxide as an oxidizer is accounted for.

### Tests[1] for Solution of Hydrogen Dioxide.

(Use the commercial solution after diluting about five times with water.)

1. To a beaker half-full of water, add 1 or 2 c.c. of solution of potassium iodide (see Reagents) and about 2 c.c. of the hydrogen dioxide solution. Is any yellow color produced? Then add a few drops of starch solution (for which, see Index). A deep blue color is produced by the action of the starch on the iodine liberated from potassium iodide by the oxidizing action of the hydrogen dioxide:

$$2KI + H_2O_2 = 2KOH + 2I.$$

The action is more intense if the water is first acidified with 5 or 10 drops of a dilute acid. This is not a decisive test, since other substances besides hydrogen dioxide give the same test.

2. To a test-tube half-full of water, add in succession, 1 c.c. of the hydrogen dioxide solution, a few drops of dilute sulphuric acid, and 2 drops of solution of potassium dichromate, and mix. A blue compound, known as perchromic acid, $HCrO_4$, is produced, which fades after a short time. The color may be made more permanent by shaking the mixture with ether, which dissolves the compound and collects on the surface on standing. This is a very delicate and decisive test.

3. Acidify a few cubic centimeters of the hydrogen dioxide solution with about 2 c.c. of dilute sulphuric acid, and add solution of potassium permanganate, a little at a time. The purple color vanishes quickly and a gas is given off (oxygen). The permanganate is an unstable oxidizing agent, which gives up its oxygen. This unites with oxygen from the dioxide, and escapes as a gas. The reaction will be understood when the chemistry of manganese is studied. Other substances also decolorize permanganate.

If a solution is colorless, odorless, practically neutral to litmus-paper, volatilizes completely upon heating, and responds to the above tests, especially number 2, it is, without doubt, hydrogen dioxide.

**The Law of Chemical Combination by Volume, or the Law of Gay-Lussac.**—We have seen that the proportions in which hydrogen and oxygen combine to form water may be stated in terms of volumes

[1] Tests are reactions to which a substance may be subjected for the purpose of recognition. Acids turn blue litmus red, and we call that a test for acids. Carbon dioxide gas gives a milky appearance to lime-water, which is a test for the gas. Some tests are much more striking than others, indeed, they are so characteristic that they tell at once the nature of the substance tested. Such tests might be called *decisive*, in distinction to others which are only *corroborative*, and to which several substances may respond.

of the two constituents. There are a number of instances like this one, and in 1808 Gay-Lussac, after a careful quantitative study of them, discovered the law of combination by volume which may be stated as follows: *When two or more gaseous constituents combine chemically to form a gaseous compound, the volumes of the individual constituents bear a simple relation to the volume of the product.* The law may be divided into two laws, thus: 1. Gases combine by volume in a simple ratio. 2. The resulting volume of the compound, when in the form of a gas, bears a simple ratio to the volumes of the constituents. For instance: 1 volume of hydrogen combines with 1 volume of chlorine, forming 2 volumes of hydrochloric acid gas; 2 volumes of hydrogen combine with 1 volume of oxygen, forming 2 volumes of water-vapor; 3 volumes of hydrogen combine with 1 volume of nitrogen, forming 2 volumes of ammonia.

If the different combining volumes of the gases mentioned are weighed, it will be found that there exists a simple relation between these weights and the combining weights of the elements.

For instance: equal volumes of hydrogen and chlorine combine, and the weights of these volumes are as 1.008 : 35.46, which numbers represent also the combining weights of the two elements. Two volumes of hydrogen combine with one volume of oxygen, and the weights of the volumes are as 2.016 : 16, the latter being the combining weight of oxygen.

From the above relationship in regard to combination of gases, the important inference is drawn that the combining weights of the elements and the formula weights of compounds, in the gaseous state, occupy at the same temperature and pressure volumes which are equal or bear a simple ratio to one another.

In Section I on Physics, reasons are given for believing that all matter is made up of particles called molecules. Gases consist of molecules and when they unite chemically, the act must involve the molecules. As stated in Gay-Lussac's law, gases unite in volumes that bear a simple ratio to one another, which means, in other words, that the numbers of the molecules in equal volumes of different gases under like conditions of temperature and pressure must bear a simple ratio to one another. In 1811 Avogadro of Turin offered the hypothesis that equal volumes of all gases under like conditions *contain the same number of molecules.* Subsequent facts and theoretical deductions have substantiated this view, which is now known as Avogadro's hypothesis.

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QUESTIONS.—Mention two processes by which hydrogen may be obtained. Show by symbols the decomposition of water by potassium, and of sulphuric acid by iron. State the chemical and physical properties of hydrogen. Define the nascent state. What explanation is offered to account for it? State the composition of water in parts by weight and by volume. Mention the most common solid and gaseous constituents of natural waters. How does a mineral water differ from other waters? Mention some different kinds of mineral waters

## 8. SOLUTION.

As stated under Water, the term solution is applied to any homogeneous liquid mixture that results when solids, liquids, or gases are brought in contact with a liquid and disappear in the liquid. (There are a few instances of solution of a gas in a solid, and of a solid in a solid.) Solutions are transparent, and the dissolved material is so thoroughly disseminated that its particles cannot be distinguished by the eye from those of the solvent. Moreover, there is perfect distribution of the dissolved matter and no tendency for it to settle. An opalescent or opaque appearance of a liquid is evidence that there is matter held in suspension, and this matter will settle in time, or may be filtered out. Dissolved substances cannot be removed by filtration, as they pass through the pores of the paper as readily as the liquid does.

For the majority of substances there is a limit to the amount that can be dissolved in a given amount of liquid. This limit ranges from an almost infinitesimal amount in some cases to a fairly large quantity in others. Thus, at ordinary temperature, the amount of ferric oxide that is dissolved by 100 c.c. of pure water is extremely small, while about 90 grams of crystallized magnesium sulphate are dissolved. No substance is absolutely insoluble, but many are so sparingly soluble that for practical purposes they are considered insoluble. In some cases two substances may be mixed in any proportions, for example, water and alcohol. But usually the solubility of one liquid in another is limited, and when two such liquids are shaken together they separate after a time into two layers, the liquid in each layer being saturated with the other liquid. Thus, when ether and water are shaken together at ordinary temperature they separate on standing with the lighter (ether) layer on top, and 100 grams of water dissolve 2.1 grams of ether, while 100 grams of ether dissolve 11 grams of water. Pairs of liquids which are only slightly soluble in each other are known as *immiscible solvents*, and are often employed in certain kinds of chemical work for transferring a substance from one liquid to another. This operation is known as *extraction*, and depends for its success upon a great difference of solubility of the given substance in the two solvents. The division of a substance between two immiscible solvents, after thorough shaking and separation of the liquids, is proportional to its solubility in each solvent. If a substance is 100 times more soluble in chloroform than in water, and its aqueous solution is shaken

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and their chief constituents. What are the characteristics of a good drinking-water? What are the purest natural waters, and by what process may chemically pure water be obtained? State composition, mode of manufacture, and properties of hydrogen dioxide. What is the explanation of efflorescence and deliquescence? State the law of chemical combination by volume, with illustrations.

thoroughly with chloroform, the concentration of the substance in the chloroform layer will be found 100 times that in the water layer. The process of extraction must be repeated several times for the complete removal of a substance from a liquid.

**Terms Employed.**—The liquid in which a substance is dissolved is called the *solvent*, while the substance, to avoid circumlocution, is often called the *solute*. The word *strength* is frequently used to refer to the amount of substance in solution, but a more exact term to employ is *concentration*. A solution that contains a small quantity, say 5 grams of a substance in 100 c.c., is said to have a small concentration, or to be *dilute*. *Concentrated* solutions contain a relatively large amount of dissolved substance; they are often spoken of as *very strong solutions*. *Concentrating* a solution is the removal of *part* of the solvent by evaporation. A *saturated solution* is one that contains the maximum amount of dissolved substance. This condition may be attained by long agitation of the liquid with an excess of the substance. If the latter is a solid, it should be finely divided. The *solubility* of a substance is its concentration in saturated solution, and is expressed in terms of the number of grams of the substance in 100 grams of the solvent, or in 100 c.c. of the solution, or of the grams of solvent required to dissolve 1 gram of the substance. The solubility of substances varies with the temperature, being, as a rule, in the case of solids, much greater at boiling than at ordinary temperature. In most cases, when a hot concentrated solution is allowed to cool, the excess of material over what corresponds to the solubility at lower temperature, separates as crystals from the solution (see Crystals, chapter 1). But in some instances the excess of material does not separate from the solution as it cools; such a solution is then said to be *supersaturated*. Crystallization can be induced by placing in the cool solution a fragment of the same substance as that in solution. A solution in contact with the solid substance cannot be more than saturated with respect to that substance. There is an equilibrium between the solid and the saturated solution. Sulphate, thiosulphate, and chlorate of sodium have a marked tendency to give supersaturated solutions, especially if the solutions are freed from all floating particles by careful filtration.

The solution of certain substances in water takes place with liberation of heat and rise in temperature of the solution, while in other cases there is an absorption of heat and a fall in temperature. *Heat of solution* is the number of calories liberated or absorbed when the weight of a substance in grams corresponding to its chemical formula (molecular weight) is dissolved in an unlimited amount of water. When 98.09 grams of sulphuric acid (corresponding to $H_2SO_4$) are thus dissolved, 39,170 calories of heat are liberated, or enough heat to raise over 39 liters of water 1° C. in temperature. When 286.16 grams of crystallized sodium carbonate ($Na_2CO_3.10H_2O$) are dissolved, 16,160 calories are absorbed, but solution of an equivalent weight

of anhydrous sodium carbonate ($Na_2CO_3$), or 106 grams, liberates 5640 calories of heat. If a substance absorbs heat during solution, it develops the same amount of heat when it comes out of solution as by crystallization. For example, a supersaturated solution of sodium sulphate, when crystallizing suddenly, produces quite an appreciable rise in temperature.

**Solution of gases. Henry's Law.** Gases dissolve in liquids to a variable degree. The range of solubility is quite wide, as may be seen from the following examples: At 0° C. and 760 mm. pressure, 1 volume of water dissolves 0.02 volume of hydrogen, or nitrogen, 0.04 volume of oxygen, 1.8 volumes of carbon dioxide, 80 volumes of sulphur dioxide, 550 volumes of hydrochloric acid gas, and 1050 volumes of ammonia gas.

The solubility of a gas varies with the nature of the solvent; thus, at 0° C., a volume of alcohol dissolves twice as much carbon dioxide as the same volume of water does. It also varies with the temperature, decreasing, as a rule, as the temperature increases. Thus, 100 volumes of water dissolve about 4 volumes of oxygen at 0° C., 3 at 20° C., 1.8 at 50° C., and none at 100° C. In many instances a gas is completely removed from its solution by boiling, but this is not possible in the case of certain very soluble gases, like hydrochloric acid. There is in such cases a chemical action, in part at least, between the gas and the solvent. A 20.2 per cent. aqueous solution of hydrochloric acid distills unchanged under normal atmospheric pressure.

The solubility of a gas increases with increased pressure on the gas. Commercial aërated water is [illegible] a good illustration. The water is charged with carbon dioxide under considerable pressure. When drawn from the container and exposed to the atmosphere the excess of gas, which cannot remain dissolved under the diminished pressure, escapes, causing effervescence. Such a solution is often called soda water. Solutions of gases in liquids fall into two classes: (1) those from which the gas is completely removed by heat or by decrease of pressure; (2) those from which the gas is not thus completely removed. Very soluble gases give rise to the second class of solutions, in which a complete chemical and physical independence of the molecules of solvent and gas is lacking. In solutions of the first class there is a fixed relationship between the solubility of a gas and pressure, which is known as *Henry's Law.* It may be stated thus: *The quantity of a gas dissolved by a given quantity of a liquid is proportional to the pressure of the gas.* Since the volume of a gas is inversely proportional to the pressure, another form in which the law may be stated is: *A given quantity of a liquid dissolves the same volume of a gas at all pressures.*

In the case of a mixture of gases in contact with a liquid, each gas dissolves as if it were present alone, and in proportion to its own partial pressure in the mixture.

Henry's law holds in the case of absorption of gases by saline solutions, if the gas has no chemical action on the salt in solution, for example, in the absorption of carbon dioxide, oxygen, or nitrogen, by a solution of sodium chloride (common salt). When the gas acts chemically on the dissolved salt, as carbon dioxide does on ordinary sodium phosphate or sodium carbonate, one portion of the gas is absorbed in accordance with Henry's law, and an additional portion is absorbed as a result of chemical action and is independent of pressure.

**Freezing-points of Solutions.**—The freezing-point of a solution is always lower than that of the pure solvent. It is also easily observed, by introducing small quantities of solutions and pure solvents over the mercury in barometer tubes, that the vapor tension of the solutions is always less than that of the pure solvents, no matter what the temperature is. This difference in vapor tension accounts for the fact that the freezing-point of solutions is depressed. Theoretical considerations show that freezing (separation of some of the solvent in the solid state) can take place only at such a temperature at which the solution and the solid state of the solvent have the same vapor tension, whereby they are in physical equilibrium and can co-exist permanently (see discussion under Efflorescence and Deliquescence, p. 85). Since the vapor tension of a solution is always less than that of the pure solvent, it follows that the freezing-point of a solution must be lower than that of the pure solvent, in order that the vapor tension of the solution and of the ice that separates may balance each other. (On this principle the low temperature of freezing mixtures, such as snow (or ice) and salt, is explained).

For a description of apparatus and details of method in making determinations of the freezing-points of solutions, the student must be referred to books on physical chemistry.

For solutions not too concentrated and in which there is no chemical action between the solvent and the substance dissolved, the following law has been found to hold: *The depression of the freezing-point is directly proportional to the weight of dissolved substance in a given amount of the solvent.* By calculations made on the results obtained with dilute solutions, the following law has been found to hold theoretically for formula quantities of substances: *The formula weights in grams of different substances dissolved in 1000 grams of the same solvent produce the same depression of the freezing-point.* The depression thus produced is called the *molecular depression constant*, and has a different numerical value for each solvent. For water it is 1.89° C.; for benzene, 4.9° C., and for phenol, 7.5° C.

The above law gives a basis for a method of determining formula (molecular) weights, which was first applied extensively by Raoult, and is sometimes called the *cryoscopic method.* It is valuable in the case of substances which cannot be volatilized without decomposition. The formula weight is calculated from the equation

$$D = d \times \frac{W \times 1000}{M \times g},$$

in which D is the amount of depression in any actual experiment, d the molecular depression constant, W the weight of the substance, M its formula (molecular) weight, and g the weight of the solvent in grams.

The above law, often called *the law of Raoult*, does not hold in some cases, especially in those of solutions of acids, bases, and salts in water. For example, one formula weight of sodium chloride, 58.46 grams, dissolved in 1000 grams of water, depresses the freezing-point about 3.5° C., or nearly twice the amount produced by a cane-sugar solution of equivalent concentration, 1.89° C., which is taken as the molecular depression of normally acting substances. It is also a noteworthy fact that aqueous solutions of substances that have abnormal freezing-point depressions are just such as conduct an electric current, while solutions of substances that give normal depressions do not conduct a current. The same number of particles of different substances in a given amount of solvent produces

the same lowering of the freezing-point, and the formula (molecular) weight in grams contain the same number of particles. The fact that the depression of the freezing-point of a solution of the formula weight in grams of sodium chloride in 1000 grams of water is much greater than that of a similar solution of cane-sugar, can be accounted for on the assumption that the number of particles in the sodium chloride solution must be increased somehow over the number of particles in the sugar solution. This increase can only take place by a decomposition of the particles of sodium chloride, thus,

$$NaCl = Na + Cl.$$

The particles Na and Cl must be different in condition from sodium and chlorine as we know them in the free state, but as far as their effect upon the freezing-point is concerned they act the same as undecomposed dissolved particles. This assumption of the decomposition of molecules is applied in the cases of all abnormally acting solutions where the freezing-point depressions are greater than normal, and will be referred to again farther on under Ionization.

In the field of medicine the determination of the freezing-point of certain fluids is sometimes carried out in order to learn something of the manner in which the organs are functioning. Normal blood has a lower freezing-point than water, the difference is 0.56° C. A greater difference than this indicates that the kidneys are not properly eliminating the solid waste products from the blood. The freezing-point depression of normal urine is 1.2°–2.3° C. Of cows' milk it is 0.55°–0.56° C. A lower depression indicates that the milk has been tampered with.

**Boiling-points of solutions.** These are always higher than the boiling-points of the pure solvents. The boiling-point of any solution is that temperature at which the vapor tension of the solution is equal to the atmospheric pressure. Since the vapor tension of solutions is less than that of the pure solvent, it follows that a solution must be heated to a higher temperature than that at which the pure solvent boils, in order to make its vapor tension equal to the atmospheric pressure; in other words, to make it boil. *The elevations in the boiling-points are proportional to the concentrations of the different solutions of any one substance.* The formula weight in grams of normally acting substances, dissolved in 1000 grams of water, elevates the boiling-point from 100° to 100.52° C. The difference, 0.52°, is called the *molecular boiling-point constant* for water. Just as in the case of freezing-points, so here a method of determining formula (molecular) weights has been devised, but for a description of the apparatus and details of working, reference must be made to special books.

The substances which show abnormalities in the depression of the freezing-point are also those which give abnormal elevations in the boiling-points of their solutions. The abnormal behavior is also accounted for by the same explanation, namely, a decomposition of some of the molecules of the dissolved substance. The deviations from normal behavior are particularly observed in aqueous solutions.

**Osmotic pressure.** Soluble substances in contact with a liquid dissolve and diffuse throughout the liquid until the concentration is uniform in every part of the solution (see Diffusion, p. 35). In the liquid the substance behaves somewhat like a gas, in that its molecules tend to spread out and fill the whole space occupied by the liquid. The cohesion between the molecules of the substance is overcome and there is freedom of motion, somewhat as in a gas.

Just as a gas exerts a pressure on any partition or membrane that resists the motion of its molecules, so likewise do the molecules of a substance in solution exert pressure upon a membrane that prevents their diffusion into a less concentrated region of the solution, or into the pure solvent. This pressure is called *osmotic pressure.* In the article on Dialysis it is shown that a substance in aqueous solution on one side of certain kinds of membranes, as bladder or parchment, will diffuse into pure water on the other side. Osmotic pressure is exhibited here, but such membranes are not suitable for its study, because the motion (diffusion) of the molecules of the dissolved substance is not stopped, but only hindered. It is possible, however, to prepare membranes which are permeable to the solvent, but impermeable to the dissolved substance. These are known as *semi-permeable membranes,* and by their means the phenomena of osmotic pressure can be studied qualitatively and quantitatively. W. Pfeffer, a botanist, was the first to successfully construct (1877) an artificial semi-permeable membrane by causing a precipitate of copper ferrocyanide to be formed within the walls of a porous unglazed porcelain cup.[1] Such cups are known as *osmotic cells.* When a solution of any substance, say, cane-sugar, is placed in the cell and the latter is placed in water, it is observed that water passes through the cell into the solution, but no sugar passes out into the water. If the flow of water is unobstructed, it will continue until the solution is so much diluted that it is practically the same as water. If the accumulation of water in the cell is obstructed by using a closed cell filled with the solution and fitted with a manometer, pressure is seen to develop in the cell, due to the tendency of the water to pass into it, and corresponding to the amount that would have passed into it had the water not been obstructed. It requires some hours for this pressure to reach a maximum, and the amount in atmospheres can be read on the manometer. At the maximum the pressure on the water within the cell causes it to tend to flow out as fast as the water outside tends to flow in, thus producing a system in equilibrium. The pressure read on the manometer is equal to the osmotic pressure of the molecules of the dissolved substance against the membrane of the cell.

In osmotic cells the pure solvent always passes into the solution, or the solvent passes from a solution of less concentration into one of greater concentration. This flow can be accounted for on the physical principle of equilibrium, namely, that in any system capable of movement or adjustment a strain in one part will cause a movement tending to remove or equalize the strain. A system of a membrane and a liquid on each side of it can be in equilibrium only when the osmotic pressure on the two sides of the membrane is the same. In the case of a semi-permeable membrane, the molecules of the dissolved substance cannot pass, so the only other way of equalizing osmotic pressure is by the solvent passing from the exterior of the cell into the solution, until the osmotic pressure is the same on each side of the membrane. If this passage is obstructed the tendency still exists, which manifests itself as pressure.

In 1887 van't Hoff deduced from theoretical considerations the laws of osmotic pressure, which are verified by experiments. These laws are analogous to the gas laws, and are as follows:

*The osmotic pressures of solutions of the same substance are proportional to their*

[1] It was rather difficult to prepare such membranes until a method was devised by Prof. H. N. Morse, by which practically flawless osmotic cups can be readily made. See Amer. Chem. Jour., July, 1905, and later.

*concentrations.* This is analogous to Boyle's law for gas pressures, and in general is independent of the nature of the solvent. It is illustrated by the following results:

| | | | | |
|---|---|---|---|---|
| Grams of cane-sugar in 1000 grams of water | 68.4 | 136.8 | 171.0 | 342.0 |
| Osmotic pressure in atmospheres . . . | 4.83 | 9.72 | 12.15 | 24.46 |

*Osmotic pressure increases in proportion to the absolute temperature.* This is analogous to the law of Charles for gases.

*Solutions which at the same temperature have equal osmotic pressure contain equal numbers of molecules of the dissolved substance in equal volumes.* This is analogous to Avogadro's law for gases.

*The osmotic pressure of a substance in solution is the same in value as the gaseous pressure which it would exhibit if the same weight of it were contained as a gas in the same volume at the same temperature.* The osmotic pressure of a solution of the formula (molecular) weight in grams of a substance in 1 liter of water at 0° C. is 22 to 23 atmospheres, and the same weight of the substance in gas form at 0° C., and occupying a liter volume, would have a gas pressure of 22 to 23 atmospheres.

Solutions of different substances having the same osmotic pressure are said to be *is-osmotic* or *isotonic.* It is not an easy matter to carry out measurements of osmotic pressure except in specially equipped laboratories, but isotonic solutions can be prepared, nevertheless, by taking advantage of the fact that such solutions have the same freezing-points, and determination of freezing-points is a routine task in laboratories. Blood-serum freezes at —0.56° C., which corresponds to an osmotic pressure of about 6.6 atmospheres. A 0.95 per cent. aqueous solution of sodium chloride freezes at —0.56° C., and, therefore, exerts the same osmotic pressure as blood-serum. It is isotonic with blood-serum. A solution of higher osmotic pressure than that of blood-serum is called *hypertonic,* and one of lower pressure is called *hypotonic.*

In regard to the laws of osmotic pressure, deviations from them are observed in the case of aqueous solutions of the same substances for which the freezing-point and boiling-point laws do not hold, namely, acids, bases, and salts. These always show greater osmotic pressures than those calculated, and than that shown by cane-sugar, which is a type of normally acting substance. The deviations are explained by the same assumption that is made to explain deviations from the freezing-point law (see above), namely, decomposition of molecules into a greater number of particles, that is, ions.

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QUESTIONS.—Give a definition of solution and its general characteristics. What are immiscible solvents and how are they employed? Define dilute, concentrated, and saturated solutions. What is meant by the solubility of a substance, and by heat of solution? What is Henry's law regarding the solution of gases in liquids? What is the relation between the freezing-points of solutions and the weights of dissolved substances? What use is made of the cryoscopic method? What is osmotic pressure? What is a semi-permeable membrane? How do the laws of osmotic pressure compare with the gas laws? What are isotonic, hypertonic, and hypotonic solutions? What is the explanation of the abnormal behavior shown by solutions of acids, bases, and salts in their freezing-points, boiling-points, and osmotic pressures?

## 9. NITROGEN.

$N^{III} = 14.01.$

**Occurrence in Nature.**—By far the larger quantity of nitrogen is found in the atmosphere in a free state. Compounds containing nitrogen are chiefly the nitrates, ammonia, and many organic substances.

**Preparation.**—Nitrogen is obtained usually from atmospheric air by the removal of its oxygen. This may be accomplished by burning a piece of phosphorus in a confined portion of air, when phosphoric oxide, a white solid substance, is formed, while nitrogen is left in an almost pure state.

Other methods for obtaining nitrogen are by heating a mixture of potassium nitrite and ammonium chloride dissolved in water:

$$KNO_2 + NH_4Cl = KCl + 2H_2O + 2N;$$

or by heating ammonium nitrite in a glass retort:

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

*Experiment* 5.—Use an apparatus as shown in Fig. 8, page 72. Place in the flask about 10 grams of potassium nitrite and nearly the same amount of ammonium chloride; add enough water to dissolve the salts, and apply heat, which is to be carefully regulated from the time the decomposition begins, as the evolution of gas may otherwise become too rapid. Collect the gas, and notice its properties mentioned below.

**Properties.**—Nitrogen is a colorless, inodorous, tasteless gas; which, at a temperature of —130° C. (—202° F.) and a pressure of 280 atmospheres, may be condensed to a colorless liquid. It is neither, like oxygen, a supporter of combustion, nor, like hydrogen, a combustible substance; in fact, nitrogen is distinguished by having very little affinity for any other element, and it scarcely enters directly into combination with any substance. Nitrogen is not poisonous, yet not being a supporter of combustion it cannot sustain animal life.

**Atmospheric Air.**—Atmospheric air is a mixture of about four-fifths of nitrogen and one-fifth of oxygen, with small quantities of aqueous vapor, argon, carbon dioxide, and ammonia, containing frequently also traces of nitrous or nitric acid, and occasionally hydrogen sulphide, sulphur dioxide, and hydrocarbons. Besides these gases there are always suspended in the air solid particles of dust and very minute cells of either animal or vegetable origin.

100 volumes of atmospheric air contain of

| | |
|---|---|
| Oxygen | 20.60 volumes. |
| Nitrogen | 77.16 " |
| Argon | 0.80 volume. |
| Carbon dioxide | 0.03–0.04 " |
| Aqueous vapor | 0.5 –1.40 " |
| Ammonia, Nitric acid | traces. |

Omitting all minor constituents, the composition of air by volume is about 79 per cent. of nitrogen and 21 per cent. of oxygen, corresponding in weight to 77 per cent. of nitrogen and 23 per cent. of oxygen.

That atmospheric air is a mixture and not a compound of oxygen and nitrogen is shown by the facts that the composition is not absolutely constant, that the two elements may be mixed in the proper quantities without showing the least evidence that chemical change has taken place, and that pure water absorbs from air the two elements in quantities different from those in which they occur in air.

*Humidity*, specifically called *relative humidity*, designates the amount of aqueous vapor in the atmosphere, compared with that which is required to saturate it at the respective temperature. When the air is completely saturated the humidity is expressed as 100; if perfectly dry, as 0. The instruments used to determine humidity are called *hygrometers*.

An *analysis of air* may be made by the following method: A graduated glass tube, containing a measured volume of air, is placed with the open end downward into a dish containing mercury. A small piece of phosphorus is then introduced and allowed to remain in contact with the air for several hours, when it gradually combines with the oxygen. The remaining volume of air is chiefly nitrogen, the loss in volume represents oxygen.

For the determination of carbon dioxide and water, a measured volume of air is passed through two U-shaped glass tubes. One of these tubes has previously been filled with pieces of calcium chloride, the other tube with pieces of potassium hydroxide, and both tubes have been weighed separately. In passing the measured air through these tubes the first one will retain all the moisture, the second one all the carbon dioxide; the increase in weight of the tubes at the end of the operation will give the amounts of the two constituents.

That oxygen is found in the atmosphere in a free state is explained by the fact that all elements having affinity for oxygen have entered into combination with it, while the excess is left uncombined. Nitrogen is found uncombined, because it has so little affinity for other elements.

Liquefaction of air on a large scale has been made possible by a process which depends on first subjecting air to a pressure of 2000 pounds to the square inch and then permitting the compressed gases to escape from a needle-point orifice. During the expansion of the gas heat is absorbed, *i. e.*, the air as well as the tubes in which it is contained are cooled off. The cold thus produced is used to cool another portion of compressed air, which, on expanding, becomes colder than the first portion. By repeating the operation a third time the temperature is brought down to —191° C. and below, and at this temperature liquefaction takes place.

Liquefied air is a mobile, slightly bluish liquid which can be kept for some little time in open vessels—*i. e.*, so long as the temperature of nearly 200° C. below freezing is maintained by the evaporation of the liquid.

As nitrogen is somewhat more volatile than oxygen, the liquefied air, when permitted to stand in open vessels, becomes gradually richer in oxygen, so that finally a liquid is left containing over 30 per cent. of oxygen. Notwithstanding the low temperature of this liquid it acts most energetically as a supporter of combustion.

Of interest are the changes which are brought about in the physical properties of different bodies when cooled down to nearly —200° by immersion in liquid air. Many malleable metals, many soft or elastic bodies, such as rubber and paraffin, when subjected to this low temperature, become as brittle as badly cooled glass; changes in color, as well as in other properties, take place also.

**Argon,** mentioned above as a normal constituent of air, is a gaseous element, discovered in 1894. It may appear strange that a normal constituent of air, present to the extent of nearly 1 per cent., should have been overlooked for so many years, although air had been carefully analyzed many hundred times.

The only explanation that can be offered is the fact that argon has scarcely any chemical affinity for other elements, and consequently its presence was not revealed by any of the ordinary reactions used in air analysis. In fact, the total of argon present had invariably been reported as nitrogen up to the time of the discovery of the new element.

**Helium** is another gaseous element discovered in 1895. It occurs absorbed in a number of rare minerals from which it is expelled by heating. It is also a constituent of the gases which are disengaged from certain spring waters, and, in very small quantities, is a constituent of atmospheric air. Both argon and helium are very inert. Helium has an atomic weight of about 4, while that of argon is 40. One volume of helium is contained in 245,000 volumes of air.

### Compounds of Nitrogen.

Nitrogen has very little tendency to combine directly with other elements, but it is an easy matter to obtain compounds of nitrogen. These, however, are all obtained in indirect ways, being either furnished ready made by processes of nature or obtained as by-products in manufacturing industries. Conversely, as a result of the inactivity of nitrogen, most of its compounds are more or less unstable, either at ordinary or elevated temperatures, or when brought together with other substances. We have already seen how easily ammonium nitrite is radically decomposed by heat, and ammonium nitrate acts in the same way, as will be seen below.

The two principal compounds of nitrogen are ammonia and nitric acid, and nearly all the others with which we have to do in inorganic chemistry are derived from these. Ammonia represents the limit of reduction while nitric acid represents the limit of oxidation of nitrogen.

**Ammonia, $NH_3$ = 17.03.**—This compound is constantly forming in nature by the decomposition of organic (chiefly animal) matter, such as meat, urine, blood, etc. It is also obtained during the process of destructive distillation, which is the heating of non-volatile organic substances in suitable vessels to such an extent that decomposition takes place, the generated volatile products being collected

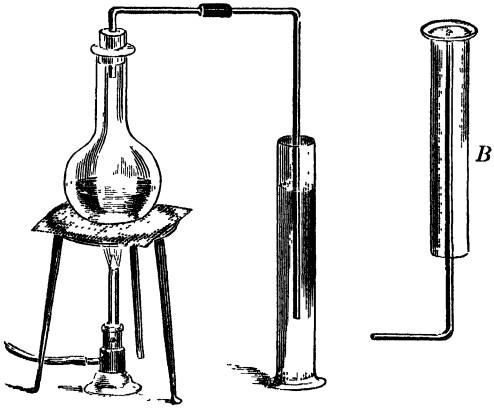
in receivers. The manufacture of illuminating gas is such a process of destructive distillation; coal is heated in retorts, and most of the nitrogen contained in the coal is converted into and liberated as ammonia gas, which is absorbed in water, through which the gas is made to pass. This is the source of nearly all the ammonium salts on the market.

Another method of obtaining ammonia is through decomposition of ammonium salts by the hydroxides of sodium, potassium, or calcium. Usually ammonium chloride is mixed with calcium hydroxide and heated, when calcium chloride, water, and ammonia are formed:

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

*Experiment* 6.—Mix about equal weights (10 grams of each) of ammonium chloride and calcium hydroxide (slaked lime) in a flask of about 200 c.c. capacity, and arranged as in Fig. 10; cover the mixture with water and apply heat.

FIG. 10.




Apparatus for generating ammonia.

As long as any atmospheric air remains in the apparatus, bubbles of it will pass through the water contained in the cylinder; afterward all gas will be readily and completely absorbed by the water. Notice the odor and alkaline reaction on litmus of the ammonia water thus obtained. When the gas is being freely liberated, move the tube upward, as shown in B, and collect the gas by upward displacement in a cylinder or tube, which when filled with gas is held mouth downward into water, which will rapidly rise in the tube by absorption of the gas. Notice that ammonia is not readily combustible, by applying a flame to the gas escaping from the delivery tube.

Ammonia is a colorless gas, of a very pungent odor, an alkaline taste, and a strong alkaline reaction. In pure oxygen it burns, forming water and free nitrogen.

By the mere application of a pressure of seven atmospheres or by intense cold (—40° C., —40° F.), ammonia may be converted into a liquid, which at —80° C. (—112° F.) forms a solid crystalline mass.

Water, at its freezing-point, dissolves as much as 1050 volumes of ammonia gas, and at 15° C. (59° F.) still retains 727 volumes of the gas in solution. This solution contains ammonium hydroxide:

$$NH_3 + H_2O = NH_4OH.$$

Certain experimental evidence indicates that only a small proportion of the gas is combined with water to form hydroxide, most of it being simply dissolved. By boiling, all the ammonia is finally driven out of solution.

It has a strong alkaline action on litmus and has basic properties like those of sodium and potassium hydroxide. It neutralizes acids forming salts, thus:

$$NH_4OH + HCl = NH_4Cl + H_2O.$$

Ammonia gas also unites with acids directly without elimination of water. For example, with hydrochloric acid gas, a dense white cloud of ammonium chloride is formed:

$$NH_3 + HCl = NH_4Cl.$$

In ammonium hydroxide and all the ammonium salts there is an association of the elements nitrogen and hydrogen in the proportion of 1 combining weight of the former to 4 combining weights of the latter, which acts exactly like a metallic element. This grouping is represented by the formula $NH_4$, and is an example of what is called a *radical* in chemistry. Because it resembles the metals in properties, it has been given the name *ammonium* in analogy to the names of metals, such as sodium, potassium, etc. This radical and its analytical reactions will be discussed under Ammonium Compounds.

*Experiment* 7.—To about 20 c.c. of dilute ammonia water, add concentrated hydrochloric acid until litmus-paper is just turned from blue to red by the liquid. Evaporate to dryness in a porcelain dish over a small flame. Note appearance of residue and compare its taste with that of the ammonia water, and dilute hydrochloric acid, and also that of ammonium chloride. What is the residue? This is an example of the formation of a salt by neutralization of an acid by an alkali.

**Ammonia Water** (*Aqua Ammoniæ*) (*Spirit of Hartshorn*).—This is a solution of ammonia gas in water or *ammonium hydroxide* in water. The common ammonia water contains 10 per cent. by weight, equal to 125 volumes of ammonia, and has a specific gravity of 0.958 at 25° C.; the *stronger ammonia water, aqua ammoniæ fortior,* contains 28 per cent., and has a specific gravity of 0.897 at 25° C. Ammonia water has the odor, taste, and reaction which characterize the gas.

**Hydrazine, $N_2H_4$** (*Diamine*), is a compound obtainable from organic compounds by processes which cannot be considered here. It is a colorless gas at summer heat, readily liquefying at a somewhat lower temperature, and solidifying at the freezing-point of water.

Exposed to the air it takes up oxygen, forming water and nitrogen. In its chemical properties hydrazine resembles ammonia, forming a hydrate of the composition $N_2H_4.H_2O$, and salts with acids, such as $N_2H_4.H_2SO_4$ and $N_2H_4(HCl)_2$.

**Hydroxylamine, $NH_2OH$.**—The term amine is used to designate compounds derived from ammonia by replacement of one or more combining weights of hydrogen by other elements or radicals, and it is in keeping with this terminology that the compound under consideration is known as hydroxylamine, while hydrazine is termed diamine.

Hydroxylamine is prepared by the action of nascent hydrogen on nitric acid:

$$HNO_3 + 6H = NH_2OH + 2H_2O.$$

The compound is known only in solution; with acids it forms well-defined salts. The formation of salts may be represented thus:

$$NH_2OH + HNO_3 = NH_3OHNO_3$$
$$NH_2OH + HCl = NH_3OHCl$$

**Triazoic acid, $N_3H$** (*Hydrazoic acid*). This remarkable substance was first isolated in 1890 from organic compounds. It is now obtained also from inorganic material by the action of sodium on ammonia, when a compound of the composition $NH_2Na$ is formed, which by treatment with nitrogen monoxide produces water and sodium triazoate. The latter, by the action of an acid, is converted into a sodium salt and free triazoic acid. The three steps of the process may be represented thus:

$$NH_3 + Na = NH_2Na + H$$
$$NH_2Na + N_2O = NaN_3 + H_2O$$
$$2NaN_3 + H_2SO_4 = Na_2SO_4 + 2HN_3.$$

Triazoic acid is a colorless gas, possessing a disagreeable odor. It is soluble in water, and this solution can be distilled, but the operation is dangerous, as the compound is apt to decompose with explosive violence. When inhaled it acts as a poison, producing violent headache.

While the three compounds of hydrogen with nitrogen considered above are of a basic nature, triazoic acid has decidedly acid properties. In fact, it is a stronger acid than acetic acid, and resembles hydrochloric acid in precipitating soluble silver and mercurous salts.

## Compounds of Nitrogen and Oxygen.

Five distinct compounds of nitrogen and oxygen are known. They are named and constituted as follows:

| | Composition. | | | |
|---|---|---|---|---|
| | By weight. | | By volume. | |
| | N | O | N | O |
| Nitrogen monoxide, $N_2O$ . . . | 28 | 16 | 2 | 1 |
| Nitric oxide, NO . . . . . | 28 | 32 | 2 | 2 |
| Nitrogen trioxide, $N_2O_3$ . . . | 28 | 48 | 2 | 3 |
| Nitrogen tetroxide, $N_2O_4 = 2(NO_2)$ . | 28 | 64 | 2 | 4 |
| Nitrogen pentoxide, $N_2O_5$ . . . | 28 | 80 | 2 | 5 |

The trioxide and pentoxide are called also acid anhydrides, or nitrous and nitric anhydride respectively, because they combine with water to give nitrous and nitric acid. Conversely, when the acids are deprived of the elements of water, the respective oxides of nitrogen are obtained. The monoxide corresponds to hyponitrous acid, $H_2N_2O_2$, but does not yield the acid with water. It is, hence, not an anhydride. All of the oxides are obtained from nitric acid, directly or indirectly. The last one is formed by abstraction of water from nitric acid, the others involve reduction of nitric acid or, in reality, of nitrogen pentoxide.

When electric sparks pass through atmospheric air some ozone is generated which oxidizes nitrogen, forming first the lower and then also the higher oxides; these combine with water to form nitrous and nitric acid, which acids are taken up by the ammonia present in the air, forming the respective ammonium salts.

**Nitrogen Monoxide** (*Nitrogenii Monoxidum*) $N_2O = 44.02$ (sometimes called *Nitrous Oxide*; also *Laughing Gas*). This compound was discovered by Priestley in 1776; its anæsthetic properties were first noticed in 1800 by Sir Humphry Davy, and it was first used in dentistry by Dr. Horace Wells, a dentist of Hartford, Conn., in 1844. It may be easily obtained by heating ammonium nitrate in a flask at a temperature not exceeding 250° C. (482° F.), when the salt is decomposed into nitrogen monoxide and water:

$$NH_4NO_3 = 2H_2O + N_2O.$$

When nitrous oxide is prepared for use as an anæsthetic it should be passed through two wash-bottles containing caustic soda and ferrous sulphate respectively; these agents will retain any impurities that may be formed during the decomposition, especially from an impure salt.

Ammonium nitrate to be used for generating pure nitrous oxide should be completely volatilized when heated on platinum foil; its solution in water should not be rendered turbid by silver nitrate, as this would indicate the presence of chlorides. These latter are objectionable because gaseous compounds of chlorine with the oxides of nitrogen may be formed. If the gas is prepared as directed above, it can be used with safety.

Impurities found in the gas when not properly made are air, nitric oxide, chlorine, and chloronitrous oxide.

If the gas is stored over water, considerable loss is experienced on account of the solubility of nitrous oxide in cold water. This loss can be diminished by using hot water or a concentrated solution of common salt in water, both of which liquids dissolve less of the gas.

*Experiment* 8.—Use apparatus as represented in Fig. 8. Place in the dry flask about 10 grams of ammonium nitrate, apply heat, collect the gas in cylinders over water, and verify by experiments and observations the correctness of the statements below regarding the physical and chemical properties of nitrogen monoxide.

Nitrogen monoxide is a colorless, almost inodorous gas, of distinctly sweet taste. It supports combustion almost as energetically as oxygen, but differs from this element by its solubility in cold water, which absorbs nearly its own volume. Under a pressure of about 50 atmospheres it condenses to a colorless liquid, the boiling-point of which is at about —90° C. (−130° F.) and the freezing-point at —102° C. (—151.6° F.). The gas does not act on potassium permanganate solution.

When inhaled it causes exhilaration, intoxication, anæsthesia, and, finally, asphyxia. The gas is used in dentistry as an anæsthetic, the liquefied compound being sold for this purpose in wrought-iron cylinders. There are two sizes of these cylinders: the smaller contain about one and a half pounds of the liquid, equal to 100 gallons of gas; the larger size contains about five times that quantity.

**Nitric Oxide, NO.**—This is a colorless gas which is formed generally when nitric acid acts upon metals or upon substances which deoxidize it. It is capable of combining directly with oxygen, thereby forming *nitrogen tetroxide*, called *nitrogen peroxide*, $NO_2$ or $N_2O_4$, which is a gas of deep red color and poisonous properties. *Nitrogen trioxide*, $N_2O_3$, exists as an indigo-blue liquid at temperatures below —21° C. (—6° F.); above this temperature it decomposes into NO and $NO_2$.

*Experiment* 9.—Use apparatus as shown in Fig. 9. Put about 20 grams of copper or brass turnings into the flask and pour through the funnel tube a mixture of 30 c.c. concentrated nitric acid and 50 c.c. water. Apply gentle heat and collect several bottles of gas. Note that the gas in the flask is at first colored. Why? Remove the cover from a bottle of the gas, and explain the result. Insert a stick with a flame into another bottle of the gas, and compare with the action of nitrous oxide. If copper is used, filter the solution after all copper is dissolved, and evaporate to get blue crystals of copper nitrate. For explanation of the reaction, see below, under Nitric Acid.

It was stated above that nitrogen monoxide supports combustion about as well as oxygen. It is decomposed by the heat of a spark on a splint of wood into nitrogen and oxygen, thus: $N_2O = 2N + O$. The liberated oxygen supports the combustion of the wood. Because of this close resemblance between nitrogen monoxide and oxygen, it becomes desirable to have a method of distinguishing between these gases and to detect the presence of oxygen in the other. There are a number of methods, one of which is easy to carry out and depends on the property that nitric oxide possesses of combining with oxygen to form a reddish gas. Nitrogen monoxide does not possess this property. Therefore, to test for the presence of oxygen in nitrogen monoxide, a cylinder is filled with the gas, covered with a glass plate, mouth up, over which is brought a like cylinder filled with nitric oxide gas, covered with a glass plate, mouth down. The glass plates are quickly drawn out, bringing the mouths

together. If oxygen is present, it will be shown by the reddish color developed as the gases diffuse into one another.

**Hyponitrous Acid, HNO,** or possibly $H_2N_2O_2$.—Hyponitrous acid is a very unstable white, flaky solid. Neither the acid, nor its salts, the hyponitrites, are of practical interest.

**Nitrous acid, $HNO_2$,** has not been obtained in a pure state, but exists in solution. Several of its salts, the nitrites, are well known and are used analytically and otherwise. Nitrous acid very readily breaks down into water and its anhydride, $N_2O_3$, which escapes as brown fumes from the solution. Hence, the salts of the acid are decomposed by nearly all other acids. Nitrous acid acts as an oxidizing agent toward some substances, being itself reduced to lower oxides, and as a reducing agent toward others, being then oxidized to nitric acid. A solution of nitrous acid in water or other acids has a pale blue color.

**Tests for Nitrous Acid and Nitrites.**

(Use about a 5 per cent. solution of sodium or potassium nitrite.)

1. To 5 c.c. of the solution, add a little strong sulphuric acid. Note the colored fumes and effervescence and the bluish color of the liquid.

2. To the same amount of the solution, add some acidified solution of potassium permanganate, which is decolorized at once. What becomes of the nitrite?

3. Carry out the directions of Test 1, under Hydrogen Dioxide, using a few drops of the nitrite solution in place of the hydrogen dioxide. Note that the blue color is not developed until an acid is added. Only free nitrous acid acts on potassium iodide:

$$HNO_2 + HI = H_2O + NO + I.$$

This is a very delicate test, but not decisive alone.

4. Dilute 1 drop of the nitrite solution in half a beakerful of water, add 1 c.c. of meta-phenylene-diamine reagent (see Nitrous Acid, under Water Analysis, at end of chapter 38). A yellow to dark brown color is produced, according to the proportion of nitrite. The test is used only for very small amounts of nitrite.

Test 1 is usually sufficient to recognize a nitrite.

**Nitric Acid** (*Acidum Nitricum*) $HNO_3$; $NO_2OH = 63.02$ (*Aqua fortis*). Nitrogen pentoxide, $N_2O_5$, a white, solid, unstable compound, is of scientific interest only. When brought in contact with water it readily combines with it, forming nitric acid:

$$N_2O_5 + H_2O = 2HNO_3.$$

The usual method for obtaining nitric acid is the decomposition of sodium nitrate by sulphuric acid:

$$NaNO_3 + H_2SO_4 = HNO_3 + \underset{\text{Sodium bisulphate.}}{HNaSO_4};$$

or

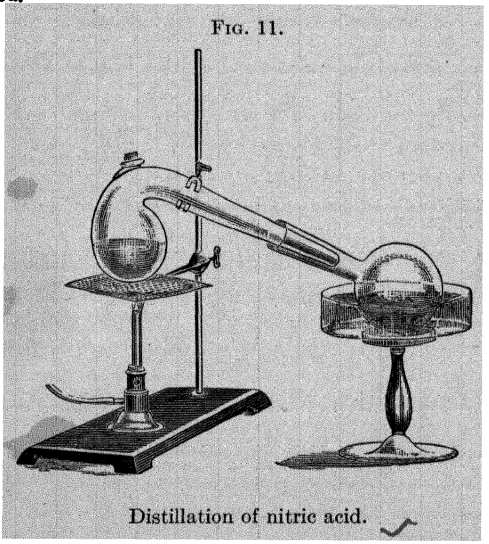
$$2NaNO_3 + H_2SO_4 = 2HNO_3 + \underset{\text{Sodium sulphate.}}{Na_2SO_4}.$$

At the present time nitric acid is produced also from the atmosphere by causing the nitrogen and oxygen to unite under the influence of electric discharges. The nitrogen tetroxide formed, when dissolved in water, gives nitric acid and nitric oxide:

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

The NO unites with oxygen to give $NO_2$, which is again dissolved. The commercial success of this method depends upon the cost of electric power. It is interesting as offering a source of nitrates when the native supply shall have been exhausted.

FIG. 11.



Distillation of nitric acid.

*Experiment* 10.—Prepare an apparatus as shown in Fig. 11. Heat in a retort of about 250 c.c. capacity a mixture of about 50 grams of potassium nitrate and nearly the same weight of sulphuric acid. Nitric acid is evolved and distils over into the receiver, which is to be kept cool during the operation by pouring cold water upon it or by surrounding it with pieces of ice. Examine the properties of nitric acid thus made, and use it for the tests mentioned below. How much pure nitric acid can be obtained from 50 grams of potassium nitrate? Weigh the acid which you obtain in the experiment and compare this weight with the theoretical quantity.

Nitric acid is an almost colorless, fuming, corrosive liquid, of a peculiar, somewhat suffocating odor, and a strongly acid reaction.

When exposed to sunlight it assumes a yellow or yellowish-red color in consequence of its partial decomposition into nitrogen tetroxide, water, and oxygen.

*Common nitric acid*, of a specific gravity 1.403 at 25° C., is composed of 68 per cent. of $HNO_3$ and 32 per cent. of water. The usual diluted nitric acid is made by mixing ten parts by weight of the common acid with fifty-eight parts of water, and contains 10 per cent. of absolute nitric acid; it has a specific gravity of 1.054 at 25° C.

*Fuming nitric acid* has a brown-red color, due to nitrogen tetroxide, and emits vapors of the same color. Specific gravity 1.45 to 1.50.

Nitric acid is completely volatilized by heat; it stains animal matter distinctly yellow and destroys the tissue; it is a monobasic acid, forming salts called nitrates. These salts are all soluble in water, for which reason nitric acid cannot be precipitated by any reagent. Nitric acid is a strong oxidizing agent, this means that it is capable of giving off part of its oxygen to substances having affinity for it.

Nitric acid of 68 per cent. has a constant boiling-point and distils unchanged. A more concentrated acid decomposes in part when distilled, $2HNO_3 = 2NO_2 + H_2O + O$, while a more dilute acid gives off water at first. In either case, repeated distillation gives a 68 per cent. acid.

The action of nitric acid upon such metals as copper, silver, and many others involves two changes, viz.: displacement of the hydrogen of the acid by the metal:

$$Cu + 2HNO_3 = Cu(NO_3)_2 + 2H;$$

and the deoxidation of another portion of nitric acid by the liberated hydrogen while yet in the nascent state. Thus:

$$HNO_3 + 3H = 2H_2O + NO.$$

The liberated nitrogen dioxide, which is colorless, readily absorbs oxygen from the air, forming red vapors of nitrogen tetroxide.

Another explanation of the chemical action of nitric acid on metals is based on our knowledge of the fact that nitric acid readily gives up part of its oxygen to any substance having affinity for it. Therefore, it may be assumed that the first action of the acid on metals is their conversion into oxides, which are immediately changed into nitrates, thus:

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

### Tests for Nitric Acid or Nitrates.

(Potassium nitrate, $KNO_3$, may be used as a nitrate.)

1. Fairly strong nitric acid with copper turnings gives copious red fumes. Rather dilute acid, however, has not a very marked action, even when heated, but the action is increased by the addition of some concentrated sulphuric acid. A nitrate, dry or in solution, has no

action on copper, but addition of concentrated sulphuric acid (to set free the nitric acid) causes evolution of red fumes.

2. The solution of a nitrate, to which a few small pieces of ferrous sulphate have been added, will show a reddish-purple or black coloration upon pouring a few drops of strong sulphuric acid down the side of the test-tube, so that it may form a layer at the bottom of the tube. The black color is due to the formation of an unstable compound of the composition $2FeSO_4.NO$. Free nitric acid also responds to this test, which is delicate and very often used.

3. Nitrates deflagrate when heated on charcoal by means of the blow-pipe flame. The high temperature causes the nitrate to decompose and liberate oxygen, which unites with the charcoal energetically. Such action is called *deflagration*. Other oxidizing substances act like nitrates.

4. When a few drops of a solution of 0.1 gram of diphenylamine in 50 c.c. of 10 per cent. sulphuric acid are added to a very dilute solution of a nitrate, and then some concentrated sulphuric acid is carefully poured down the side of the test-tube, a deep blue color is produced at the line of contact.

A similar reaction is also produced by hypochlorites, chlorates, chromium trioxide, ferric salts, and similar oxidizing agents.

When the test is made with a similar solution of pyrogallic acid instead of the diphenylamine solution, a deep brown color is produced.

The tests with diphenylamine and pyrogallic acid show 1 part of nitric acid in three and ten million parts of water respectively, and are used chiefly to detect traces of nitric acid in drinking-water. As sulphuric acid may contain nitric acid, the tests should also be made with the sulphuric acid alone in order to prove its purity.

Tests 1 and 2 are sufficient to identify nitric acid or its salts. Nitrites also respond to these tests, but they give red fumes by merely adding a dilute acid, thus differing from nitrates.

**Poisonous properties; antidotes.** Strong nitric acid is a corrosive, violent poison. It first stains the tissues with which it comes in contact a bright-yellow color, and then corrodes them.

As an antidote in cases of poisoning by nitric acid a solution of sodium carbonate, or a mixture of magnesia and water, milk of lime, or other alkalies well diluted may be administered with the view of neutralizing the acid.

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QUESTIONS.—State the physical and chemical properties of nitrogen. Mention the principal constituents of atmospheric air and the quantity in which they are present. By what processes can the four chief constituents of atmospheric air be determined? Mention some decompositions by which ammonia is generated. Explain the process of making ammonia water. State the physical and chemical properties of ammonia gas and ammonia water. How is nitrogen monoxide obtained, and what are its properties? Describe the process for making nitric acid, and give symbols for decomposition. How does nitric acid act on animal matter, and what are its properties generally? Give tests and antidote for nitric acid.

## 10. ATOMIC THEORY. VALENCE. RADICALS. CONSTITUTIONAL OR GRAPHIC FORMULAS. NOMENCLATURE.

**Atomic Theory.**—One of the objects of men of science, besides experimenting and observing facts and laws, is to determine causes, that is, to furnish an answer to the question, Why do things take place as they do? If the senses, even when fortified with delicate instruments, are not sufficiently refined to perceive the causes, the philosopher, with the aid of his reasoning faculties, tries to imagine a cause which will account in the most satisfactory manner for what he observes. Such an imagined cause is called an hypothesis or theory. For example, to account for the uniform behavior of all gases as summed up in the Laws of Boyle, Charles, and Avogadro, it was imagined that the nature of gases is that they are made up of exceedingly minute particles in motion, acting as elastic bits of matter and with practically no cohesion between them. This is known as the kinetic-molecular theory of gases, and from it all the behaviors of gases can be deduced mathematically. We may never be able to actually see a gas particle, nevertheless we are willing to accept that it exists as long as the hypothesis accounts satisfactorily for what is observed.

There must be some reason for the chemical behavior of the elements as set forth in the Laws of Definite and Multiple Proportions and the fact that the elements unite in proportions represented in the system of figures called combining weights. This cause must lie in the constitution or physical make-up of matter. Reflection upon the constitution of matter is not peculiar to modern science, for the ancients had their conceptions, and some (Democritus, Lucretius) advocated a theory of atoms. But the views of the ancients were speculative and had no physical basis resting upon experiments, and therefore were of no service to science. It was not until 1804 that a theory or conception of matter was proposed by John Dalton, of England, that had the merits of being capable of being put to tests and from which deductions could be made that lent themselves to experimental verification. Dalton's *atomic theory* holds that (1) elements are made up of inconceivably small particles which are indivisible in chemical actions and called atoms (from the Greek ἄτομος, uncut, or not yet divided); (2) the atoms not only have definite weights, but the atoms of any one element have the same weight, which is different from the weight of the atoms of some other element; (3) when the elements unite chemically, the action takes place between the atoms. If we assume this theory to be correct and argue from it as a basis, we can deduce the laws of definite proportions and multiple proportions. Let us suppose that two certain elements, A and B, unite, and the union is of the simplest kind possible, that is, in each instance an atom of A is united with an atom of B. No matter what the mass of the resulting product may be, whether an ounce, pound,

or ton, the whole chemical action is simply a repetition throughout the mass of what might be called the unit action, that is, the union of one atom of A with one atom of B. Hence the ratio between the weights of the elements in the resulting compound, that is, its composition, must be the same as the ratio between the weights of the atom of A and the atom of B. But the weights of these atoms are definite and constant, hence the composition of the compound must be constant, or, in other words, the compound is an illustration of the law of definite proportions. By a simple extension of the above argument, the law of multiple proportions may be deduced. The theory also accounts for the fact that if two elements are brought together in other than certain proportions, say 56 parts of iron to 32 parts of sulphur, after union has taken place, part of the one or the other element is found uncombined. It is easy to see, too, that if the theory is correct, the elements ought to combine according to a system of figures such as were discussed earlier as combining weights, for these weights are bound to be proportional to the weights of atoms, which are definite. The atomic theory has been found in accord with the facts of chemistry for a century or more, and we are justified in accepting it, although we cannot prove absolutely the existence of atoms.

**Atomic Weight.**—If atoms exist, they must have weight, since they are concrete masses of matter, and all matter is attracted by the earth. But, of course, it is impossible to weigh single atoms, and we have no knowledge of the absolute weight of an atom. It is possible, however, to determine the *relative* weights of the atoms, that is, how many times heavier one atom is than another. How this is done will be briefly indicated in a later chapter. In any process of weighing, we adopt a unit with which to make a comparison. For example, in commerce we have a mass of iron which is called a pound, and we say a body weighs so many times the mass of iron, or so many pounds. We proceed similarly in the case of atomic weights. We use the weight of an atom of one element as the unit, and compare the weight of the atoms of the other elements with it. The thing to decide is, Which atom shall be chosen as the unit weight? As was said in discussing combining weights, hydrogen is the lightest known substance, and it unites with other elements in the smallest proportions, hence its atom may be chosen as the unit weight for measuring the weights of atoms of the other elements. Formerly this was done, and the figures that were assigned to the other elements as atomic weights signified how many times heavier those atoms are than the atom of hydrogen. Thus the atomic weight of oxygen is 15.88 on the hydrogen basis, that is, the matter in an atom of oxygen is 15.88 times as heavy as that in an atom of hydrogen.

Since atomic weights are simply a series of figures or ratios showing the relative heaviness of atoms, any series of figures in which the ratios are maintained may be adopted. Thus, we may choose a

series of figures in which the atomic weight of oxygen is 16, and on this scale the atomic weight of hydrogen is 1.008. The ratio 1.008:16 is the same as the ratio 1: 15.88, or, in other words, an atom of oxygen is represented to be 15.88 times heavier than an atom of hydrogen, whatever may be the scale on which the atomic weight ratios are expressed. Chemists prefer the scale oxygen = 16 because then many of the atomic weights are either whole numbers or so close to them that the small decimals may be omitted in ordinary calculations without any appreciable effect in the results, thus greatly curtailing the work in calculations. Another reason for adopting the oxygen = 16 system of atomic weights is the fact that oxygen unites readily with nearly all elements, whereas hydrogen unites with relatively few of them, and atomic weights are established by very careful quantitative analysis of the compounds of elements, and these usually are oxygen compounds. In this way a direct weight relationship with oxygen is obtained.

On the page preceding the Index is a table of the elements, with symbols and atomic weights on the scale oxygen = 16. These weights are what have been hitherto designated *combining* or *chemical unit weights* (see Chapter IV).

**Atoms and Molecules.**—In Section I, on Physics, we learned that all matter is made up of exceedingly minute particles, called molecules, and, from a chemical study of matter, we are led to believe that there is another kind of small particle, the atom. The atoms unite in chemical action and form the larger masses called molecules. The molecules of compounds consist of atoms of different kinds. The elements also, like any kind of matter, consist of molecules, which evidently must be made up of atoms of the same kind. There are a few exceptional elements of which the molecule consists of only one atom, that is, the molecule and atom of these are identical. The atoms of an element have the power of uniting not only with atoms of a different kind, but also with themselves, to form molecules of the element. The present conception as to atoms may be summed up in the following definition: "Atoms are the indivisible constituents of molecules. They are the smallest particles of the elements that take part in chemical reactions, and are, for the greater part, incapable of existence in the free state, being generally found in combination with other atoms, either of the same kind or of different kinds" (Remsen).

We may define molecules as the smallest particles of matter that can exist in the free state and still retain all the properties of the substance to which they belong. If we divide the molecule, we destroy the properties of the substance as we know it in the free state.

Taking the law of combination by volume and Avogadro's Law as a basis of argument, we can prove directly in the case of some of the elementary gases that their molecules consist of more than one atom. One volume of hydrogen combines with one volume of chlorine to give two volumes of hydrochloric acid

gas. According to Avogadro's Law the volume of hydrogen and chlorine contain the same number of molecules, and the volumes of product formed must contain twice as many molecules as does the volume of hydrogen or chlorine. Hence the molecules of hydrogen and chlorine must be divided to form part of a product consisting of twice as many molecules, since each molecule of hydrochloric acid contains some hydrogen and some chlorine. But if the molecules of hydrogen and chlorine can be divided, they must consist of more than one atom. Everything that is known about hydrochloric acid justifies the assumption that its molecule contains one atom each of hydrogen and chlorine. If this is true, it follows then that the molecule of hydrogen and of chlorine contains two atoms. The same kind of argument in the case of the union of hydrogen and oxygen to form water-vapor, leads to the conclusion that the molecule of oxygen contains at least two atoms. In fact, from various experiments and processes of reasoning, it has been established that the molecule of nearly all the elements, in the gaseous state, consists of two atoms.

**Formulas and Equations in the Light of the Atomic Theory.**—The atomic theory furnishes a mechanical basis for picturing what takes place when elements unite or when one compound acts on another, with formation of new substances. Our insight into chemical transformations is made much clearer by it, and descriptions of them are made much more precise and intelligible.

The symbols of elements and formulas of compounds that have been used in previous chapters simply indicate the kinds of substances and the relative proportions by weight which were involved. Adopting the atomic theory, a symbol now stands for an atom of the element and a quantity by weight represented by its atomic weight. Thus O represents one atom and 16 parts by weight of oxygen; Na stands for one atom and 23 parts by weight of sodium.

In terms of the atomic theory the molecule is the smallest physical unit that can exist and retain the properties of the substance to which it belongs, and also is the unit of matter concerned in the first instance in chemical changes. The molecules are made up of atoms which of course are the ultimate seat of chemical combination. It is possible for the chemist to determine how many atoms are united in the molecule of the various substances, or, in other words, to determine the actual size of molecules in terms of atoms. Formulas which express the actual size of molecules are called *molecular formulas*, and the sum of the atomic weights of all the atoms composing the molecule is called the *molecular weight*. The ratio between the molecular weight of any substance and the atomic weight of hydrogen or oxygen indicates how many times heavier such molecule is than the atomic weight of hydrogen or oxygen. The molecular weight represents the relative proportion by weight which is concerned when the substance undergoes chemical change. A formula primarily represents the composition of a molecule, but as any quantity of a substance is simply the sum of a great multitude of molecules all alike, the formula, in a broader sense, stands

for the substance itself. Thus we say HgO is mercuric oxide, although it shows the composition of a molecule of the oxide, namely, that it consists of one atom of mercury and one atom of oxygen.

The unit of chemical change is the molecule, and chemical equations in keeping with the atomic theory are intended to show the action taking place between molecules. Thus, the action between hydrochloric acid and silver nitrate is written, $HCl + AgNO_3 = AgCl + HNO_3$, which means that one molecule of hydrochloric acid is required for one of silver nitrate, producing one molecule each of silver chloride and nitric acid. When more than one molecule is represented, a numeral is placed before the symbol. The symbols 2NaCl and $Na_2Cl_2$ represent the same number of atoms and the same proportions by weight of the elements, but they are quite different, for NaCl is the actual size of the molecule, and 2NaCl stands for two molecules, while $Na_2Cl_2$ represents a molecule double the size of that of sodium chloride, NaCl, as actually known. Often in writing equations, for convenience we represent elements in the atomic state, while in reality they exist in the molecular state. The equations are true, however, as far as proportions are concerned. For example, we represent the union of hydrogen and oxygen to form water thus, $H_2 + O = H_2O$, but to be in keeping with the fact that molecules of hydrogen and oxygen are really involved, we should write $2H_2 + O_2 = 2H_2O$.

**Valence.**—If we accept the atomic theory as correct and grant that it is possible to establish the molecular formulas of compounds, then upon inspection of these formulas we soon become aware of a rather interesting property inherent in the atoms of the elements. In the first place we observe that the compounds formed by any two or more elements are restricted in number. For example, potassium and iodine give only one compound, mercury and iodine only two, zinc and oxygen only one, iron and chlorine only two, etc. Secondly, we observe that the atoms of the different elements have not all the same capacity for holding other atoms in combination to form molecules. When one element unites with another, or replaces another in a compound, the quantities involved are said to be equivalent to each other. Formerly it was believed that all elements were equivalent atom for atom; accordingly, atomic weights were frequently designated as equivalent weights.

This view, however, is not correct, as it is found that one atom of one element frequently displaces two or more atoms of another element. This fact, as well as other considerations, has led to the assumption of the quantivalence of atoms. This property will be understood best by selecting for consideration a few compounds of different elements with hydrogen.

| I. | II | III | IV |
|---|---|---|---|
| HCl | $H_2O$ | $H_3N$ | $H_4C$ |
| HBr | $H_2S$ | $H_3As$ | $H_4Si$ |
| HI | $H_2Se$ | $H_3P$ | |

We see here that Cl, Br, and I combine with H in the proportion of atom for atom; O, S, Se combine with H in the proportion of 2 atoms of hydrogen for 1 atom of the other element; N, As, P combine with 3; C and Si with 4 atoms of hydrogen.

Moreover, it has been found that the compounds mentioned in column I. are the only ones which can be formed by the union of the elements Cl, Br, and I with H. They invariably combine in this proportion only. Other elements show a similar behavior. For instance, the metal sodium combines with chlorine or bromine in one proportion only, forming the compound NaCl or NaBr.

Looking at columns II., III., and IV., we see that the elements mentioned there combine with 2, 3, and 4 atoms of hydrogen, respectively. It is evident, therefore, that there must be some peculiarity in the power of attraction of different elements toward other elements, and to this property of the atoms of elements of holding in combination one, two, three, four, or more atoms of other elements the name *atomicity, quantivalence,* or simply *valence,* has been given.

According to this theory of the valence of atoms, we distinguish univalent, bivalent, trivalent, quadrivalent, quinquivalent, sexivalent, and septivalent elements. All elements which combine with hydrogen in the proportion of one atom to one atom are univalent, as, for instance, Cl, Br, I, F, and all elements which combine with these in but one proportion, that is, atom with atom, bear the same valence, or are also univalent, as, for instance, Na, K, Ag, etc.

Those elements which combine with hydrogen or other univalent elements in the proportion of one atom to two atoms are bivalent, such as O, S, Se.

Trivalent and quadrivalent elements are those the atoms of which combine with 3 or 4 atoms of hydrogen, respectively. Figuratively speaking, we may say that the atoms of univalent elements have but one, those of bivalent elements two, of trivalent elements three, of quadrivalent elements four *bonds* or points of attraction, by means of which they may attach themselves to other atoms.

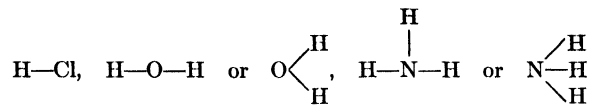
To indicate the valence of the elements frequently dots or numbers are placed above the chemical symbols, thus $H^{I}$, $O^{II}$, $N^{III}$, $C^{IIII}$ or $C^{IV}$

The bonds are often graphically represented by lines, thus:

$$H\text{—},\quad \text{—}O\text{—},\quad \text{—}\overset{|}{N}\text{—},\quad \text{—}\overset{|}{\underset{|}{C}}\text{—}$$

It is needless to say that such representations are merely symbolical, and express the view that atoms have a definite power to combine with others.

When atoms combine with one another the bonds are said to be satisfied, which is graphically expressed thus:



While the valence of some elements is invariably the same under all circumstances, other elements show a different valence (this means a different combining power for other atoms) under different conditions. For instance: Phosphorus combines both with 3 and 5 atoms of chlorine, forming the compounds $PCl_3$ and $PCl_5$. As chlorine is a univalent element, we have to assume that phosphorus has in one case 3, in another case 5 points of attraction. Many similar instances are known, and will be spoken of later.

An explanation which is sometimes given in regard to the variability of the valence of atoms is the assumption that sometimes one or more of the bonds of an atom unite with other bonds of the same atom. If, for instance, in the quinquivalent phosphorus atom two bonds unite with one another a trivalent atom will remain.

It is noticed that the valence of atoms in nearly all cases increases or diminishes by two, which could not be otherwise, if the explanation given be correct. Thus chlorine, the valence of which generally is I., may also have a valence equal to III., V., or VII., while sulphur shows a valence either of II., IV., or VI. Atoms whose valence is even, as in the case of sulphur, are called *artiads;* those whose valence is expressed in uneven numbers, as chlorine and phosphorus, are called *perissads.*

While it is now being assumed that most of the elements possess more than one valence, in consequence of the assumed power of bonds in the same atom to saturate one another, in this book will be mentioned chiefly that valence which the element seems to possess predominantly.

The doctrine of the valence of atoms has modified our views of the equivalence of atoms. We now say that all atoms of a like valence are equivalent to each other. The atoms of each univalent element are equivalent to each other, and so of the atoms of any other valence, but two atoms of a univalent element are equivalent to one atom of a bivalent element, or two atoms of a bivalent element to one atom of a quadrivalent element, etc.

The student should be careful not to confuse valence and affinity, as they involve entirely different conceptions. Affinity is the term used to refer to the force or energy with which atoms unite, while valence determines the complexity of the combinations of atoms. Thus, the affinity or energy of union between hydrogen and chlorine is great, but the valence of the elements is small, each having a valence of one. The affinity between carbon and hydrogen is much weaker than that between chlorine and hydrogen, although the valence of carbon is four.

It is not necessary for the student to memorize the valence of the elements, as he can often easily reason out the valence of an element by recalling the formula of a compound that it forms with hydrogen

or chlorine. Thus, if he can hold in mind the formula for calcium chloride, $CaCl_2$, he can see at once that an atom of calcium is equivalent to two atoms of the univalent chlorine, and that, therefore, the atom of calcium must be bivalent. He then can use this information in constructing the formulas of other compounds of calcium. For example, if he wished to write the formula for calcium carbonate and learned that it is derived from carbonic acid, $H_2CO_3$, by replacement of the hydrogen in the molecule by calcium, he would be justified in writing $CaCO_3$, on the argument that an atom of a bivalent element is equivalent to and can replace two atoms of a univalent element.

**Radicals and Valence.**—In the chapter on Nitrogen, under Ammonium Hydroxide, it was pointed out that often groups of elements exist in compounds, which remain intact and are transferable like a single element from one compound to another in chemical reactions. These groups are atomic combinations which have no separate existence, but exist only in combination with other atoms, although they behave in chemical interchanges like single atoms. Such a group is known as a *residue*, *radical*, or *compound radical*. For example, the molecule of water consists of two atoms of hydrogen united to one atom of oxygen, H–O–H. When metallic sodium acts on water, some hydrogen is given off and a substance is left having the formula, NaOH, and known in chemistry as sodium hydroxide (caustic soda). In this an atom of sodium is combined with the residue of the water molecule (OH), which is called *hydroxyl*. This residue or radical can be transferred from sodium hydroxide so as to form new compounds containing it. Thus when a solution of sodium hydroxide is added to a solution of iron chloride, a reddish-brown gelatinous insoluble substance is precipitated, which upon analysis is found to have the composition $Fe(OH)_3$, and is called iron hydroxide, $3NaOH + FeCl_3 = Fe(OH)_3 + 3NaCl$. There is a large class of substances in chemistry called metallic hydroxides or *bases*, each member of which contains the hydroxyl radical in combination with a metal.

To show the indentity or molecular size of the radicals, they are written in brackets, and the number of radicals is indicated by a figure outside the bracket. Thus, we write $Fe(OH)_3$ instead of $FeO_3H_3$.

A radical, like an atom, has valence, which can be determined by noting the valence of the other constituent with which it is in combination. Thus, the radical (OH) is united with one atom of univalent hydrogen in water, or with one atom of univalent sodium in sodium hydroxide, hence we conclude that (OH) is univalent. Some radicals are bivalent, others trivalent.

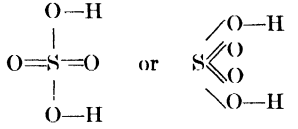
The formula for nitric acid is $HNO_3$, and the hydrogen in the molecule is easily replaceable by metals, giving rise to nitrates which belong to the class of substances known as salts. In every

nitrate there is the same group of atoms ($NO_3$), which is called the radical of nitric acid, and evidently is univalent, as shown by the fact that it is united with one atom of univalent hydrogen in nitric acid. These facts will enable the student to construct the formula of any nitrate, if he knows the valence of the element that replaces hydrogen, or, in other words, that unites with the ($NO_3$) radical. Thus $K'(NO_3)'$, $Ca''(NO_3)_2'$, $Fe'''(NO_3)_3'$, would be the formulas of potassium, calcium, and ferric nitrate, respectively. Similarly, all other acid molecules have a part or radical that remains unchanged in interactions and has a definite valence.

**Constitutional or Graphic Formulas and Valence.**—Though it is impossible to examine the structure of a molecule by means of a microscope, yet we may obtain some information of the atomic arrangement within the molecules by a study of the formation and decomposition which they undergo under different conditions.

Such investigations lead to the conclusion that molecules are not merely clusters of atoms held together irregularly, but that the atoms are arranged systematically and occupy a definite position within the molecules of each individual substance.

In order to represent figuratively our views regarding the atomic arrangement the so-called constitutional or graphic formulas are often used. Thus, while sulphuric acid is represented by the molecular formula $H_2SO_4$, we may assign to it the graphic formula $SO_2''.(OH)_2$, which indicates that sulphuric acid is made up of the bivalent radical $SO_2$ and of two univalent radicals OH. In order to give a yet fuller expression of our views regarding the linkage of the atoms, sulphuric acid may be graphically represented thus:




In these formulas we show that sulphur exerts the valence of six, that four of its affinities are saturated by oxygen, while the two remaining are attached to two oxygen atoms, the unsaturated affinities of which are satisfied by hydrogen.

Compounds consisting of but two elements are called *binary compounds*, and in these there is, as a rule, not much difficulty in recognizing the valence of the elements by an inspection of the formulas. But when three or more elements are united, it is impossible to tell the valence of all the elements by an inspection of the molecular formula. Unless we know the internal structure of such molecules, which involves the distribution of atoms according to their valence, we are left in doubt in regard to the valence of some of the elements in the compound. Thus, from the molecular formula of sulphuric acid, $H_2SO_4$, it would be impossible to tell what the valence of sulphur is in the molecule, whereas in the graphic formula given above, its valence is six.

It is sometimes rather difficult to determine experimentally the structural formulas of compounds, and such formulas are often used without sufficient basis of facts. In the case of the oxides of nitrogen, it is impossible to say what the valence of nitrogen is in some of them, namely, $N_2O$ and $NO_2$, because there is no way of learning by experiment how the atoms are linked together. In nitric oxide, NO, the valence of nitrogen is apparently two, and very probably three and five in the trioxide and pentoxide, respectively,

$$O=N-O-N=O \text{ and } \begin{matrix} O \\ O \end{matrix}\!\!\rangle N-O-N\langle\!\!\begin{matrix} O \\ O \end{matrix}$$

It is known that the most prevalent valence of nitrogen is three, as in ammonia, $NH_3$, or five, as in ammonium chloride, and nitric acid,

$$\begin{matrix} H \\ H \\ H \end{matrix}\!\!\rangle N\langle\!\!\begin{matrix} H \\ Cl \end{matrix} \text{ and } H-O-N\langle\!\!\begin{matrix} O \\ O \end{matrix}$$

**Nomenclature.**—The chemical nomenclature of compound substances has undergone considerable changes within the last twenty-five years. These changes were made in conformity with our present views of the constitution of the compounds.

Whenever the syllable *ide* is used to replace the ending of a non-metallic element it designates that this element has entered into combination with another element or with a radical. Thus, we speak of ox*ides*, sulph*ides*, carb*ides*, chlor*ides*, etc., when referring to compounds formed by the union of oxygen, sulphur, carbon, or chlorine with another element or with a radical.

When two elements combine in one proportion only, little difficulty is experienced in the formation of a name, as, for instance, in iodide of potassium or potassium iodide, KI, chloride of sodium or sodium chloride, NaCl.

When two elements combine in more than one proportion, the syllables, *mono*, *di*, *tri*, *tetra*, and *penta* are frequently used to designate the relative quantity of the elements. For instance: Carbon *mon*oxide, CO, carbon *di*oxide, $CO_2$, phosphorus *tri*chloride, $PCl_3$, nitrogen *tetr*oxide, $N_2O_4$, phosphorus *penta*chloride, $PCl_5$.

In many cases the syllables *ous* and *ic* are used to distinguish the proportions in which two elements combine; the syllable *ous* being used for the simpler or lower, the syllable *ic* for the more complex or higher form of combination. For instance: Phosphor*ous* chloride, $PCl_3$, and phosphor*ic* chloride, $PCl_5$; ferr*ous* oxide, FeO, ferr*ic* oxide, $Fe_2O_3$.

The syllable *sesqui* is used occasionally to indicate that a compound contains one-half more of an element than another compound formed from the same elements. Thus, ferr*ic* chloride, $FeCl_3$, is sometimes

called *sesqui*chloride of iron, as it contains one-half more of chlorine than does ferr*ous* chloride, $FeCl_2$.

The syllables *proto* or *sub* and *per* have also been used as prefixes to differentiate between compounds formed by the same elements. For instance, mercur*ous* chloride, HgCl, is called *proto*chloride or *sub*chloride, while mercur*ic* chloride, $HgCl_2$, is often designated as *per*chloride of mercury.

When two oxides of the same element ending in *ous* and *ic* form acids (by entering in combination with water), the same syllables are used to distinguish these acids. Phosphor*ous* oxide, $P_2O_3$, forms phosphor*ous* acid; phosphor*ic* oxide, $P_2O_5$, forms phosphor*ic* acid.

The salts formed by these acids are distinguished by using the syllables *ite* and *ate*. Phosph*ite* of sodium is derived from phosphorous acid, phosph*ate* of sodium from phosphoric acid. Sulph*ites* and sulph*ates* are derived from sulphurous and sulphuric acid, respectively.

When an element forms more than two acids the syllables *hypo* and *per* are often used to designate the nature of these acids, as also that of their respective salts. *Hypo* is prefixed to the compound containing less oxygen than the *ous* acid; and *per* is prefixed to the compound containing more oxygen than the *ic* acid. For instance, *hypo*chlor*ous* acid, HClO; chlor*ous* acid, $HClO_2$; chlor*ic* acid, $HClO_3$; *per*chlor*ic* acid, $HClO_4$. The salts formed from these acids are called hypochlorites, chlorites, chlorates, and perchlorates.

According to the new nomenclature, the name of the metal precedes that of the acid or acid radical in an acid. For instance, sodium phosphite, instead of phosphite of sodium; potassium sulphate, instead of sulphate of potassium. The acids themselves are looked upon as hydrogen salts, and are sometimes named accordingly: hydrogen nitrate for nitric acid, hydrogen chloride for hydrochloric acid, etc.

When the number of elements and the number of atoms increase in the molecule, the names become in most cases more complicated. The rules applied to the formation of such complicated names will be spoken of later.

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QUESTIONS.—Give in full Dalton's atomic theory and show how it accounts for the laws of combination. What is the relation of atoms to molecules? Define atomic and molecular weight. Define valence. What were considered formerly equivalent quantities of elements, and what are such at present? Mention some uni-, bi-, tri-, and quadrivalent elements. What explanation is offered for variable valence? What is the distinction between valence and affinity? If the valence of calcium is 2, and the formula of sulphuric acid is $H_2SO_4$, what theoretically should be the formula of calcium sulphate? What is a radical? Give an example of a univalent radical. What is meant by constitutional or graphic formulas? State the principles employed in the construction of names of compounds.

## 11. ACIDS, BASES, SALTS, NEUTRALIZATION. TYPES OF CHEMICAL CHANGE. REVERSIBLE ACTIONS AND CHEMICAL EQUILIBRIUM. MASS ACTION.

**Acids.**—The many compounds formed by the union of elements are so various in their nature that no system of classification proposed up to the present time can be called perfect. There are, however, a few groups or classes of compounds, the properties of which are so well marked, that a substance belonging to either of them may be easily recognized. These groups are the acids, bases, and neutral substances.

The term *acid* is applied to those compounds of hydrogen with an electro-negative element or group of elements which are characterized by the following properties:

1. The hydrogen present is replaceable by metals, the compound thus formed being a salt.

2. They change the color of many organic substances. Thus, litmus, a coloring-matter obtained from certain lichens, is changed from blue to red.

3. They have (when soluble in water) usually an acid or sour taste.

The great majority of acids are the result of union between water and the oxides of those elements which are devoid of characteristic metallic properties. We might, therefore, classify non-metallic elements as acid-forming elements. There are a few exceptional metals which form a series of oxides, some of which, when united with water, give acids; for example, chromic acid, $H_2CrO_4$, permanganic acid, $HMnO_4$. The formation of acids from oxides is shown by the following equations:

$$\underset{\text{Sulphur trioxide.}}{SO_3} + H_2O = \underset{\text{Sulphuric acid.}}{H_2SO_4}.$$

$$\underset{\text{Phosphorus pentoxide.}}{P_2O_5} + 3H_2O = \underset{\text{Phosphoric acid.}}{2H_3PO_4}.$$

$$\underset{\text{Carbon dioxide.}}{CO_2} + H_2O = \underset{\text{Carbonic acid.}}{H_2CO_3}.$$

Evidently in the acids containing oxygen, often called *oxyacids*, the hydrogen is derived from the water molecules with which the acidic oxides unite. Those oxides which unite with water to give acids are called *acidic oxides* or *acid anhydrides*. As was said before, the great majority of acidic oxides are derived from the non-metals, but there are some oxides of the non-metals which do not form acids, for example, carbon monoxide, CO, and nitrogen monoxide, $N_2O$.

A few acids contain no oxygen, and these are sometimes called *hydracids*. They have no corresponding oxides and are combinations of hydrogen with non-metallic elements, or groups of elements called radicals. The principal ones are hydrochloric acid, HCl, hydrobromic acid, HBr, hydriodic acid, HI, hydrofluoric acid, HF, or $H_2F_2$, hydrogen sulphide, $H_2S$, hydrocyanic acid, H(CN).

However much the acids may differ in certain properties, such as consist-

ency, that is, whether solid, liquid, or gas, solubility in water, degree of acid taste and action on litmus paper, corrosiveness to organic matter, such as skin, wood, cloth, etc., they are all alike in one respect, namely, in containing hydrogen which is separable from the rest of the molecule, and replaceable by metals, either by direct action of a metal on the acid, as when zinc acts on a solution of sulphuric or hydrochloric acid, or in a round-about way. There seems to be a strong tendency to separation between the hydrogen and the rest of the molecule of an acid which remains intact as a unit.

According to the number of hydrogen atoms replaceable by metals, we distinguish monobasic, dibasic, and tribasic acids. Hydrochloric acid, HCl, is a monobasic; sulphuric acid, $H_2SO_4$, is a dibasic; phosphoric acid, $H_3PO_4$, is a tribasic acid.

Many of the acids sold in trade, as well as the reagents used in the laboratory, are solutions of acids in water. It is customary to call these solutions by the names given to the acids themselves.

**Bases or Basic Substances.**—Bases or basic substances show properties which are chemically opposite to those of acids. As a general rule bases are compounds of electropositive elements (metals) with oxygen (oxides) or more generally with oxygen and hydrogen (hydroxides). Thus, silver oxide, $Ag_2O$, and sodium hydroxide, NaOH, are basic substances. Other properties characteristic of bases are:

1. When acted upon by acids, they form salts; for instance, when sodium hydroxide and nitric acid are brought together water and the salt sodium nitrate are formed:

$$NaOH + HNO_3 = H_2O + NaNO_3.$$

2. They have (when soluble in water) an alkaline reaction, *i. e.*, they restore the color of organic substances when previously changed by acids: for instance, that of litmus, from red to blue.

3. They have (when soluble in water) the taste of lye, or an alkaline taste.

The term *base* was originally applied to the metallic oxides, because when salts of the metals were highly heated they were decomposed, leaving a non-volatile calx or ash, the oxide of the metal, while the acid radical of the salt was driven off. Thus the metallic oxides were regarded as the base or stable groundwork of the salts. In the present-day classification, metallic hydroxides are called bases, but as the oxides bear such a close relationship to the hydroxides, in fact, many of them being converted into hydroxides in contact with water, many authors also include metallic oxides in the class of bases. The relationship between metallic oxides and hydroxides is well shown in the case of quick-lime, calcium oxide. Nearly everyone is familiar with the process of slaking lime by adding water to quick-lime. The action takes place thus, $CaO + H_2O = Ca(OH)_2$. The slaked lime, $Ca(OH)_2$, is a hydroxide of calcium. The relation might be made more striking by writing the formula thus, $CaO \cdot H_2O$.

Some oxides do not unite with water to form hydroxides, but, as far as they

are acted upon by acids, they give the same end product (a salt) as the hydroxides do, as may be illustrated in the following reactions:

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O.$$
$$Zn(OH)_2 + H_2SO_4 = ZnSO_4 + 2H_2O.$$

It should be noted that one of the products that is always formed when an acid acts on a metallic hydroxide, or oxide, is water. This is shown in the above reactions.

The hydroxides evidently are compounds derived from water by the replacement of part of the hydrogen in the water molecule by metal, thus leaving the radical, (OH), which is known as *hydroxyl*, in combination with metal. Hence, these compounds are called hydroxides. In a few cases hydroxides can be obtained by the direct action of the metals on water, the displaced hydrogen escaping as a gas. This seems to be good evidence of the relationship between the hydroxides and water. Most metals, however, do not act on water, and their hydroxides are obtained in an indirect way. (See *Remarks on Tests for Metals*, in the chapter on Magnesium.)

There are some hydroxides of radicals which can unite with acids just as the metallic hydroxides do, and these are also classed as basic substances. In them the radical plays the part of a metal.

Most of the metallic oxides and hydroxides are practically insoluble in water, and therefore have no appreciable action on litmus paper and no taste. Hence, alkaline action and taste are not a sure criterion of a basic substance. But the hydroxides insoluble in water can act on acids and replace their hydrogen by metal, just as the soluble hydroxides do.

The hydroxides differ very much in regard to specific properties, such as solubility in water, color, taste, etc., but there is one feature common to all of them, namely, the presence of the hydroxyl group, which is responsible for the class properties upon which such compounds are classified as basic substances.

It should be noted that there appears to be a tendency to easy separation between the metal and the hydroxyl radical in the bases, just as there is between the hydrogen and the acid radical in the case of acids. The significance of these facts will appear when the Ionic Theory is discussed.

**Neutralization.**—Neutralization is the term applied to the interaction between acids and bases with the result that both acid and basic properties, disappear—*i. e.*, are neutralized.

All substances which are acid in character contain hydrogen as one of their constituents. This hydrogen can readily be replaced by metals, for instance, by magnesium, when hydrogen is liberated. Not all substances containing hydrogen behave in this manner; for example, magnesium does not liberate hydrogen from petroleum, olive oil, sugar, etc., which all contain hydrogen. Hence the hydrogen of acids must be in a peculiar condition. That it is this hydrogen, and the peculiar condition in which it is present, which impart to acids their peculiar properties, are demonstrated by the fact that the acid properties disappear as soon as the hydrogen is replaced by a metal. Thus, the acid characteristics of hydrochloric acid, HCl,

vanish when it is acted on by sodium, or by the basic substance caustic soda (sodium hydroxide, NaOH), both of which cause a replacement of the acid hydrogen by sodium. These actions can be represented by the equations:

$$HCl + Na = NaCl + H.$$
$$HCl + NaOH = NaCl + H_2O.$$

In both cases sodium chloride, NaCl (common salt), is formed, which possesses neither acid nor basic properties.

**Neutral Substances.**—All substances having neither acid nor basic properties are neutral. Water, for instance, is a neutral substance, having no acid or alkaline taste, and no action on red or blue litmus. Many neutral substances, to some extent even water, appear to possess the characteristic properties of both classes, acids and bases; of neither class, however, to a very great extent.

**Salts.**—Salts are acids in which hydrogen has been replaced by metals or by basic radicals. There are several general methods by which salts may be obtained:

1. By the action of an acid on a metal. This is illustrated in the preparation of hydrogen from sulphuric or hydrochloric acid and zinc or iron.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$
$$Fe + 2HCl = FeCl_2 + H_2.$$

2. By the action of an acid on an oxide or hydroxide of a metal. This is of wider application than the previous method.

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O.$$
$$MgO + 2HCl = MgCl_2 + H_2O.$$
$$NaOH + HCl = NaCl + H_2O.$$

3. By the action of an acid on a salt of a volatile acid. This finds most extensive and useful application in the case of carbonates, which are decomposed by nearly all other acids, and are found ready-formed in nature or can be easily made.

$$MgCO_3 + H_2SO_4 = MgSO_4 + H_2O + CO_2.$$
$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

Other volatile acids whose salts are decomposed by acids are sulphurous, nitrous, hydrogen sulphide, hydrocyanic, etc. The manufacture of hydrochloric and nitric acids by the aid of concentrated sulphuric acid is an example of the method, and large quantities of sodium sulphate are obtained as a by-product for the market.

4. By the action of one salt upon another salt. This method is chiefly used when one of the products is insoluble or very nearly so, and is known as *precipitation*. Usually the insoluble product is the desired one, but the soluble one may also be isolated. A great many of the analytical reactions, called tests, fall under this method. Nearly all carbonates and phosphates are obtained by precipitation.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl.$$
$$CaCl_2 + Na_2HPO_4 = CaHPO_4 + 2NaCl.$$

Calcium carbonate and phosphate are precipitated and may be removed.

An example of the use of the method to get the soluble product is shown by the equation:

$$CuSO_4 + BaCl_2 = BaSO_4 + CuCl_2.$$

A solution of copper chloride is obtained by filtering off the barium sulphate.

In the case of certain salts it is simpler or more economic to follow special methods, which may be seen under the respective salts. Some of these salts are ferrous iodide, ammonium iodide, sodium hypochlorite, iodide, and thiosulphate, potassium permanganate, dichromate and chlorate, sodium carbonate, mercurous and mercuric chloride, etc.

According to the number of hydrogen atoms replaced in an acid, we distinguish normal and acid salts. A *normal salt* is one formed by the replacement of all the replaceable hydrogen atoms of an acid. For instance: Potassium chloride, KCl, potassium sulphate, $K_2SO_4$, potassium phosphate, $K_3PO_4$. (As monobasic acids have but one atom of hydrogen which can be replaced, they form normal salts only.)

Normal salts often have a neutral reaction to litmus, but they may have an acid or even an alkaline reaction.

It is found that soluble normal salts derived from a weakly ionizing acid, as carbonic, boric, phosphoric, sulphurous, hypochlorous, silicic, hydrogen sulphide, and a strongly ionizing base, as sodium and potassium hydroxide, and some others, have an alkaline reaction, while those derived from a strongly ionizing acid and a weakly ionizing base, as the hydroxide of many of the heavy metals, such as $Fe(OH)_2$, $Al(OH)_3$, $Cu(OH)_2$, etc., have an acid reaction. The reason for this is that such salts are partially decomposed or *hydrolyzed* by water. Thus, in the case of ferrous sulphate,

$$FeSO_4 + 2H_2O = Fe(OH)_2 + H_2SO_4,$$

the small quantity of free acid formed affects litmus-paper, $Fe(OH)_2$ being neutral. Sodium carbonate is acted on thus:

$$Na_2CO_3 + H_2O = NaHCO_3 + NaOH,$$

the free alkali causes litmus to turn blue, while $NaHCO_3$ is neutral.

*Acid salts* are acids in which there has been replaced only a portion of their replaceable hydrogen atoms. For instance: $KHSO_4$, $K_2HPO_4$, $KH_2PO_4$. While acid salts have generally an acid reaction to litmus, there are many exceptions to this rule. Indeed, the reaction may be

neutral or even alkaline, as, for instance, in the case of the ordinary sodium phosphate, $Na_2HPO_4$, which is slightly alkaline to litmus.

*Basic salts* are salts containing a higher proportion of a base than is necessary for the formation of a normal salt. Instances are basic mercuric sulphate, $HgSO_4.(HgO)_2$, basic lead nitrate, $Pb(NO_3)_2$, $Pb(OH)_2$. According to modern views basic salts are looked upon as derived from bases by replacement of part of their hydroxyl by acid radicals. In the base lead hydroxide, $Pb(OH)_2$, one hydroxyl radical may be replaced by the radical of nitric acid, when basic lead nitrate, $Pb\begin{matrix}NO_3\\OH\end{matrix}$, is formed.

In bismuth hydroxide, $Bi(OH)_3$, one, two, or three hydroxyl radicals may be replaced by nitric acid, when the salts $Bi\begin{matrix}NO_3\\(OH)_2\end{matrix}$, $Bi\begin{matrix}(NO_3)_2\\OH\end{matrix}$ and $Bi(NO_3)_3$ are formed. The first two compounds are basic salts, while the third one is the normal salt.

*Double salts* are salts formed by replacement of hydrogen in an acid by more than one metal. For instance: Potassium-sodium sulphate, $KNaSO_4$.

**Types of Chemical Changes.**—There are four principal ways in which chemical actions take place. These may be represented by the following equations, in which the letters stand for elements or groups of elements:

1. $A + B = AB$ *direct combination or addition.*
2. (*a*) $AB = A + B$
   (*b*) $ABC = AB + C$
   (*c*) $ABC = AC + BC$
   } *simple decomposition.*
3. $AB + C = CB + A$ *displacement.*
4. $AB + CD = AD + CB$ *double decomposition* or *metathesis.*

The following concrete examples will serve to illustrate the above types of change:

1. $Mg + O = MgO$.

When magnesium metal is heated to the ignition point it unites with oxygen of the air, and gives a white ash known as magnesium oxide.

2. (*a*) $HgO = Hg + O$.

Mercuric oxide, when heated to a sufficient temperature, decomposes into its elements—mercury and oxygen.

(*b*) $KClO_3 = KCl + 3O$.

When potassium chlorate is heated sufficiently high and long it decomposes into the compound potassium chloride and the element oxygen.

(*c*) $CaCO_3 = CaO + CO_2$.

When calcium carbonate is heated to redness it is decomposed into two new compounds, namely, calcium oxide and carbon dioxide.

3. $Fe + 2HCl = FeCl_2 + 2H.$

When a solution of hydrochloric acid is poured upon some iron, a brisk evolution of hydrogen gas takes place, and a new compound, ferrous chloride, remains in the solution.

Although in a sense there is a displacement of one element by another in every chemical action between two substances in which two new substances result, by custom the term *displacement* is used in those cases where the element displaced is left in the free or uncombined state.

4. $HCl + AgNO_3 = AgCl + HNO_3.$

When a solution of hydrochloric acid is added to a solution of silver nitrate, silver chloride is obtained as a white precipitate, and nitric acid is left in solution. This type of change, known as *double decomposition* or *metathesis*, is one of the most frequently occurring kinds of chemical change in analysis and chemical industry.

While in many cases of chemical decomposition the change which is to take place cannot be foretold, but has to be studied experimentally, there are other chemical changes which can be predicted with certainty. This is more especially true in the case of the action of acids on bases and the action of one salt on another salt. This will be easily seen from the previous discussion of acids, bases, neutralization and salts. Among these classes of compounds the results can usually be foretold, and there is little difficulty in representing the change by the proper equation. *In doing this it must be borne in mind that equivalent quantities replace one another;* that, for instance, two atoms of a univalent element are required to replace one atom of a bivalent element, as, for instance, in the case of the decomposition taking place between potassium iodide and mercuric chloride, when two molecules of the first are required to decompose one molecule of the second compound:

$$\begin{matrix} K-I \\ K-I \end{matrix} + Hg\begin{matrix} /Cl \\ \backslash Cl \end{matrix} = Hg\begin{matrix} /I \\ \backslash I \end{matrix} + \begin{matrix} K-Cl \\ K-Cl \end{matrix}$$

or

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

Whenever the exchange of atoms takes place between univalent and trivalent elements, three of the first are required for one of the second, as in the case of the action of sodium hydroxide on bismuth chloride:

$$\begin{matrix} Na-OH \\ Na-OH \\ Na-OH \end{matrix} + Bi\begin{matrix} /Cl \\ -Cl \\ \backslash Cl \end{matrix} = Bi\begin{matrix} /OH \\ -OH \\ \backslash OH \end{matrix} + \begin{matrix} Na-Cl \\ Na-Cl \\ Na-Cl \end{matrix}$$

or

$$3NaOH + BiCl_3 = Bi(OH)_3 + 3NaCl.$$

In the following examples of double decomposition an exchange takes place between the atoms of metallic elements, or between the metallic elements and the hydrogen. The student, in completing the equations, has also to select the correct quantity, *i. e.*, the correct number of molecules of the factors required for the change. The interrogation marks indicate that more than one atom or one molecule of the substance is needed for the reaction.

| | | | | | |
|---|---|---|---|---|---|
| $Na'$ | + $H'Cl$ | = | $Cu''SO_4$ | + $H_2'S$ | = |
| $H_2'SO_4$ | + $K'(?)$ | = | $Ba''Cl_2$ | + $Na_2'SO_4$ | = |
| $Ca''$ | + $H'Cl(?)$ | = | $Na_2'CO_3$ | + $H_2'SO_4$ | = |
| $Fe''$ | + $H_2'SO_4$ | = | $Bi'''(NO_3)_3$ | + $K'OH(?)$ | = |
| $H'Cl$ | + $Ag'NO_3$ | = | $Al_2'''(SO_4)_3$ | + $K'OH(?)$ | = |
| $Ca''Cl_2$ | + $Ag'NO_3(?)$ | = | $Al_2'''(SO_4)_3$ | + $Ca''(OH)_2(?)$ | = |
| $Bi'''Cl_3$ | + $Ag'NO_3(?)$ | = | $Fe_2'''Cl_6$ | + $Ag'NO_3(?)$ | = |

**Reversible actions and chemical equilibrium.** Experimental study has shown that in many instances a chemical action, when once started, runs to completion, that is, continues until the substance, or one of two substances, undergoing change is used up. For example, when a piece of magnesium is ignited the action continues until all the metal is used up, or the oxygen in the supply of air is exhausted. Moreover, this action cannot be reversed, that is, made to proceed in the opposite manner, no matter how much heat, or what degree of heat, available in the laboratory, we apply to the magnesium oxide. In other words, we cannot decompose the latter into magnesium element and oxygen by heat alone.

On the other hand, there are many instances in which chemical action, under a given set of conditions, is not complete, but proceeds to a certain point beyond which the products formed tend to act in a reverse manner, and reproduce the original substance or substances. Such changes are known as *reversible actions*, and evidently, while the conditions are maintained, the whole chemical process comes apparently to a standstill. But in the light of the kinetic-molecular theory of matter it is believed that action is constantly going on, although there is no progress made in either direction. The forward action of the system is counterbalanced by the reverse action which proceeds at the same speed, and thus is produced a condition of seeming rest, or *chemical equilibrium*. An example of equilibrium as a result of two equal and opposite actions is the case of a liquid in a closed container. At a definite temperature, the space above the liquid is saturated with its vapor which exerts a constant pressure. Although there is apparent rest, molecules of the liquid are passing off into the space above it, while vapor molecules are flying back into the liquid. These opposite actions finally balance each other, and then the system is in equilibrium. If the conditions are changed, for example, by a rise in temperature, the equilibrium is disturbed, a readjustment and new equilibrium follow, in which more vapor molecules exist in the space above the liquid, and a higher vapor pressure is produced.

Reversible chemical actions are represented by equations which differ from the ordinary chemical equations, in that the equality sign is replaced by two oppositely directed arrows, thus:

$$AB + CD \rightleftarrows AD + CB.$$

Such an equation indicates that the action takes place in two directions, forward and backward, and when equilibrium has been reached as much material continues to be transformed in one direction as in the reverse direction.

While in many cases the action is reversible, yet it runs far toward completion in one direction. This condition may be represented by making one of the arrows heavier than the other, thus:

$$MN + PR \rightleftharpoons MR + PN.$$

The following is a good example of a reversible chemical change. If finely divided iron and water vapor be heated in a sealed glass tube so that none of the products can escape, a state of equilibrium will result, in which four products exist in the tube—namely, iron, iron oxide, water vapor, and hydrogen.

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 8H.$$

This means that at the equilibrium stage the hydrogen reduces the iron oxide reversely as fast as the iron reduces the water vapor in the forward direction.

When the experiment is performed in the same manner as above, with iron oxide and hydrogen sealed in the tube at the equilibrium point, the same kinds of products exist as in the first case, thus:

$$Fe_3O_4 + 8H \rightleftharpoons 3Fe + 4H_2O.$$

Evidently a necessary condition for maintaining a chemical equilibrium in any reversible action is the keeping intact of all the factors taking part. If one of the products of an action be removed from the field of action as fast as it is formed, we might reasonably predict that the action would proceed to completion in the direction made easiest by the removal of such product. This is exactly what happens, as may be shown in the above instances. When steam is passed over highly heated iron through an open tube, the action takes place to completion, thus:

$$Fe_3 + 4H_2O = Fe_3O_4 + 8H.$$

The hydrogen is swept out of the tube and away from contact with the iron oxide by the current of steam. The action continues until all the iron is exhausted.

Conversely, when hydrogen gas is passed over heated iron oxide in an open tube, the action runs to completion reversely thus:

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

The current of hydrogen sweeps the water vapor (steam) out of the tube as fast as it is produced. The action continues until all the iron oxide is exhausted by conversion to elementary iron.

If one considered only the first action he would conclude that iron has a greater affinity for oxygen than hydrogen has, whereas if he considered only the second action, he would say that hydrogen has a greater affinity for oxygen than iron has, which apparently is a contradiction. But both conclusions are correct, depending on circumstances. In fact, in reversible actions affinity plays a minor part in determining which direction a chemical change will take, this being controlled in largest measure by the physical conditions of the experiment, which have nothing to do with affinity. This is admirably shown by the following example: When common salt (sodium chloride, NaCl) is dis-

solved in 20 per cent. aqueous solution of sulphuric acid ($H_2SO_4$), nothing apparently happens except solution of the salt. Yet a reversible action takes place, thus:

$$2NaCl + H_2SO_4 \rightleftarrows Na_2SO_4 + 2HCl.$$

Four products are present in solution in equilibrium. When, however, concentrated sulphuric acid, which is about 95 per cent., is poured upon salt, a brisk evolution of hydrochloric acid gas takes place, because of the fact that it is nearly insoluble in concentrated sulphuric acid. One of the factors in the equilibrium equation above is thus removed from the field of action, which thus allows the action to go forward nearly to completion and leaves the impression that the sulphuric acid has a greater affinity for the metal sodium than has the hydrochloric acid, or, as it is put sometimes in text-books, that sulphuric acid is a "stronger" acid than hydrochloric, which, in fact, is not true.

On the other hand, when hydrochloric acid gas is passed into a saturated aqueous solution of sodium sulphate until no more is absorbed, nearly all of the sodium is precipitated as sodium chloride, because the latter is almost insoluble in concentrated hydrochloric acid solution, and sulphuric acid is liberated and remains in the solution. In this case one of the factors in the above equilibrium equation is practically removed from the field of action by precipitation, thus allowing the reverse action to proceed nearly to completion, and leaving the impression that hydrochloric acid is a "stronger" acid than sulphuric.

**Mass action.** The vigor and extent of a chemical action depends upon the freedom with which the molecules can clash as well as upon the affinity between substances. Hence it is found that chemical action is aided far better in homogeneous mixtures, as when the substances are present in the gaseous state or in solution. Such physical systems as gas and solid, gas and liquid, liquid and solid, solid and solid, offer only limited contact between molecules, and, therefore, more or less impede chemical change. In homogeneous mixtures, in the case of reversible actions, the proportion of the substances changed chemically is different in different cases. The range extends all the way from slight change to nearly complete change. But in each individual case the amount of transformation is found to depend upon the concentration of each substance as well as upon the affinity between the substances. This is often called the *Law of Mass Action*, which may be stated thus: *The amount of a chemical change taking place in a given time will be dependent upon the molecular concentration of each substance.*

In chemical operations it is usually desirable to obtain one or other of the products of a chemical change in as large a yield as possible. If the action employed is a non-reversible one, little difficulty will be experienced in obtaining a full yield. In reversible actions, according to the law of mass action, the amount of the new product formed can be increased in two ways, either (1) by increasing the concentration of one or the other of the reacting substances, or (2) by removing one or the other of the products formed. The second method—namely, the removal of one of the products of the action, thus affecting the equilibrium of the system in such a way that the action tends toward completion—is the more effective way of increasing the yield. This is most conveniently done by selecting such actions that automatically remove

one of the products of the system in the form of an escaping gas or an insoluble body (precipitate[1]).

As instances of the removal of one of the products, and, therefore, more or less complete action, may be mentioned the formation of all the hundreds of insoluble metallic salts which are produced by the action of one salt solution upon another salt solution, the first solution containing a metal which, with the acid of the second solution, may form an insoluble compound, which is then invariably produced as a precipitate. For instance: Calcium carbonate, $CaCO_3$, is insoluble; if we bring together two solutions containing a soluble calcium salt and a soluble carbonate, such as calcium chloride, $CaCl_2$, and sodium carbonate, $Na_2CO_3$, calcium carbonate is precipitated.

Examples of complete action because of the removal of one of the products as a gas are: Action of any acid on any carbonate, whereby carbon dioxide gas is liberated; action of caustic alkalies, lime or magnesia, on ammonium salts, whereby ammonia gas is liberated.

## 12. CARBON. SILICON. BORON.

$C^{iv} = 12.$ $Si^{iv} = 28.3.$ $B^{iii} = 11.$

**Occurrence in Nature.**—Carbon is a constituent of all organic matter. In a pure state it is found crystallized as diamond and graphite, amorphous in a more or less pure condition in the various kinds of coal, charcoal, boneblack, lampblack, etc. As carbon dioxide, carbon is found in the air; as carbonic acid, in water; as carbonates (marble, limestone, etc.), in the solid portion of our earth.

**Properties.**—The three different allotropic modifications of carbon differ widely from each other in their physical properties.

*Diamond* is the purest form of carbon, in which it is crystallized in regular octahedrons, cubes, or in some figure geometrically connected with these. Diamond is the hardest substance known; when heated intensely in the presence of oxygen it burns, forming carbon dioxide.

*Graphite, plumbago,* or *black-lead,* is carbon crystallized in short six-sided prisms; it is a somewhat rare, dark gray mineral, having an almost metallic lustre. It feels soft and greasy between the fingers and leaves a black mark when drawn over a white surface. It is

[1] The term *precipitate* is used to designate an insoluble substance which separates by chemical action in a liquid, while *sediment* is applied to the collection of insoluble matter that may be floating in a liquid, and does not imply chemical action.

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QUESTIONS.—Give a general discussion of acids and bases. Give an example of an oxyacid and of a hydracid. What is an acid anhydride and an anhydrous acid? By what names are the acids distinguished in regard to the number of replaceable hydrogen atoms in the molecule? Why are bases called hydroxides? What is neutralization? Define a salt chemically and state various methods for obtaining salts. Define normal salt, acid salt, basic salt, and double salt. Mention the principal types of chemical change, with examples. Define reversible actions and chemical equilibrium. How may a reversible action be made to run to completion in one direction? Give an example. What is the law of mass action?

used to make lead-pencils, and also as a lubricator, in stove polish, as an admixture with clay used for crucibles, etc.

*Amorphous carbon* is always a black solid, but the hardness and specific gravity of the different kinds of amorphous coal differ widely. Amorphous carbon in the various kinds of coal is the chief agent for generating heat by combustion. In the form of lampblack it is used in printer's ink; in boneblack it serves for decolorizing sugar syrups and other liquids.

Neither form of carbon is soluble in any of the common solvents, but it dissolves to some extent in melted iron. On cooling, under ordinary conditions, most of the dissolved carbon separates in the form of graphite; when cooling takes place under high pressure small diamond-like crystals may be obtained. By the intense heat produced by electricity carbon becomes softened and in small quantities also volatilized.

Carbon is a quadrivalent element; it has little affinity for metals, though at high temperatures it combines with many, forming compounds, termed *carbides*. It does not enter into combination with oxygen at ordinary temperature, but at red heat it combines eagerly with free or combined oxygen, serving in many cases as a deoxidizing agent. Compounds of carbon with other non-metallic elements are mostly formed by indirect processes.

## Carbon Compounds.

The chemistry of the carbon compounds is very extensive and intricate. There are more compounds containing carbon than the total of all other compounds, and for good reasons they are studied in a subdivision of chemistry, called Organic Chemistry. A few simple compounds are taken up in Inorganic Chemistry because of their similarity in properties to the other inorganic compounds. These are the two oxides of carbon, the carbonates, carbon disulphide, and sometimes the cyanides and sulphocyanates.

Nearly all animal and vegetable substances contain carbon, and when heated they usually undergo decomposition and char, that is, leave a residue of black carbon. This is because the other elements go off first in various combinations, while carbon remains last. But some of the carbon also passes off as volatile products. If the heat is high enough and air has access, the carbon finally disappears, or, as is said, the substance burns up. Carbon compounds that are volatile when heated do not char. For example, alcohol, ether, chloroform, and many others simply vaporize when heated, although they contain carbon. Carbon may be shown to be present in such compounds by burning them in the air (when combustible) under a funnel and drawing the products through lime-water, or by causing the vapors to come in contact with copper oxide heated to redness in a tube and passing the products through lime-water. When carbon compounds are

burned up, either in air or by oxidizing agents, as copper oxide, the carbon passes off as gaseous carbon dioxide, $CO_2$, which unites with lime-water to form insoluble white calcium carbonate. In fact, this is the only common gas which acts in this way with lime-water.

When carbon compounds containing non-volatile metals are charred, the metals remain as carbonates or oxides mixed with the residue of carbon. Many carbon compounds char when heated with concentrated sulphuric acid because the acid extracts hydrogen and oxygen in the proportions to form water, for which it has a powerful affinity, thus leaving a residue of carbon.

*Experiment* 11. *a.* Heat a little starch on charcoal with the blow-pipe flame. Note that it blackens and burns up completely.

*b.* Heat a small knifepointful of sugar in a dry test-tube, gradually increasing the temperature. Note the melting, browning, condensation of water on the walls of the tube, odor, and final charring.

*c.* Heat gradually a little Rochelle salt ($K.Na.C_4H_4O_6$) in a porcelain crucible held in a triangle. The salt melts, effervesces, evolves inflammable vapors, and chars. Heat finally to redness, cool, and add some dilute acid. Any effervescence? Explain. Make the same experiment with tartaric acid. Note any difference in results. Note also the odor while heating.

*d.* Insert a burning stick of wood into a pint bottle or flask, mouth down, until the flame is extinguished; then remove the stick (is it charred?), pour into the bottle about 50 c.c. of lime-water and shake it. Explain results.

*e.* Heat slowly about 2 c.c. concentrated sulphuric acid in a dry test-tube with a bit of starch, sugar, Rochelle salt, and wood respectively. Describe and explain the results.

**Carbon Dioxide, $CO_2$.**—(Formerly named *carbonic acid*, or *anhydrous carbonic acid*.) This compound is always formed during the combustion of carbon or of organic matter; also during the decay (slow combustion), fermentation, and putrefaction (process of decomposition) of organic matter; it is constantly produced in the animal system, exhaled from the lungs, and given off through the skin.

Many spring waters contain considerable quantities of the gas, a part of which escapes from the water as it rises to the surface.

By heating, many carbonates are decomposed into oxides of the metals and carbon dioxide.

Lime-burning is such a process of decomposition:

$$\underset{\text{Calcium carbonate}}{CaCO_3} = \underset{\text{Calcium oxide}}{CaO} + CO_2.$$

Another method for the generation of carbon dioxide is the decomposition of any carbonate by an acid:

$$\underset{\text{Calcium Carbonate}}{CaCO_3} + \underset{\text{Hydrochloric acid}}{2HCl} = \underset{\text{Calcium chloride.}}{CaCl_2} + H_2O + CO_2.$$

The reason the action takes place readily and proceeds to completion is because carbonic acid is only slightly soluble in water and

easily breaks up into water and carbon dioxide gas, which escapes and is removed from the field of action, thus permitting the decomposition to be constantly renewed. Almost any acid will liberate carbon dioxide from a carbonate. The same principle is involved here as in the case of the liberation of nitrous acid from nitrites, nitric acid from nitrates, sulphurous acid from sulphites, or hydrochloric acid from chlorides. (See Reversible Actions, p. 127.)

*Experiment* 12.—Use the apparatus represented in Figure 9. Place about 20 grams of marble, $CaCO_3$, in small pieces (sodium carbonate or any other carbonate may be used) in the flask, cover it with water, and add hydrochloric acid through the funnel-tube. The escaping gas may be collected over water, as in the case of hydrogen, or by downward displacement, *i. e.*, by passing the delivery-tube to the bottom of a tube or other suitable vessel, when the carbon dioxide, on account of its being heavier than atmospheric air, gradually displaces the latter. This will be shown by examining the contents of the vessel with a burning taper, which is extinguished as soon as most of the air has been expelled.

Examine the gas for its high specific gravity by pouring it from one vessel into another; for its power of extinguishing flames, by mixing it with an equal volume of air, which mixture will be found not to support the combustion of a taper notwithstanding that oxygen is contained in it. Add to one portion of the collected gas some lime-water, shake it, and notice that it becomes turbid. Blow air exhaled from the lungs through a glass tube into lime-water, and notice that it also turns turbid.

Continue to pass the gas through the turbid liquid, and notice that it becomes clear in consequence of the dissolving action of carbonic acid water on calcium carbonate. On heating the solution carbon dioxide is expelled and calcium carbonate is reprecipitated. (So-called "hard" waters often contain calcium carbonate dissolved by carbonic acid. On heating these hard waters they become "soft," because the dissolved carbonate is precipitated.)

If marble has been used for the experiment, neutralize the liquid in the flask, if acid, by adding more marble until action ceases, filter, and evaporate it in a dish to dryness. The solid residue is a salt, calcium chloride. Expose some of it to the air for a long time and note that it absorbs moisture or deliquesces. What method of salt formation is illustrated by this experiment?

If sodium carbonate has been used, neutralize the liquid by adding acid or carbonate, as may be required, filter, and evaporate it to dryness. Taste the residue. What is it? Taste also sodium carbonate and the acid.

Carbon dioxide is a colorless, odorless gas, having a faintly acid taste. By a pressure of 38 atmospheres, at a temperature of 0° C. (32° F.), carbon dioxide is converted into a colorless liquid, which by intense cold (—79° C., —110° F.) may be converted into a white, solid, crystalline, snow-like substance. The specific gravity of carbon dioxide is 1.529; it is consequently about one-half heavier than atmospheric air. One liter at 0° C. and 760 mm. pressure weighs 1.977 grams.

Cold water absorbs at the ordinary pressure about its own volume of carbon dioxide, but the solubility is increased one volume for every increase of one atmosphere in pressure (soda water).

Carbon dioxide is not combustible, and not a supporter of combustion; on the contrary, it has a decided tendency to extinguish flames, air containing one-tenth of its volume of carbon dioxide being unable to support the combustion of a candle. While not poisonous when taken into the stomach, carbon dioxide acts indirectly as a poison when inhaled, because it cannot support respiration, and prevents, moreover, the proper exchange between the carbon dioxide of the blood and the oxygen of the atmospheric air. The pure gas causes immediate suffocation by spasm of the glottis.

Common atmospheric air contains about 4 volumes of carbon dioxide in 10,000 of air, or 0.04 per cent. In the process of respiration this air is inhaled, and a portion of the oxygen is absorbed in the lungs by the blood, which conveys it to the different portions of the animal body, and receives in exchange for the oxygen a quantity of carbon dioxide, produced by the union of a former supply of oxygen with the carbon of the different organs to which the blood is supplied.

The air issuing from the lungs contains this carbon dioxide, in quantity about 4 volumes in 100 of exhaled air, which is 100 times more than that contained in fresh air.

Exhaled air is, moreover, contaminated by other substances than carbon dioxide, such as ammonia, hydrocarbons, and most likely traces of other organic bodies, the true nature of which has not been fully recognized. The fact that stagnant air of an occupied room becomes uncomfortable and makes those who are exposed to it listless was formerly assumed to be due either to lack of oxygen or excess of carbon dioxide, or to the presence of some specific organic poison of exhalation. But the researches of Flügge, Haldane, Hill, Benedict and others have shown pretty conclusively that the more obvious effects experienced in a badly ventilated room are due to the heat and moisture produced by the bodies of the occupants, rather than to the carbon dioxide or other substances given off in the breath. The percentage of carbon dioxide in the air of a room was used as a measure of its fitness for respiration, but in the light of the latest researches, the carbon dioxide is rather an indication of excessive heat and moisture than an index of poisons in the air of the room. As a general rule, it may be stated that it is not advisable to breathe, for any length of time, air containing more than 0.1 per cent. of exhaled carbon dioxide; in air containing 0.5 per cent. most persons are attacked by headache, still larger quantities produce insensibility, and air containing 8 per cent. of carbon dioxide causes death in a few minutes.

The bad effects of stagnant air are corrected by ventilation, which keeps down the temperature and degree of moisture within proper limits. This is necessary for comfort, even though there were enough air supplied to the room to support respiration. A room may have plenty of air supplied to it and yet lack ventilation and the occupants may feel bad effects from excess of moisture and temperature. Ventilation is the displacement of the old air in a room by new fresh air, and the carbon dioxide standard may still be used as a measure of the air change which is required to carry off heat, moisture and odors. Thirty cubic feet of air per minute per capita is considered necessary to be supplied to an occupied room to keep it cool and fresh.

Mentioned above are many processes by which carbon dioxide is constantly produced in nature, and we might assume that the amount of 0.04 per cent. of carbon dioxide contained in atmospheric air would gradually increase. This, however, is not the case, because plants, and more especially all their green parts, are capable of absorbing carbon dioxide from the air, while at the same time they liberate oxygen.

This process of vegetable photosynthesis, which takes place under the influence of sunlight, is, consequently, the reverse of that of animal respiration. The animal uses oxygen and liberates carbon dioxide; the plant consumes this carbon dioxide and liberates oxygen.

**Difference between Vegetable and Animal Life.**—As a general rule it may be stated that the chemical changes in a plant are *progressive* or *constructive*, in an animal *regressive* or *destructive*. That is to say, plants take up as food a small number of inorganic substances of a comparatively simple composition, convert them into organic substances of a more and more complicated composition with the simultaneous liberation of oxygen, while animals take up as food these organic vegetable substances of a complex composition, assimilating them in their system, where they are gradually used (burned up) and finally discharged as waste products, which are identical (or nearly so) with those substances serving as plant food.

| *Plant food.* | *Waste products of animal life.* |
|---|---|
| Carbon dioxide. | Carbon dioxide. |
| Water. | Water. |
| Ammonia, $NH_3$. | Urea, $CO(NH_2)_2$. |
| Nitrates, $MxNO_3$. | Urates, $MxC_5H_2N_4O_3$. |
| Phosphates, Sulphates, Chlorides } of { Calcium. Magnesium. Sodium. Potassium. | Phosphates, Sulphates, Chlorides } of { Calcium. Magnesium. Sodium. Potassium. |

It should be remembered that no sharply defined line of demarcation can be drawn between plants and animals. Synthetic processes occur in the body of animals, and cleavage processes take place in some plants. However, in the animal organism the processes of oxidation and cleavage are predominant, while in plants those of deoxidation and synthesis are prevalent.

**Formation of Organic Substances by the Plant.**—As shown in the preceding table, plants take up the necessary elements for organic matter from a comparatively small number of compounds. All carbon is derived from carbon dioxide; hydrogen chiefly from water; oxygen from either of the two substances named, as well as from the various salts; nitrogen either from ammonia, or from nitrates and nitrites; while sulphur and phosphorus are derived from sulphates and phosphates respectively. These substances are taken into the plant chiefly by the roots, the assimilation of the necessary mineral constituents being facilitated by an acid secretion (discharged from the roots) which has a tendency to render these salts, present in the soil and surrounding the roots, soluble.

Water having absorbed more or less of carbon dioxide, of ammonia or ammonium salts, and of nitrates, phosphates, and sulphates of potassium, calcium, etc., enters the plant through the roots by a simple process of diffusion, and is carried

to the various green parts of the plant (chiefly to the leaves), where, under the influence of sunlight, a chemical decomposition and the formation of new compounds take place, the liberated oxygen being discharged directly through the leaves into the atmosphere.

It is difficult to explain fully the process of the formation of highly complex organic compounds in the plant, because we know so little in regard to the intermediate products which are formed. However, it is fair to assume that the various compounds above mentioned as plant food are first decomposed (with liberation of oxygen) in such a manner that residues or unsaturated radicals are formed which combine together. From these compounds, produced at first, more complicated ones will be formed gradually by replacement of more hydrogen, oxygen, or other atoms by other residues.

The following equations, while not showing the various radicals and intermediate compounds formed, may illustrate some of the results obtained by the plant in forming organic compounds:

$$CO_2 + H_2O = H_2CO_3$$
$$H_2CO_3 - O = H_2CO_2 = \text{Formic acid.}$$
$$2CO_2 + H_2O = H_2C_2O_5$$
$$H_2C_2O_5 - O = H_2C_2O_4 = \text{Oxalic acid.}$$
$$6CO_2 + 6H_2O = C_6H_{12}O_{18}$$
$$C_6H_{12}O_{18} - 12O = C_6H_{12}O_6 = \text{Glucose.}$$
$$10CO_2 + 8H_2O = C_{10}H_{16}O_{28}$$
$$C_{10}H_{16}O_{28} - 28O = C_{10}H_{16} = \text{Oil of turpentine.}$$
$$10CO_2 + 4H_2O + 2NH_3 = C_{10}H_{14}O_{24}N_2$$
$$C_{10}H_{14}O_{24}N_2 - 24O = C_{10}H_{14}N_2 = \text{Nicotine.}$$

The above formulas show that the formation of organic compounds in the plant is always accompanied by the liberation of oxygen, and it may be stated, as a general rule, that no organic substance (produced in nature) contains a quantity of oxygen sufficient to convert all carbon into carbon dioxide and all hydrogen into water, which fact also explains the combustibility of all organic substances.

Why it is that the living plant has the power of forming organic substances in the manner above indicated, we know not, and we know very little even in regard to the means by which the living cell accomplishes this formation, but we do know that sunlight furnishes the kinetic energy necessary in the formation of complex substances from the simpler ones. This kinetic energy is transformed into the potential energy, or chemical tension, of the new compounds and of the liberated oxygen.

**Carbonic Acid, $H_2CO_3$ or $CO(OH)_2$.**—Carbon dioxide is an acid oxide, which combines with water, forming carbonic acid: $CO_2 + H_2O = H_2CO_3$. It is not known in a pure state, but always diluted with much water, as in all the different natural waters. Carbonic acid is a dibasic, extremely weak acid, the salts of which are known as carbonates. Many of these carbonates (calcium carbonate, for instance) are abundantly found in nature. Only the alkali carbonates and bicarbonates are soluble in water. Acid carbonates of some other metals, such as magnesium, calcium, zinc, iron, are also slightly soluble in water, but these do not exist in the dry state. The

bicarbonates when heated to about 100° C. give up carbon dioxide and form carbonates:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

At high temperatures only alkali carbonates are not decomposed.

**Tests.**—Since nearly all carbonates are insoluble in water, these are formed as precipitates whenever a solution of an alkali carbonate (those of potassium, sodium, or ammonium) is added to a solution of a salt of any other metal. This is a corroborative test for a soluble carbonate, but the best and decisive test for all carbonates and carbonic acid is found in Experiment 12, namely, the liberation of carbon dioxide and its action on lime-water.

**Carbon Monoxide, Carbonic Oxide, CO.**—While carbon, as a general rule, is quadrivalent, in this compound it exerts a valence of 2. Carbon monoxide is a colorless, odorless, tasteless, neutral gas, almost insoluble in water; it burns with a pale blue flame, forming carbon dioxide; it is very poisonous when inhaled, forming with the coloring matter of the blood a compound which prevents the absorption of oxygen. Carbon monoxide is formed when carbon dioxide is passed over red-hot coal:

$$CO_2 + C = 2CO.$$

The conditions necessary for the formation of carbon monoxide are, consequently, present in any stove or furnace where coal burns with an insufficient supply of air. The carbon dioxide formed in the lower parts of the furnace is decomposed by the coal above. The blue flames frequently playing over a coal fire are burning carbon monoxide. This gas is formed also by the decomposition of oxalic acid (and many other organic substances) by sulphuric acid:

$$\underset{\text{Oxalic acid}}{H_2C_2O_4} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = H_2SO_4.H_2O + CO_2 + CO.$$

Carbon monoxide is now manufactured on a large scale by causing the decomposition of steam by coal heated to red heat. The decomposition takes place thus:

$$H_2O + C = 2H + CO.$$

The gas mixture thus obtained, known as *water-gas*, may be used for heating purposes directly, but has to be mixed with hydrocarbons when used as an illuminating agent, for reasons which will be pointed out below when considering the nature of flames.

**Carbonyl Chloride, $COCl_2$.**—This is formed when a mixture of carbon monoxide and chlorine is exposed to sunlight, and, hence, is also known as *phosgene*. Commercially it is made by passing a mixture of the two gases over animal charcoal, which acts as a catalytic agent. Carbonyl chloride is gaseous above 8° C., has a suffocating odor, and dissolves readily in benzene. Water decomposes it at once into carbonic and hydrochloric acids, $COCl_2 + 2H_2O = H_2CO_3 + 2HCl$ It is used in making certain synthetic organic compounds.

### Compounds of Carbon and Hydrogen.

There are no other two elements which are capable of forming so large a number of different combinations as are carbon and hydrogen. Several hundred of these hydrocarbons are known, and their consideration belongs to the domain of organic chemistry.

Two of these hydrocarbons, however, may be briefly mentioned, as they are of importance in the consideration of common flames. These compounds are: *methane* (marsh-gas, fire-damp), $CH_4$; and *ethene* (olefiant gas), $C_2H_4$.

Both compounds are colorless, almost odorless gases, and both are products of the destructive distillation of organic substances. Destructive distillation is the heating of non-volatile organic substance in such a manner that the oxygen of the atmospheric air has no access, and to such an extent that the molecules of the organic matter are split up into simpler compounds. Among the gaseous products formed by this operation, more or less of the two hydrocarbons mentioned above is found.

Marsh-gas is formed frequently by the decomposition of organic matter in the presence of moisture (leaves, etc., in swamps); and during the formation of coal in the interior of the earth, the gas often giving rise to explosion in coal mines. During these explosions of the methane (mixed with air and other gases), called *fire-damp* by the miners, carbon is converted into carbon dioxide, which the miners speak of as *choke-damp*, or *after-damp*.

**Flame.**—Flame is gas in the act of combusion. Of combustible gases, have been mentioned: hydrogen, carbon monoxide, marsh-gas, and olefiant gas. These four gases are actually those which are found chiefly in any of the common flames produced by the combustion of organic matter, such as paper, wood, oil, wax, or illuminating gas itself.

These gases are generated by destructive distillation, the heat being supplied either by a separate process (manufacture of illuminating gas by heating wood or coal in retorts), or generated during the combustion itself.

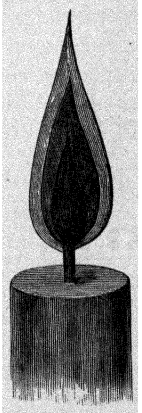
In burning a candle, for instance, fat is constantly decomposed by the heat of the flame itself, the generated gases burning continuously until all fat has been decomposed, and the products of decomposition have been burned up, *i. e.*, have been converted into carbon dioxide and water.

An ordinary flame (Fig. 12) consists of three parts or cones. The inner portion is chiefly unburnt gas; the second is formed of partially burnt and burning gas; the outer cone, showing scarcely any light, is that part of the flame where complete combustion takes place. The highest temperature is found between the second and third cone.

The light of a flame is caused by solid particles of carbon heated to a white heat. The changes that take place in a flame are difficult to study, but sufficient has been done experimentally to permit the conclusion to be drawn that the separation of carbon in a flame is due to dissociation of some of the hydrocarbons, of which ethylene (ethene) is the most important. It is well known that when ethylene ($C_2H_4$) is heated it yields acetylene ($C_2H_2$), which in turn gives carbon and hydrogen. Evidence that acetylene is present in a gas flame is furnished by the fact that when a Bunsen flame "strikes back," that is, burns at the base of the tube so that incomplete combustion of the gases takes place, a large quantity of acetylene is formed.

If a sufficient amount of air be previously mixed with the illuminating gas, as is done in the *Bunsen burner*, no separation of carbon takes place, and, therefore, no light is produced, but a more intense heat is generated. A similar effect is produced by the aid of the *blow-pipe* or by means of the *blast lamp*, which serve to direct a current of air directly into the cone of the flame. The luminous and non-luminous Bunsen flame, using the same flow of gas, must produce the same amount of heat for a definite amount of gas burned, since the end-products of combustion are the same in both cases. But the non-luminous flame is much shorter than the luminous one, and thus the heat is concentrated within a smaller space, and, therefore, the temperature is much higher than in the luminous flame.

FIG. 12.



Structure of flame.

The cause of non-luminosity of a flame when air or oxygen is admitted into the interior, as in a Bunsen burner, is difficult to explain. That it is due to other causes than the presence of the oxygen is shown by the fact that nitrogen or carbon dioxide will also destroy luminosity. The introduction of cold gases into a flame lowers the temperature of the inner cone, where the dissociation of ethylene takes place. It seems probable that this lowering of temperature and dilution of the gases diminish the decomposition of ethylene to such an extent that not enough carbon is separated to give luminosity.

## Silicon or Silicium, Si = 28.3.

Silicon is found in nature very abundantly as silicon dioxide, or silica, $SiO_2$ (rock-crystal, quartz, agate, sand), and in the form of silicates, which are silicic acid in which the hydrogen has been replaced by metals. Most of our common rocks, such as granite, porphyry, basalt, feldspar, mica, etc., are such silicates or a mixture of them. Small quantities of silica are found in spring-waters, as well as in vegetable and animal matters.

Silicon resembles carbon both in its physical and chemical properties. Like carbon, it is known in the amorphous state, and forms two kinds of crystals, which resemble graphite and diamond. Like carbon, silicon is quadrivalent, forming silicon dioxide, $SiO_2$, silicic acid, $H_2SiO_3$, silicon hydride, $SiH_4$, silicon chloride, $SiCl_4$, which compounds are analogous to the corresponding carbon compounds, $CO_2$, $H_2CO_3$, $CH_4$, and $CCl_4$.

The compounds formed by the union of silicon with hydrogen, chlorine, and fluorine are gases. The latter compound, silicon fluoride, $SiF_4$, is obtained by the action of hydrofluoric acid on silica or silicates, thus:

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

This reaction is used in the analysis of silicates, which are decomposed and rendered soluble by the action of hydrofluoric acid.

Silicon fluoride is decomposed by water into silicic acid and hydrofluosilicic acid, $H_2SiF_6$, thus:

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6.$$

Several varieties of silicic acid are known, of which may be mentioned the *normal silicic acid*, $H_4SiO_4$, and the *ordinary silicic acid*, $H_2SiO_3$, from the latter of which, by heating, water may be expelled, when *silicon dioxide*, $SiO_2$, is left.

## Tests for silicic acid and silicates.

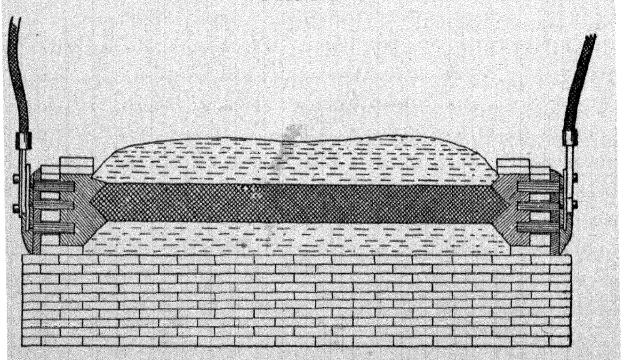
(Soluble glass or flint may be used.)

1. Silicic acid and most silicates are insoluble in water and acids. By fusing silicates with about 5 parts of a mixture of the carbonates of sodium and potassium the silicates of these metals (known as soluble glass) are formed. By dissolving this salt in water and acidifying the solution with hydrochloric acid a portion of the silica separates as the gelatinous hydroxide.

Complete separation of the silica is accomplished by evaporating the mixture to complete dryness over a water-bath, and re-dissolving the chlorides of the metals in water acidulated with hydrochloric acid; silica remains undissolved as a white amorphous powder.

2. Silica or silicates when added to a bead of microcosmic salt (see index) form on heating before the blowpipe the so-called silica-skeleton.

FIG. 13.

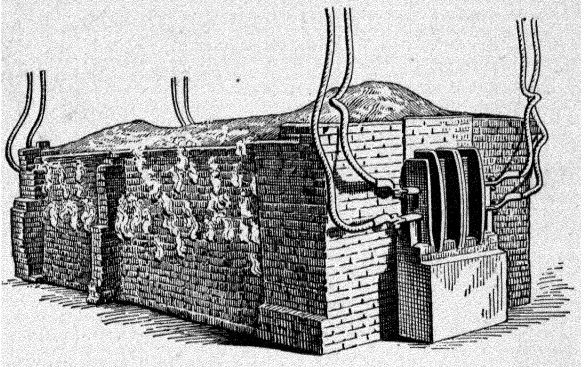


Longitudinal section of carborundum furnace.

**Silicon Carbide, SiC** (*Carborundum, Carbon silicide*).—This compound furnishes a typical illustration of the possibilities of the electric furnace for manufacturing purposes. Figs. 13 and 14 give a sectional and an exterior view of the furnace used. The current enters and leaves the furnace through cables terminating in carbon electrodes fastened in the wall. Between them is placed a core of coke, surrounded by a mixture of carbon, sand, and salt. The current heats the mass to about 3500° C. (6332° F.), when the carbon combines with both elements of the sand, thus:

$$SiO_2 + 3C = 2CO + SiC.$$

FIG. 14.



Exterior view of carborundum furnace.

Carborundum forms beautiful, dark green, iridescent crystals of extreme hardness, in the latter quality being exceeded only by the diamond. It is extensively used as a polishing agent, gradually replacing emery, to which it is far superior.

## Silica Ware.

Silica is a very refractory substance, and must be heated above 1500° C. before it melts. When melted it is not mobile, but rather a thick viscid fluid which makes it more difficult to work into apparatus than glass. In recent years, however, by the use of the electric furnace, every variety of apparatus, large and small, has been manufactured out of fused silica, which has displaced glass, porcelain and platinum to a great extent, especially in those instances in which the properties of silica give it an advantage over other materials. Fused silica ware possesses a low coefficient of expansion (about one-seventeenth of that of glass) and is, therefore, unaffected by sudden and extreme changes of temperature. It is not attacked by acids (except hydrofluoric). Apparatus made of silica is not transparent as in the case of glass, but opaque because of entrapped air which cannot escape easily from the viscous melted silica.

## Boron, $B''' = 11$.

Boron is found in but few localities, either as boric (boracic) acid or sodium borate (borax). Formerly the total supply of boron was

derived from Italy: large quantities of borax are now obtained from Nevada and California.

Boron exists as a greenish-brown amorphous powder and also in the form of hard and often highly lustrous crystals. Boron combines with many of the non-metals, forming such compounds as boron trichloride, $BCl_3$, trifluoride, $BF_3$, and hydride, $BH_3$. It is one of the few elements which at a high temperature combine directly with nitrogen, forming boron nitride, BN.

**Boric Acid** (*Acidum Boricum*) $\mathbf{H_3BO_3}$, $\mathbf{B(OH)_3}$ = **62.02** (*Boracic acid*), is a white, crystalline substance, which is sparingly soluble in cold water or alcohol, but more soluble in glycerin; it has but weak acid properties. When heated to 100° C. (212° F.) it loses water, and is converted into *metaboric acid*, $HBO_2$, which when heated to 160° C. is converted into *tetraboric acid*, $H_2B_4O_7$, from which *borax*, $Na_2B_4O_7 + 10H_2O$, is derived. At a white heat boric acid loses all water, and is converted into boron trioxide, $B_2O_3$. From a boiling solution boric acid readily volatilizes with the steam.

Boric acid is obtained by adding hydrochloric acid to a hot saturated solution of borax, when boric acid separates on cooling. The chemical change is this:

$$Na_2B_4O_7 + 2HCl + 5H_2O = 4H_3BO_3 + 2NaCl.$$

It is rather odd that while the usual form of boric acid in the uncombined state is the orthoboric acid, $H_3BO_3$, salts of this form are hardly known. Salts of metaboric acid occur, but the best-known salts are derived from tetraboric acid, and the best representative is the sodium salt, borax. On the other hand, when the acid is liberated from the salts, it assumes the ortho form. From the formula of tetraboric acid, it appears that four molecules of the ortho acid combine with elimination of water to form a more complex molecule:

$$4H_3BO_3 = H_2B_4O_7 + 5H_2O.$$

There are other cases of this kind, as will be seen later.

Borax may be looked upon as containing sodium metaborate and boric oxide, $2NaBO_2 + B_2O_3$. When it is heated with basic oxides, these unite with the excess of $B_2O_3$, forming a fused mixed metaborate. This action explains the use of borax on hot metal surfaces which are to be welded. Some of these metaborates have distinctive colors. For this reason borax beads are used as tests for certain metals (see under Sodium Borate).

Boric acid is such a weak acid that its solution has only a slight action on litmus-paper, and it is displaced from its salts by nearly every other acid. The borates of the alkali metals only are easily soluble in water, the others being either insoluble or nearly so. Hence, when a solution of an alkali borate (but not of free boric acid) is added to a solution of a salt of other metals, a precipitate is obtained. Alkali borates show a strong alkaline reaction to litmus because they are partly hydrolyzed in solution to free alkali and boric acid. It will be seen that boric acid is very much like carbonic acid in behavior.

Boric acid and borax are practically the only compounds of boron that are

used. Both are used in medicine and as preservatives. When powdered they look much alike, but can be distinguished by the fact that the acid is soluble in alcohol while borax is not, and that borax has a marked alkaline reaction to litmus, and when held in a Bunsen flame on platinum wire gives a yellow color, while free boric acid gives a green color.

### Tests for Boric Acid and Borates.

1. When borax is heated on the loop of a platinum wire in a Bunsen flame it first puffs up very much, and then gradually melts into a transparent, colorless bead. If the bead is moistened with concentrated sulphuric acid and heated again, a green color is produced. Boric acid also melts into a colorless bead. Note any difference in color of the flame.

2. Mix in a porcelain dish some borax with 2 c.c. of concentrated sulphuric acid, add about 10 c.c. of alcohol, and ignite. The flame has a mantle of green color, which is best seen by alternately extinguishing and relighting the alcohol. Repeat the experiment, omitting the acid; no green color is seen. Free boric acid is volatilized with alcohol, but not its salts.

3. A solution of boric acid, or of a borate acidulated with dilute hydrochloric acid, colors a strip of turmeric paper dark red, which becomes more intense on drying. The color is changed to bluish black by dilute ammonia water.

## 13. THEORY OF ELECTROLYTIC DISSOCIATION, OR IONIZATION. ELECTROLYSIS. DISSOCIATION THEORY APPLIED TO ACIDS, BASES, SALTS, AND NEUTRALIZATION.

### Theory of Electrolytic Dissociation.

It was observed long ago that aqueous solutions of certain kinds of substances, of which cane-sugar is a good type, do not conduct an

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QUESTIONS.—How is carbon found in nature? State the physical and chemical properties of carbon in its three allotropic modifications. Mention three different processes by which carbon dioxide is generated in nature, and some processes by which it is generated by artificial means. State the physical and chemical properties of carbon dioxide. Explain the process of respiration from a chemical point of view. What is the percentage of carbon dioxide in atmospheric air, and why does its amount not increase? State the composition of carbonic acid and of a carbonate. How can they be recognized by analytical methods? Under what circumstances will carbon monoxide form, and how does it act when inhaled? What is destructive distillation, and what gases are generally formed during that process? Explain the structure and luminosity of flames. How does silicon occur in nature? Point out how silicon resembles carbon. What is carborundum and how is it made? How does boron occur? Give the composition and properties of boric acid and borax. How are they distinguished and detected?

electric current, while aqueous solutions of other substances, of which common salt or hydrochloric acid is a good example, are excellent conductors of electricity. Moreover, it was also observed that substances which conduct electricity in aqueous solution do not conduct when they are dissolved in certain solvents, like benzene, ether, chloroform, etc. This fact evidently points to the conclusion that water has some peculiar action on some substances whereby they become possessed of the power to conduct a current. The same kind of effect is also noticed in regard to chemical behavior. For example, dry hydrochloric acid gas dissolved in dry benzene neither conducts electricity nor has an acid reaction on litmus, nor appreciably acts on zinc, whereas an aqueous solution of the gas conducts well, has a marked acid reaction on litmus, and attacks zinc vigorously. It appears, therefore, that hydrochloric acid molecules in aqueous solution must be in a state different from that when they are dissolved in benzene. It should be noted that pure water itself is not a conductor, nor are the other substances when *dry*, but their solutions in water conduct. There are a few other liquids which show this property, but to a far less extent than water does, to which this discussion will be confined.

Substances whose aqueous solutions conduct electricity are known as *electrolytes*, those whose solutions do not are called *non-electrolytes*. It is found experimentally that acids, bases, and salts are electrolytes, and it is precisely these substances whose aqueous solutions show abnormally large values of freezing-point depressions, boiling-point elevations, and osmotic pressures. In the discussion of the latter subjects (which see) it is pointed out that the abnormally acting substances behave as if there are more particles in solution than the number of molecules corresponding to the weights of the substances dissolved, which fact can be accounted for only on the supposition that some molecules are decomposed by the solvent into smaller particles. Further, since molecules, which, like those of sugar, act normally in regard to freezing-point, boiling-point, and osmotic pressure phenomena, and thus show no indication of decomposition by the solvent, do not conduct electricity, it follows that the fragments of decomposed molecules must be responsible for the ability to conduct in the case of solutions of electrolytes. In electrolysis (chapter 3) these fragments are the particles that are attracted to the charged poles, hence the further assumption is made that the fragments (or ions as they are called) are themselves charged with electricity, because it is known that electricity attracts only bodies that possess a charge of electricity. Briefly summed up, then, the THEORY OF ELECTROLYTIC DISSOCIATION *assumes that molecules of electrolytes when dissolved in water break up to a varying degree into independent particles charged with electricity, and that the nature and number of these charged particles determine to a large degree certain physical and chemical properties of solutions.*

This theory was proposed by the Swedish physicist Arrhenius in 1887; its general adoption has been hastened by the work of van't Hoff, Ostwald, and Nernst.

The dissociation of molecules in solution is also called IONIZATION, and the electrically charged particles are called *ions*. These are always of two kinds, namely, electropositive ions, or *cations*, because they are attracted to the negative pole or *cathode* during electrolysis, and electronegative ions, or *anions*, because they are attracted to the positive pole or *anode*. Since solutions are themselves electrically neutral, that is, show no charge of electricity as a whole, it follows that the sum of the electric charges of the positive ions equals the sum of the charges of the negative ions. The two kinds of ions are in electrical balance.

**Composition of Ions.**—This is learned from a study of the products that are attracted to the anode and cathode, respectively, in electrolysis, and from the manner in which molecules of electrolytes exchange their parts or radicals in chemical actions. In molecules of acids hydrogen is readily separated in chemical actions from the rest of the molecule, which is a radical, consisting of a non-metallic element, or a group of atoms acting as a unit and remaining intact. In electrolysis, division occurs in the same manner, hydrogen separating at the cathode, and acid radical being attracted to the anode. Salts behave in the same manner as acids in regard to the division of the molecules, which is only what we should expect, since they are so closely related to acids. Indeed, some chemists put both in the same class, regarding acids as salts of hydrogen. Bases in chemical action and in electrolysis show a division between the metal and the hydroxyl (OH) radical, the metal going to the cathode, and the hydroxyl radical to the anode. It appears, then, from the side of chemical action as well as that of electrolysis that *an aqueous solution of an acid contains positive hydrogen ions and negative acid radical ions; a solution of a salt contains positive ions of a metal and negative acid radical ions; and a solution of a base contains positive ions of a metal and negative hydroxyl ions.*

**Ions and Atoms not the Same.**—The student should note particularly that a substance in the ionic state is quite different from the substance in the free state. Simple ions are atoms plus a charge of electricity, while atoms of free elements are not charged, and this difference is sufficient to account for the difference of behavior. Thus, when sodium chloride (NaCl) is dissolved in water, many of the molecules break up into Na-ions and Cl-ions, but there is no chemical action between the water and Na-ions or Cl-ions, whereas sodium in the free state acts violently on water, and chlorine dissolves in water with some chemical action and imparts its odor and bleaching properties to the water. A solution of sodium chloride has no odor or bleaching action.

**Symbols Representing Ions.**—Ions are represented by the usual

chemical symbols, with the addition of marks to indicate positive and negative charges. Thus, $Na^+$, or $Na^{\cdot}$, stands for a positively charged sodium ion, and $Cl^-$, or $Cl'$, stands for a negatively charged ion of chlorine. Quantitative experiments in electrolysis show that the amounts of electricity possessed by ions are proportional to the valence of the atoms or radicals constituting the ions. If the charge on a sodium or on a chlorine ion is taken as the unit charge, then the charge on an ion of a bivalent atom or radical is two units, and is represented thus, $Ca^{++}$, or $Ca^{\cdot\cdot}$, and $SO_4^{--}$, or $SO_4''$. The ion of trivalent aluminum is written $Al^{+++}$, or $Al^{\cdot\cdot\cdot}$, etc.

**Ionic Equilibrium.**—The dissociation of molecules into ions must be considered as a species of chemical change, and, like many others, it is a reversible action (see page 127). In ordinary dilute solutions there is always a certain proportion of undissociated molecules which are in equilibrium with the ions. The degree of dissociation varies with the concentration of the solution, and of course with the nature of the dissolved substance, since for the same concentration different substances vary widely in the amount of dissociation. If the solution is made more concentrated, as by evaporation, more and more of the ions unite to form molecules, until finally, when all the solvent is removed, the dry substance is left entirely in the molecular state. On the other hand, diluting a solution results in more molecules being dissociated. Many substances in highly diluted solutions are almost completely dissociated. The reversible character of dissociation is represented by *reversible ionic equations*, thus:

$$HCl \rightleftarrows H^{\cdot} + Cl'; \quad NaCl \rightleftarrows Na^{\cdot} + Cl'; \quad NaOH \rightleftarrows Na^{\cdot} + (OH)'.$$

The first equation means that in any given solution of hydrochloric acid there is a certain proportion of molecules and a certain proportion of ions. The molecules tend to form ions, but only as fast as the ions tend to revert to the molecular state, so that an equilibrium is maintained. By changing the conditions, ions may be forced to unite to form molecules, or *vice versa*. In other words, the equilibrium may be displaced forward or backward. Likewise for the other two equations dealing with sodium chloride and sodium hydroxide respectively.

Theoretical deductions, as well as experimental results, show that in varying solutions of the same substance there is a constant relationship, which is expressed thus: *The product of the concentration of the ions divided by the concentration of the undissociated molecules is a constant quantity (or nearly so in some cases), expressed by a numeral,* and called the IONIZATION CONSTANT. The concentration is expressed in terms of the number of molecular weights or ion weights in grams in a liter of solution. A solution containing one molecular weight or ion weight per liter is taken as unit concentration.

**Effect of Ionic Equilibrium in Chemical Reactions. Some Familiar Results.**—If in any manner, as by precipitation, one kind of the ions of a substance is removed from solution, some molecules of the substance are dissociated to replace the kind of ions removed, until the balance between ions and molecules, as indicated in the ionization constant, is restored. This process may go on until all the molecules are dissociated. Conversely, if the concentration of one kind of ion is increased, as by the addition of a substance giving the same kind of ion—for example, addition of hydrochloric acid to a solution of sodium chloride (both having a common ion, $Cl'$)—the result is a reunion of some of the ions of the original substance to form molecules, until the balance between its molecules and *all* of the ions of the kinds that it gives satisfies the demands of the ionization constant. If the solution is saturated in the beginning, and therefore contains all the undissociated molecules that it can hold, the formation of an additional number of molecules by union of ions gives rise to supersaturation and precipitation of some of the substance. Thus, the addition of hydrochloric acid gas to a saturated solution of common salt causes a copious precipitate of the salt. Likewise, addition of some saturated solution of the very soluble sodium chlorate to one of the less soluble potassium chlorate causes precipitation of some of the latter salt. The reason the sodium chlorate is not also reciprocally precipitated is that the additional molecules formed by union of its ions, $Na^{\cdot}$ and $ClO_3'$, are not sufficient to supersaturate the volume of liquid through which the sodium chlorate is distributed. The principle just discussed furnishes an explanation of the fact that is often observed in practical work, namely, that many substances are much less soluble in solutions of other substances of similar composition than in pure water.

In the case of a solution of a slightly dissociating substance, the addition of another substance having a common ion with the first may so far cause a reversal of dissociation of the first substance that practically only its undissociated molecules exist in the solution, with an accompanying loss of some of its properties. Thus, in a solution containing per liter the molecular weight of sodium acetate and the molecular weight of acetic acid, the latter no longer is able to affect the indicator methyl orange, because there are too few hydrogen ions of the acid left in solution.

**Precipitation.**—When molecules of a substance are dissolved, some dissociate until a balance is established between ions and molecules, as represented by the ionization constant. Conversely, when there are present in a solution two substances which between them produce ions corresponding to a third substance, some molecules of the third substance are formed up to the point that corresponds to its ionization constant. The following ionic equations for a mixture of potassium chloride and sodium nitrate in solution will illustrate:

$$\left.\begin{array}{l} KCl \rightleftarrows K^{\cdot} + Cl' \\ NaNO_3 \rightleftarrows NO_3' + Na^{\cdot} \\ \qquad\downarrow\uparrow \\ \qquad KNO_3 \end{array}\right\} \rightleftarrows NaCl.$$

Evidently molecules of four products will be present in this mixture, and likewise in all similar ones. If all the products are readily soluble and of large dissociating power, and the solution is rather dilute, there are few undissociated molecules present. The mixture then is practically a mixture of ions, and nothing can be observed by the eye to have taken place. But if one of the new products is "insoluble" in water, there are more of its ions present than can be maintained in a saturated solution of the same, the excess of ions unite to form molecules, and the excess of molecules are removed by precipitation. In this way one factor in the equilibrium is removed and the action runs to completion. *This principle is at the basis of all cases of precipitation in chemical reactions.* The precipitation of silver chloride is a good example, and is represented thus:

$$\left.\begin{array}{l} AgNO_3 \rightleftarrows NO_3' + Ag^{\cdot} \\ NaCl \rightleftarrows Na^{\cdot} + Cl' \\ \qquad\downarrow\uparrow \\ \qquad NaNO_3 \text{ soluble.} \end{array}\right\} \rightleftarrows AgCl \text{ precipitate.}$$

A simple equation, in which only the ions are represented, may be used:

$$Ag^{\cdot} + NO_3' + Na^{\cdot} + Cl' = AgCl + Na^{\cdot} + NO_3'.$$

The simplest equation of all is one which shows only those ions that are actually involved in the precipitation, thus:

$$Ag^{\cdot} + Cl' = AgCl.$$

Reasoning parallel to the above may be applied when one of the new products formed is a gas with slight solubility in water at ordinary or higher temperatures, or a liquid which is volatile at elevated temperature. In either case, the new product is removed as fast as it is formed and the action runs to completion. In the liberation of ammonia, the ionic equations are:

$$\left.\begin{array}{l} 2NH_4Cl \rightleftarrows 2Cl' + 2NH_4^{\cdot} \\ Ca(OH)_2 \rightleftarrows Ca^{\cdot\cdot} + 2(OH)' \\ \qquad\downarrow\uparrow \\ \qquad CaCl_2 \text{ soluble.} \end{array}\right\} \rightleftarrows 2NH_4OH = 2H_2O + 2NH_3 \text{ (gas) undissociated.}$$

Or, more simply,

$$Ca^{\cdot\cdot} + 2(OH)' + 2NH_4^{\cdot} + 2Cl' = Ca^{\cdot\cdot} + 2Cl' + 2NH_4OH.$$

Ammonium hydroxide is only slightly ionized, and by heating is easily broken up and driven out of solution as ammonia gas.

For the liberation of carbon-dioxide gas the representation is this:

$$\left.\begin{array}{l} Na_2CO_3 \rightleftarrows 2Na^{\cdot} + CO_3'' \\ H_2SO_4 \rightleftarrows SO_4'' + 2H^{\cdot} \end{array}\right\} \rightleftarrows H_2CO_3 = H_2O + CO_2 \text{ (gas)}.$$

$\downarrow\uparrow$

$Na_2SO_4$ soluble.

Or simply

$$2Na^{\cdot} + CO_3'' + 2H^{\cdot} + SO_4'' = 2Na^{\cdot} + SO_4'' + H_2CO_3.$$

Carbonic acid is only slightly ionized and very little soluble. Hence it escapes as fast as it is liberated. This description will serve also for the liberation of nitrous acid from nitrites.

The formation of nitric acid is represented thus:

$$\left.\begin{array}{l} 2KNO_3 \rightleftarrows 2K^{\cdot} + 2NO_3' \\ H_2SO_4 \rightleftarrows SO_4'' + 2H^{\cdot} \end{array}\right\} \rightleftarrows 2HNO_3 \text{ volatile by heating.}$$

$\downarrow\uparrow$

$K_2SO_4$ non-volatile.

Or simply

$$2K^{\cdot} + 2NO_3' + 2H^{\cdot} + SO_4'' = 2K^{\cdot} + SO_4'' + 2HNO_3.$$

As concentrated sulphuric acid and dry potassium nitrate are used in this process, only a relatively small number of ions are present at one time, but as fast as ions are removed as nitric acid, new ions are formed to replace them until the operation is completed.

The above discussions on the formation of precipitates, gases, and volatile liquids, and consequent completion of chemical reactions, is a presentation in terms of the ionic theory of the same subjects discussed in a simpler form on p. 129 under Reversible Actions and Chemical Equilibrium, and furnish an explanation of what is there stated.

Chemical actions in aqueous solutions are nearly always actions between ions. Indeed, there are some who claim that chemical action does not take place except between ions, and the fact that action does occur is itself evidence of the presence of ions. This is an extreme view and is not well taken, as there are undoubted examples of action in solution in which ions do not exist. In the case of acids, bases, and salts in solution, action is practically always ionic.

## Electrolysis.

This name is given to the series of changes that take place when an electric current is passed through a solution of an electrolyte, and the subject is briefly discussed on page 53. The process is carried out in an electrolytic cell, which consists of a suitable vessel holding a solution into which are immersed the electrodes of the circuit. Fig. 6 illustrates one form of such a cell, which is designed to collect gases. The electrodes are made of materials which are not affected by the products that collect on them. Platinum plates are often used.

The results of passing a current through a solution of an electrolyte is a chemical decomposition. The products that appear at the electrodes are always

different. For illustration, one of the simplest cases of electrolysis may be considered, namely, the decomposition of hydrochloric acid. When the apparatus (Fig. 6) is filled with the concentrated acid and a current is turned on, hydrogen gas is found to collect and rise into the tube from the cathode or (—) electrode, and chlorine gas collects in the other tube from the anode or (+) electrode. The mechanism of the process is conceived to be as follows: The solution of the acid contains some ions of hydrogen ($H^{\cdot}$) and of chlorine ($Cl'$), the presence of which is entirely independent of the electric current. These ions, before the current is turned on, are attracted no more in one direction than in any other. When the current is turned on, one electrode receives from the battery or dynamo, or whatever the source of electricity, a positive charge, and the other receives a negative charge, and a constant difference of voltage or electromotive force is maintained between the electrodes. If the latter should be connected by a continuous conductor, as a piece of copper wire, a current would flow from the positive to the negative electrode by their discharge through the wire. But the source of electricity would constantly renew the charges on the electrodes, and thus a continuous current would be kept up. When the connecting wire is replaced by hydrochloric acid, the positive electrode attracts the negatively charged chlorine ions and repels the positive hydrogen ions, while the negative electrode attracts the positive hydrogen ions and repels the negative chlorine ions. In this way there is a general movement of all positive ions to one electrode, and of all negative ions to the other. When the ions come in contact with the electrodes, they lose their charges by neutralizing the charges of opposite kind on the electrodes. The discharged ions then unite and pass off as molecules of hydrogen and chlorine respectively. The discharged electrodes receive new charges as before, and the process is repeated until all of the electrolyte is removed from the solution. The effect as far as the conduction of the current is concerned is the same as if a wire connected the electrodes, and the current flowed through a circuit entirely metallic. In the light of this ionic explanation of electrolysis, we can understand why solutions of substances which do not dissociate into ions like sugar do not conduct electricity, and why substances which conduct in aqueous solution do not conduct in solvents in which they are not dissociated.

**Secondary changes in electrolysis.** In the electrolysis of hydrochloric acid the products liberated consist of the same elements of which the ions are constituted, but the majority of cases are not so simple as this one. Many ions are atomic groups which are not known in the free state, but exist only as ions in solution. When these lose their charges, secondary chemical changes occur and the resulting products accumulate around the electrodes. Thus in the case of sulphuric acid, the $H^{\cdot}$ ions become molecules of hydrogen gas, but the $SO_4''$ ion when discharged becomes a group not known in the free state. It reacts with water thus: $H_2O + SO_4 = H_2SO_4 + O$. Sulphuric acid accumulates around the positive electrode, but is gradually disseminated again through the solvent by diffusion. The oxygen escapes and can be collected. The amount of hydrogen and oxygen liberated are in the same proportion as in water, and thus we have an explanation of the "decomposition of water by electrolysis."

When copper sulphate is electrolyzed metallic copper is deposited on the negative electrode, and sulphuric acid and oxygen collect at the other. In the

case of sodium sulphate the sodium ion when discharged acts on water, resulting in the accumulation of sodium hydroxide and hydrogen around the negative electrode, and as before sulphuric acid and oxygen collect at the positive electrode.

**Faraday's laws of electrolysis.** Michael Faraday, of England, was the first to make a careful quantitative study of electrolysis, and announced the following two laws:

I. *The amount of a substance liberated in an electrolytic cell is proportional to the quantity of electricity that has passed through it.*

II. *Chemically equivalent quantities of ions are liberated by the passage of equal quantities of electricity.* Chemically equivalent quantities are determined by valence. Thus for every divalent ion liberated, two univalent ions are liberated, etc., by the same amount of electricity.

The liberation of 1 gram of hydrogen requires the passage of 96,540 units (coulombs) of electricity. A current strength of 1 ampère is such that 1 coulomb of electricity flows through a circuit in 1 second. Hence a current of 1 ampère will require 96,540 seconds (26 hours and 49 minutes) to liberate 1 gram of hydrogen (nearly 11 liters). A current of 5 ampères would do the same work in one-fifth of the time.

One coulomb (a current of 1 ampère flowing 1 second) will liberate 0.0000104 gram of hydrogen, 0.0000828 gram of oxygen, 0.0003294 gram of copper, 0.001118 gram of silver, etc. These quantities are proportional to the chemical equivalents, and are called in electrical science, *electrochemical equivalents.*

An instrument constructed for determining the amount of substance as silver or copper liberated by a current in a given time, and from this the current strength, is called a *voltameter.* Suppose a current flowing for 1 hour through a voltameter liberates 0.59292 gram of copper upon the cathode, the current strength is—

$$\frac{0.59292 \text{ gm. copper}}{3600 \text{ seconds} \times 0.0003294 \text{ elect. chem. equiv. of copper}} = \tfrac{1}{2} \text{ ampère.}$$

**Conductivity.**—Every solution of an electrolyte offers a certain resistance to the flow of the current, which can be measured in ohms. If the resistance is small, the solution offers an easy passage for the current, hence it is said to have a high *conductivity.* A solution of great resistance is said to have a low conductivity. The numerical value for conductivity is the reciprocal of the resistance,

$$\text{Conductivity} = \frac{1}{\text{resistance}}.$$

In order that results may be compared, conductivity measurements are made with electrodes 1 cm. apart. The algebraic character used to represent conductivity is $\lambda_v$, which means the conductivity shown by the molecular weight of the substance in v liters of solution.

The conductivity increases with dilution. This is what we should expect, since conductivity is proportional to the number of ions, which also increases with dilution. By measuring the conductivity in a given dilution and also in very large dilution, it is a simple matter to calculate the degree of ionization of the substance in the given dilution. This method of study is called the *conductivity method.*

**Electromotive Force Required in Electrolysis.**—The amount of work that can be done by any form of energy depends not merely on the quantity, but also on the intensity of the energy. Thus, the quantity of steam in a locomotive boiler, however large, will not cause the driving-wheels to turn if the pressure (intensity factor) is not sufficiently large. Likewise, in electrolysis, different substances require for decomposition currents of different electromotive force. If the latter is less than the required minimum, there is no liberation of ions at the electrodes, that is, no electrolysis. The quantity of current only controls the amount of material liberated, but the electromotive force decides whether there will be any decomposition at all. The reason for the latter fact is that as soon as the electrodes are coated with the products of electrolysis, a reverse electromotive force and current tend to develop which oppose the original current. The electrodes are then said to be *polarized*. To overcome this polarization current requires a certain minimum electromotive force in the electrolyzing current. The electromotive force required for a few common electrolytes are as follows:

| | |
|---|---|
| Hydriodic acid | 0.53 volts. |
| Silver nitrate | 0.70 " |
| Hydrochloric acid | 1.41 " |
| Sulphuric acid | 1.92 " |
| Zinc sulphate | 2.70 " |

**Electrochemical series of the metals.** If the metals are arranged in the order of the electromotive force required to liberate them in electrolysis, we have the following electropositive series:

*Electrochemical series of metals.*

Potassium
Sodium
Lithium
Calcium
Strontium
Barium
Magnesium
Aluminum
Manganese
Zinc
Chromium
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
*Hydrogen*
Arsenic
Copper
Antimony
Bismuth
Mercury
Silver
Palladium
Platinum
Gold

The electromotive force required decreases from the potassium end of the series to the gold end. If the metals are arranged in a series according to the decreasing intensity of their chemical activity in the free state toward other substances, the same order is observed as that in the above series. Metals higher up in the series will displace others following from solutions of their salts, but not vice versâ. All the metals, from potassium to hydrogen, will displace hydrogen from dilute acids, but those following hydrogen will not. The metals, down to copper inclusive, will rust in the air. The oxides of the

metals, down to manganese inclusive, cannot be reduced to the metal by heating in hydrogen, but oxides of cadmium and the metals following can. The metals down to hydrogen do not occur in the free state in nature.

The non-metals and negative radicals into which they enter (acid radicals) can also be arranged into a similar electronegative series.

## Dissociation theory applied to acids, bases, salts, and neutralization.

**Acids.** A general discussion of acids, bases, and salts is given in Chapter 11. In terms of the ionic theory, acids are substances which give positive hydrogen ions in solution, associated with negative ions that may be either simple, as $Cl'$, or complex, as $SO_4''$, or $CO_3''$. The properties common to all acids are due to the hydrogen ions; for example, sour taste, action on litmus, action on metals with displacement of the hydrogen. The latter action is represented in the case of zinc by the ionic equation, $Zn + 2H^{\cdot} + SO_4'' = Zn^{\cdot\cdot} + SO_4'' + H_2$. This stands as a type for all acids, and it will be observed that the action is essentially between the metal and hydrogen ions, and is independent of the negative ion. The charges on the hydrogen ions are transferred to the zinc atoms, which then become ionic, and the discharged hydrogen ions escape as molecules.

The specific properties of the acids in solution are due to the different composition of the negative radicals. These radicals are the same whether acids or their salts are used. When a solution of silver nitrate is added to one of potassium chloride, a white precipitate of silver chloride is obtained, but when added to potassium chlorate in solution, no visible change takes place. Both of these salts contain chlorine, but the first gives the ion $Cl'$, and the second the ion $ClO_3'$. In other words, the composition of the negative radicals is different, which results in a different behavior toward the positive silver ion. Silver chloride is an insoluble substance and is formed in solutions only when silver ions and chlorine ions are brought together. Chlorine ions are formed only from hydrochloric acid or the chlorides. Silver chlorate is a soluble body, and, therefore, nothing that we can see happens when silver ions and chlorate ions are brought together in solution.

**Independence of ions.** The above discussion leads to the conclusion that the ions of acids are distinct substances with individual physical and chemical properties. Each kind of ion behaves as if it were alone present in the solution. This is true of all ions. To illustrate, two instances may be given that have to do with a physical property, namely, color of salts or acids. All copper salts of colorless acids have a blue color in dilute solutions. The blue color is due to the copper ion, and all copper salts that are soluble give the copper ion. The molecules of copper salts in solution are not blue, as can be shown by the following experiment: If to a solution of copper chloride concentrated hydrochloric acid be added, there will be a point at which the blue changes to a yellowish-green color. The effect of the acid is to reverse the ionization of the copper chloride so far that the color of the remaining ions of copper is overbalanced by the color of the molecules of the salt.

Again, permanganic acid in dilute solution is deeply colored, due to the $MnO_4'$ ion (hydrogen ion is colorless). Likewise all its salts in dilute solu-

tions are deeply colored, because they all form the common ion, $MnO_4'$. For equivalent concentrations, the tint of the color is the same in all the solutions.

**Analytical reactions or tests.** Since acids, bases, and salts ionize, and chemical actions concern primarily the ions, it is not difficult to see that the tests made in solutions (wet way) for identifying substances are *tests for ions.* Thus, when we test for carbonic acid by lime-water we are testing, not for the acid $H_2CO_3$, but for the ion $CO_3''$. Nevertheless we infer the nature of the molecules from a study of the reactions of the ions. Since the tests apply to ions, we have an explanation of the fact that tests for a given ion can be used in the case of all substances which give that ion in solution, irrespective of the nature of the other ions. Thus, the silver nitrate test for "chlorine" succeeds for all chlorides that are soluble. Likewise, the barium chloride test for all soluble sulphates. It is evident also that two kinds of tests must be made in the case of each substance, namely, one kind for the positive ion and the other kind for the negative ion.

**Kinds of ions formed by acids.** Monobasic acids, as HCl, $HNO_3$, etc., can form only one hydrogen ion from each molecule. Dibasic acids, like $H_2SO_4$, form one or two hydrogen ions, according to concentration. In rather concentrated solution of sulphuric acid the ionization is principally thus: $H_2SO_4 \rightleftarrows H^{\cdot} + HSO_4'$. The ion $HSO_4'$ is an acid, but much less active than sulphuric. When the acid is highly diluted, further ionization takes place to a great degree, thus, $HSO_4' \rightleftarrows H^{\cdot} + SO_4''$. All dibasic acids dissociate in two stages, like sulphuric. Tribasic acids show a similar behavior.

**Activity or "strength" of acids.** A proper comparison of acids can only be made under like conditions of temperature, concentration, etc. For this purpose like concentration means solutions containing in a given volume chemically equivalent weights of the respective acids. These are such weights in grams as contain the same weight of replaceable hydrogen. For example, two molecular weights of HCl are equivalent to one molecular weight of $H_2SO_4$. All conditions being equal, the activity of acids is proportional to the degree of dissociation, that is, to the concentration of the hydrogen ions. Those acids that ionize most are the "strongest," and *vice versa.*

**Bases.** Bases are substances which give negative hydroxyl (OH) ions in solution, associated with a positive ion, which is usually metallic, but may be a group of atoms not containing a metal, as $NH_4$. The properties common to bases in general when dissolved are due to the hydroxyl ion, for example, action on litmus, soapy taste, neutralization of acids. Most of the bases are so sparingly soluble that not enough (OH) ions are present to affect litmus. Zinc and iron hydroxides are examples of such. In other cases, just enough (OH) ions dissolve to give a faint action on litmus, for example, magnesium hydroxide. Just as in the case of acids, the activity of bases is proportional to the degree of ionization. The most active common bases are potassium and sodium hydroxides, called alkalies, and sometimes caustic alkalies. Their solutions are called lyes. The hydroxides of barium, strontium, and calcium are next in activity. Ammonium hydroxide is a rather weak base. The rest are either sparingly soluble or insoluble.

**Salts.** The relationship between salts and acids has already been discussed.

As a rule, salts ionize to a considerable degree, and do not show as wide a range in the degree as do the acids. Non-metals are never found in the positive ion of salts, except they occur in a composite radical, as $NH_4$. Hence we have no such salts as nitrogen carbonate, carbon sulphate, or sulphur phosphate. The ions of salts do not affect litmus, it is only $H^{\cdot}$ and $(OH)'$ ions that have an effect.

**Acid salts.** These may be acid, neutral, or alkaline to litmus, depending on the mode of ionization. An acid salt of a highly ionizing acid shows an acid reaction in solution, because of the presence of hydrogen ions. For example, sodium bisulphate acts thus in solution:

$$\begin{aligned} NaHSO_4 &\rightleftarrows Na^{\cdot} + HSO_4' \\ HSO_4' &\rightleftarrows H^{\cdot} + SO_4'' \end{aligned}$$

Acid salts of weak acids, like carbonic, phosphoric, boric, etc., may be neutral or even alkaline, because the remaining hydrogen of the acid does not become ionic. Sodium bicarbonate is neutral to litmus, because it ionizes thus:

$$NaHCO_3 \rightleftarrows Na^{\cdot} + HCO_3'.$$

The ion $HCO_3'$ does not furnish sufficient $H^{\cdot}$ ions by further dissociation to affect litmus.

**Basic salts.** These are the reverse of acid salts. They are derived from bases containing more than one (OH) group in the molecule, and the union with acids is such that not all of the (OH) groups are replaced by acid radical. Thus $Mg(OH)_2$ can form $Mg\begin{smallmatrix}Cl\\OH\end{smallmatrix}$ which shows the plan of structure of all basic salts. They are, in nearly all cases, insoluble in water and show slight or no action on litmus.

**Hydrolysis of salts.** Some salts, which we would expect from their formulas, such as normal salts, to have a neutral reaction in solution, show a noticeable acid reaction, while others show an alkaline one. Such salts are related to an acid or to a base of slight dissociating power, and the cause is found in the slight ionization of water, which, though extremely minute, makes itself felt in some cases. The acid reaction of copper sulphate is explained by the following ionic reaction:

$$\left.\begin{aligned} CuSO_4 &\rightleftarrows SO_4'' + Cu^{\cdot\cdot} \\ 2H_2O &\rightleftarrows 2H^{\cdot} + 2(OH)' \end{aligned}\right\} \rightleftarrows Cu(OH)_2.$$

Copper hydroxide dissociates very slightly, being in this respect on a par with water. As a consequence, some $Cu^{\cdot\cdot}$ and $(OH)'$ ions unite to form molecules of $Cu(OH)_2$. The removal of $(OH)'$ ions of water allows more to be formed, and more $Cu(OH)_2$ results. This process soon comes to a stop, but not before enough $H^{\cdot}$ ions have been produced to give the solution an acid reaction. The molecules of $Cu(OH)_2$ are not precipitated, but remain in solution. The quantity is too small.

The ionic equation for sodium carbonate which shows marked alkaline reaction is:

$$\left.\begin{aligned} Na_2CO_3 &\rightleftarrows 2Na^{\cdot} + CO_3'' \\ H_2O &\rightleftarrows (OH)' + H^{\cdot} \end{aligned}\right\} \rightleftarrows HCO_3'.$$

Here a small quantity of $(OH)'$ ions are produced, which give the solution an alkaline reaction. This action of water on salts is called *hydrolysis*. The changes are usually represented by the simpler reactions:

$$CuSO_4 + 2H_2O = Cu(OH)_2 + H_2SO_4$$
$$Na_2CO_3 + H_2O = NaOH + NaHCO_3$$

Soap always shows an alkaline reaction, which is due to hydrolysis. Salts containing bivalent or trivalent radicals, metallic or acid, are more prone to undergo hydrolysis than those containing univalent radicals only.

**Neutralization.**—Broadly speaking, the replacement of hydrogen of an acid by metal is neutralization, but, as shown in the preceding paragraph, certain salts have an acid or alkaline reaction in solution, and consequently it is impossible in such instances to produce an exactly neutral solution by bringing the acid and base together in the proportions to form the salt. A great many salts, however, are neutral, and in these cases it is possible to bring together the corresponding acids and bases, and have complete reactions and neutral solutions. In the more restricted sense *neutralization* refers to such complete reactions. They can be employed for quantitative determinations of the acids or bases in solutions. This subject is treated under *Acidimetry* and *Alkalimetry* in the section on Volumetric Analysis.

Neutralization is an example of double decomposition and of a complete reaction. The interpretation of this is found in the ionic theory. In the beginning before mixing, there are $H^\cdot$ ions which have an acid reaction, and $(OH)'$ ions which are alkaline. When they are brought together by mixing the acid and base and the neutral point is established, both $H^\cdot$ and $(OH)'$ ions disappear, as is proved experimentally by conductivity tests. This disappearance results from the fact that water is practically undissociated, and, therefore, these ions cannot exist in the same solution, but unite to form molecules of water. Of course, the metal ions and acid radical ions also unite to some extent to form molecules, but if the solutions are quite dilute the proportion of undissociated molecules is negligible.

The ionic equation for the neutralization of sodium hydroxide and nitric acid serves as a type for all instances:

$$\left.\begin{array}{l} NaOH \rightleftarrows Na^\cdot + (OH)' \\ HNO_3 \rightleftarrows NO_3' + H^\cdot \\ \quad\downarrow\uparrow \\ \quad NaNO_3 \end{array}\right\} \rightarrow H_2O$$

As fast as $H^\cdot$ and $(OH)'$ unite more NaOH and $HNO_3$ dissociate, until finally all is dissociated, and only ions of sodium nitrate and some undissociated molecules of the same are left in the solution at the point of neutrality.

The essential reaction may be shown in the simplified equation:

$$Na^\cdot + (OH)' + H^\cdot + NO_3' = Na^\cdot + NO_3' + H_2O,$$

or by the following still simpler equation, which expresses the fact that neutralization is a reaction between $H^\cdot$ and $(OH)'$ ions:

$$H^\cdot + (OH)' = H_2O.$$

**Heat of Neutralization.**—Heat is produced when an acid and a base neutralize each other. If what is stated above is true, then the heat is due to the formation of water molecules, and should be the same for all active acids and bases in dilute solutions. This is exactly what is found by experiment to be true. The heat of neutralization refers to such weights of acids and bases that will furnish enough $H^\cdot$ and $(OH)'$ ions to form one molecular weight of water, and is 13,700 calories.

**Degree of Dissociation.**—The degree of dissociation of electrolytes varies with the nature of the substance and the concentration of the solution. Usually it is small in concentrated solutions, and increases rapidly with dilution. In 62 per cent. nitric acid only about 9 per cent. of the molecules are ionized, while in the 6.3 per cent. acid about 80 per cent. are ionized. Comparisons for degree of dissociation must be made with solutions of the same relative concentrations. Usually normal solutions at 18° C. are used, except when the substance is not sufficiently soluble. The following table gives the per cent. of dissociation in normal solutions[1] at 18° C., except when otherwise specified, of some acids, bases, and salts.

| Electrolyte. | Per cent. dissociation. | Electrolyte. | Per cent. dissociation. |
|---|---|---|---|
| Nitric acid | 82 | Sodium phosphate, very dilute | 83 |
| Hydrochloric acid | 78.4 | Ammonium chloride | 74 |
| Sulphuric acid | 51 | Sodium chloride | 67.5 |
| Hydrofluoric acid | 7 | Potassium nitrate | 64 |
| Acetic acid | 0.4 | Potassium acetate | 64 |
| Carbonic acid $\left(\frac{n}{10}\right)$ | 0.17 | Silver nitrate | 58 |
| Hydrogen sulphide $\left(\frac{n}{10}\right)$ | 0.07 | Potassium sulphate | 53 |
| | | Sodium acetate | 53 |
| Boric acid $\left(\frac{n}{10}\right)$ | 0.01 | Sodium bicarbonate | 52 |
| Hydrocyanic acid $\left(\frac{n}{10}\right)$ | 0.01 | Potassium carbonate | 49 |
| | | Sodium sulphate | 44.5 |
| Phosphoric acid $\left(\frac{n}{2}\right.$ at 25° C.$\left.\right)$ | 17 | Zinc sulphate | 24 |
| Potassium hydroxide | 77 | Zinc chloride | 48 |
| Sodium hydroxide | 73 | Copper sulphate | 22 |
| Calcium hydroxide, sat sol. at 25° C. | 90 | Mercuric chloride, less than | 1 |
| Ammonium hydroxide | 0.4 | Mercuric cyanide | minute |

Mathematical formulas have been constructed for calculating the degree of dissociation from the results obtained by four methods of work, namely, freezing-point, boiling-point, osmotic pressure, and conductivity methods. The results of calculation all agree. The simplest method in execution is the conductivity method.

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QUESTIONS.—State the theory of electrolytic dissociation or ionization. Upon what experimental facts does it rest? What is an electrolyte? What substances are found to be electrolytes? What is a cation; an anion? Write the ionic equation for the dissociation of sodium chloride in solution. Write the ionic equation for the precipitation of silver chloride from solution. What is electrolysis, and how is it explained? How are acids, bases, and salts defined in terms of the ionic theory? How is the activity or "strength" of acids and bases related to dissociation? How is the fact that some acid salts have an acid action on litmus, while others are neutral, accounted for? What is hydrolysis?

[1] The concentration of normal solutions is defined in the section on Volumetric Analysis.

## 14. SULPHUR.

$S^{II} = 32.07$

**Occurrence in Nature.**—Sulphur is found in the uncombined state, mixed with earthy matter, in volcanic districts, the chief supply having been derived until lately from Sicily. Considerable quantities are now also mined in the United States, chiefly in Louisiana, Utah, California, and Nevada. In combination sulphur is widely diffused in the form of sulphates (gypsum, $CaSO_4.2H_2O$), and frequently occurs as sulphides (iron pyrite, $FeS_2$, galena, PbS, cinnabar, HgS, etc.). Sulphur enters also into organic compounds, being a normal constituent of all proteins, during the decomposition of which sulphur is often evolved as hydrogen sulphide, which gas is also a constituent of some waters.

**Properties.**—Sulphur is a yellow, brittle, solid substance, having neither taste nor odor. It is insoluble in water and nearly so in alcohol; soluble in benzene, benzin, ether, chloroform, carbon disulphide, oil of turpentine, and fat oils. Sulphur is polymorphous; it crystallizes, from a solution in carbon disulphide, in octahedrons with a rhombic base; when, however, liquefied by heat it crystallizes in six-sided prisms, and is obtained as a brown, amorphous plastic substance by pouring melted sulphur into cold water.

Sulphur melts at 115° C. (239° F.) to an amber-colored liquid, which is fluid as water; increasing the heat gradually, it becomes brown and thick, and at about 200° C. (392° F.) it is so tenacious that it scarcely flows; when heated still further it again becomes a thin liquid, and, finally, boils at a temperature of about 440° C. (824° F.).

In its chemical properties sulphur resembles oxygen, being like this element generally bivalent, and supporting, when in the form of vapor, the combustion of many substances, especially the metals. Many compounds of oxygen and sulphur show an analogous composition, as, for instance, $H_2O$ and $H_2S$, $CO_2$ and $CS_2$, CuO and CuS. While the valence of sulphur as a general rule is 2, in some compounds it shows a valence of 4 or 6, as in $SO_2$ and $SO_3$.

**Crude Sulphur.**—Crude sulphur is obtained by heating the rock containing sulphur sufficiently high to cause the sulphur to melt, and thus to separate from the earthy matters. As peculiar conditions (great depth and quicksand) prevented successful working of the sulphur deposits in Louisiana by the ordinary methods, sulphur is now mined there by the following ingenious process: Superheated water, forced through iron pipes to the deposits of sulphur, causes the latter to melt, and this liquefied sulphur is raised through other pipes to the surface by means of compressed air. Crude sulphur generally contains from 2 to 4 per cent. of earthy impurities.

**Sublimed Sulphur** (*Sulphur Sublimatum*) (*Flowers of Sulphur*).—Obtained by heating sulphur to the boiling-point in suitable vessels,

and passing the vapor into large chambers, where it deposits in the form of a powder, composed of small crystals. Sublimed sulphur when melted and poured into round moulds, is known as *roll-sulphur* or *brimstone*.

**Washed Sulphur** (*Sulphur Lotum*) is sublimed sulphur washed with a very dilute ammonia water, and then with pure water; the object of this treatment being to free the sulphur from all adhering sulphurous and sulphuric acid, as also from arsenic compounds which are sometimes present.

**Precipitated Sulphur** (*Sulphur Præcipitatum* (*Milk of Sulphur*).—Made by boiling one part of calcium hydroxide with two parts of sulphur and thirty parts of water, filtering the solution, adding to it dilute hydrochloric acid until nearly neutral, washing and drying the precipitated sulphur.

By the action of sulphur on calcium hydroxide are formed calcium polysulphide, calcium thiosulphate, and water:

$$3Ca(OH)_2 + 12S = 2CaS_5 + CaS_2O_3 + 3H_2O.$$

On adding hydrochloric acid to the solution, both substances are decomposed and sulphur is liberated:

$$2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 12S.$$

While the above equation gives the final result, the decomposition takes place in stages, thus:

$$\begin{aligned} CaS_5 + 2HCl &= CaCl_2 + H_2S + 4S \\ CaS_2O_3 + 2HCl &= CaCl_2 + H_2S_2O_3 \\ 2H_2S + H_2S_2O_3 &= 3H_2O + 4S. \end{aligned}$$

Precipitated sulphur differs from sublimed sulphur by being in a more finely divided state, and by having a much paler yellow, almost white color.

*Experiment* 13.—Mix in a beaker about 10 grams of powdered sulphur, 20 grams of slaked lime, and 200 c.c. of water, and boil until the liquid has a deep brown color. Renew the water that is lost by evaporation occasionally. Note that the color deepens as boiling is continued. This is due to the polysulphide of calcium, which is colored. Finally, filter into a large flask or beaker, wash the filter, dilute to about half a liter, and add dilute hydrochloric acid until the solution is nearly neutral. Note the milk-like appearance of the liquid. Let the sulphur settle fully, decant the liquid, filter and wash the sulphur, and let it dry in the air. Compare its appearance with that of lump sulphur.

The following four oxides are known: Sulphur sesquioxide, $S_2O_3$; sulphur dioxide, $SO_2$; sulphur trioxide, $SO_3$; sulphur heptoxide, $S_2O_7$. The three last named are acid oxides, which, on combining with one molecule of water, form sulphurous, sulphuric, and persulphuric acid respectively.

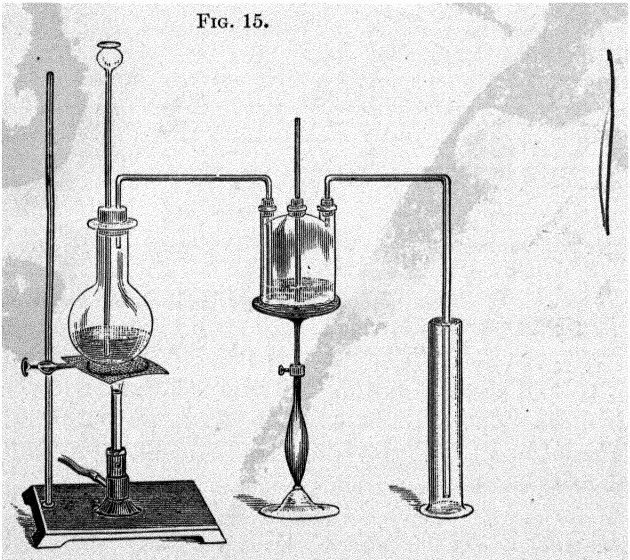
**Sulphur Dioxide, $SO_2$ = 64.07** (*Sulphurous anhydride*, improperly also called *sulphurous acid*), is formed when sulphur or substances containing it in a combustible form ($H_2S$, $CS_2$, etc.) burn in air. It is generated also by the action of strong sulphuric acid on many metals (Cu, Hg, Ag, etc.), or on charcoal:

$$2H_2SO_4 + Cu = CuSO_4 + 2H_2O + SO_2.$$
$$2H_2SO_4 + C = CO_2 + 2H_2O + 2SO_2.$$

Sulphur dioxide is a colorless gas, having a suffocating, disagreeable odor; it liquefies at a temperature of—10° C. (14° F.), and solidifies at —75° C. (—103° F.); it is very soluble in water, forming sulphurous acid; it is a strong, deoxidizing, bleaching, and disinfecting agent; when inhaled in a pure state it is poisonous; when diluted with air it produces coughing and irritation of the air-passages.

**Sulphurous Acid, $H_2SO_3$ or $SO_2.H.OH$.**—This acid, similar to carbonic acid, is not known in a pure state, but is believed to exist in aqueous solution, which decomposes into water and sulphur dioxide when attempts are made to concentrate it. One volume of cold water absorbs about 40 volumes of sulphur dioxide, equal to about 11 per cent. by weight. The acid may be conveniently made by generating sulphur dioxide from charcoal and sulphuric acid in a flask, and passing the gas through a wash-bottle containing water, into distilled water for absorption.

FIG. 15.



Apparatus for making sulphurous acid.

*Experiment* 14.—Use an apparatus as shown in Fig. 15. Place in the flask about 20 grams of charcoal in small pieces, cover it with sulphuric acid, apply heat, and pass the generated gas first through a small quantity of water contained in the wash-bottle, and then into pure water, contained in the cylinder.

The solution, sulphurous acid, may be used for the tests mentioned below; when the neutral solution of a sulphite is required, make this by adding solution of sodium carbonate to a portion of the sulphurous acid until litmus-paper shows neutral reaction. Examine also the contents of the wash-bottle by means of the tests given below for sulphuric acid; most likely some of the latter

will be found. How much carbon and how much $H_2SO_4$ are required to make 100 grams of a 6.4 per cent. sulphurous acid?

Sulphurous acid is a colorless acid liquid, which has the odor as well as the disinfecting and bleaching properties of sulphur dioxide; it is completely volatilized by heat. Sulphurous acid is a dibasic acid, the salts of which are termed *sulphites.* Both the acid and its salts are easily oxidized by the air, and hence almost always give the tests for sulphuric acid. In its chemical behavior sulphurous acid is very much like carbonic acid. It is a weak acid, being displaced from its salts by all acids except carbonic and boric. The sulphites of the alkali metals are freely soluble in water, but the normal sulphites of all other metals are insoluble or nearly so; hence addition of a solution of an alkali sulphite to a solution of salts of the other metals causes precipitates. A few sulphites are soluble in a solution of sulphurous acid, like carbonates, but are precipitated on boiling. Acid sulphites of the alkali metals can be obtained in the solid state. These show an acid reaction to litmus, but the normal sulphites of these metals have an alkaline reaction, due to hydrolysis by water into bisulphite and free alkali. All the common sulphites are white.

The ionic equations for the liberation of sulphurous acid from a sulphite, and the ionization of normal and bisulphites in solution, are in all respects like those pertaining to the liberation of carbonic acid and the ionization of normal and bicarbonate of sodium, which are given on pages 149 and 155. The reason that bisulphites are slightly acid in solution, and not neutral as bicarbonates are, is that an appreciable amount of hydrogen ions are formed, thus:

$$NaHSO_3 \rightleftarrows Na^{\cdot} + HSO_3'$$
$$HSO_3' \rightleftarrows H^{\cdot} + SO_3''.$$

The second reaction takes place only to a small degree.

### Tests for Sulphurous Acid and Sulphites.

(Sodium sulphite, $Na_2SO_3.7H_2O$, may be used.)

1. Add sulphur dioxide gas, or a solution of it in water, or a solution of a sulphite to an acidified solution of potassium permanganate. The latter is decolorized, due to its giving up oxygen, which oxidizes the sulphurous acid, thus:

$$H_2SO_3 + O = H_2SO_4.$$

Make the same experiment with acidified solution of potassium dichromate. The same kind of change takes place, but the decomposition products of the dichromate are green. The reaction will be understood when chromium is studied.

2. Add a few drops of a solution of sulphurous acid or of a sulphite to a tube containing some zinc and dilute sulphuric acid (nascent hydrogen). Hydrogen sulphide is liberated, which can be detected by the odor, or a piece of filter-paper, wet with solution of lead acetate, which blackens when held in the mouth of the tube:

$$H_2SO_3 + 6H = H_2S + 3H_2O.$$

3. Add to a few drops of the sulphite solution about 2 c.c. of silver nitrate solution. A white precipitate of silver sulphite is formed, which darkens on heating, due to reduction to metallic silver:

$$Ag_2SO_3 + H_2O = 2Ag + H_2SO_4.$$

Silver sulphite is soluble in an excess of the sulphite solution.

4. A strip of filter-paper, moistened with mercurous nitrate solution, turns black when suspended in sulphur dioxide, due to reduction to metallic mercury:

$$2HgNO_3 + 2H_2O + SO_2 = 2Hg + H_2SO_4 + 2HNO_3.$$

Tests 1 and 4, along with the odor of sulphur dioxide, are usually sufficient to recognize sulphurous acid or sulphites.

**Sulphur Trioxide, $SO_3$** (*Sulphuric acid anhydride*).—This is a white, silk-like solid substance, having a powerful affinity for water. It may be obtained by the action of phosphoric oxide on strong sulphuric acid, or by passing sulphur dioxide and oxygen together over heated platinum-sponge. It is now made on the large scale by the latter method for producing fuming sulphuric acid.

**Sulphuric Acid** (*Acidum sulphuricum*), **$H_2SO_4$, $SO_2(OH)_2$ = 98.01** (*Oil of Vitriol*).—There is no other acid, and perhaps no other substance, manufactured by chemical action which is so largely used in chemical operations and in the manufacture of so many of the most important articles, as is sulphuric acid.

Impure sulphuric acid was known in the eighth century; in the fifteenth a purer acid was obtained by heating ferrous sulphate (green vitriol) in a retort. To the liquid distilling over the name of oil of vitriol was given, in allusion to its thick or oily appearance and the green vitriol from which it was obtained. The change is shown in the following reaction:

$$4FeSO_4 + H_2O = 2Fe_2O_3 + 2SO_2 + H_2SO_4.SO_3.$$

Sulphuric acid is found in nature in combination with metals as sulphates. Thus calcium sulphate (gypsum), barium sulphate (heavy spar), magnesium sulphate (Epsom salt), and others occur in nature.

**Manufacture of Sulphuric Acid.**—Sulphuric acid is manufactured on a very large scale by passing into large leaden chambers simultaneously, the vapors of sulphur dioxide (obtained by burning sulphur or pyrite in furnaces), nitric acid, and steam, a supply of atmospheric air also being provided for. The most simple explanation that can be given for the manufacture of sulphuric acid is the fact that sulphur dioxide when treated with an oxidizing agent, in the presence of water, is converted into sulphuric acid:

$$SO_2 + O + H_2O = H_2SO_4.$$

Only a portion of the oxygen necessary for oxidation is derived from the nitric acid directly; the larger quantity is obtained from

the atmospheric air, the oxides of nitrogen serving as agents for the transfer of the atmospheric oxygen.

By the action of nitric acid on sulphur dioxide and steam are formed sulphuric acid and nitrogen trioxide:

$$2SO_2 + H_2O + 2HNO_3 = 2H_2SO_4 + N_2O_3.$$

Nitrogen trioxide next takes up sulphur dioxide, water, and oxygen, forming a compound called nitrosyl-sulphuric acid:

$$2SO_2 + N_2O_3 + 2O + H_2O = 2(SO_2.OH.NO_2).$$

This complex compound is readily decomposed by steam into sulphuric acid and nitrogen trioxide:

$$2(SO_2 OH.NO_2) + H_2O = 2H_2SO_4 + N_2O_3$$

The nitrogen trioxide again forms nitrosyl-sulphuric acid, which again suffers decomposition, and so on indefinitely, as long as the constituents necessary for the changes are supplied. These facts show that a given quantity of nitric acid will convert an unlimited amount of sulphurous acid into sulphuric acid. There is, however, an unavoidable loss of small portions of nitric acid, or oxides of nitrogen, for which reason some nitric acid has to be supplied daily.

It is likely that other chemical changes than the ones mentioned take place in the acid chamber, but according to modern investigations these are the principal ones.

The liquid sulphuric acid formed in the lead-chamber collects at the bottom of the chamber, whence it is drawn off. In this state it is known as chamber acid (specific gravity 1.50), and is not pure, but contains about 36 per cent. of water, and frequently either sulphurous or nitric acid. By evaporation in shallow leaden pans it is further concentrated, until it shows a specific gravity of 1.72. When this point is reached the acid acts upon the lead, wherefore the further concentration is conducted in vessels of glass or platinum, until a specific gravity of 1.84 is obtained. This acid contains about 95 per cent. of sulphuric acid; the remaining 5 per cent. of water cannot be expelled by heat.

**Properties of Sulphuric Acid.**—Pure acid has a specific gravity of 1.848; it is a colorless liquid, of oily consistence, boiling at 330° C. (626° F.). When cooled it forms crystals, which melt at 10° C. (50° F.). When heated to about 160° C. (320° F.), the acid begins to fume and gives off sulphur trioxide. The 100 per cent. acid gives off sulphur trioxide, and diluted acid gives off water when heated, until an acid of 98.33 per cent. is reached, which boils at the constant temperature of 330° C. It has a great tendency to combine with water, absorbing it readily from atmospheric air. Upon mixing sulphuric acid and water, heat is generated in consequence of the combination taking place between the two substances. To the same tendency of sulphuric acid to combine with water must be ascribed its property of destroying and blackening organic matter. It is due to this decomposing action of sulphuric acid upon organic matter that traces of the latter color sulphuric acid dark yellow,

brown, and, when present in larger quantities, almost black. The poisonous caustic properties are due to the same action. (See Experiments, page 132.)

Sulphuric acid is a very strong dibasic acid, which expels or displaces most other acids; its salts are known as sulphates.

The *sulphuric acid* of the U. S. P. should contain not less than 92.5 per cent. of $H_2SO_4$, corresponding to a specific gravity of not less than 1.826 at 25° C.

The *diluted sulphuric acid, Acidum sulphuricum dilutum,* is a mixture of 100 parts by weight of acid and 825 parts of water, or of about 60 c.c. of acid and 900 c.c. of water. This corresponds to 10 per cent. of $H_2SO_4$, and a specific gravity of 1.067 at 25° C.

*Great care should be taken in diluting concentrated sulphuric acid. The acid should always be poured slowly into water with constant stirring. It is dangerous to pour the hot acid into water and foolhardy to pour water into the hot acid. Ignorance or disregard of these rules may lead to sad consequences.*

When diluted sulphuric acid acts on metals, hydrogen is liberated and escapes as a gas; but if these same metals are acted on by concentrated sulphuric acid, which usually requires heating, other products are formed, such as sulphur dioxide, hydrogen sulphide, or sulphur. This is due to the fact that the concentrated acid acts as an oxidizing agent toward the hydrogen that would otherwise be evolved, and itself is reduced. Certain metals do not act on dilute sulphuric acid at all, but only on the hot concentrated acid, and under these conditions hydrogen is never evolved. This is illustrated in the preparation of sulphur dioxide by heating the concentrated acid with copper. Other substances, as charcoal, sulphur, etc., that can be oxidized, act in the same way on the hot, strong acid.

Most sulphates are soluble in water. There are practically only three which are insoluble in water or dilute acids, namely, barium, strontium, and lead. Calcium sulphate is slightly soluble in water, and more so in hydrochloric acid. A solution of it is used as a reagent.

Most sulphates are more or less easily decomposed when heated, but those of potassium, sodium, lithium, calcium, strontium, and barium can stand red heat.

Sulphuric acid, like all dibasic acids, has two modes of ionizing according to concentration (see page 154). In more concentrated solutions, the ions $H^\cdot$ and $HSO_4'$ predominate; in dilute solutions, $2H^\cdot$ and $SO_4''$ predominate. Upon diluting a more concentrated solution, $HSO_4'$ ions dissociate further, thus:

$$HSO_4' \rightleftarrows H^\cdot + SO_4''.$$

The same thing takes place when $SO_4''$ ions are removed by precipitation, which has an effect equivalent to diluting the acid.

Tests 1 and 2 below are examples of reversible reactions that run practically to completion, because of the removal of one of the factors by precipitation, due to its insolubility (page 129). These tests, like all similar ones that follow, are explained in terms of the ionic theory on pages 148 and 154.

**Tests for Sulphuric Acid and Sulphates.**

1. When a solution of barium chloride is added to dilute sulphuric acid, or a solution of any sulphate, a white precipitate of barium sulphate is obtained, which is insoluble in all dilute acids:

$$Na_2SO_4 + BaCl_2 = BaSO_4 + 2NaCl$$
$$2Na^{\cdot} + SO_4'' + Ba^{\cdot\cdot} + 2Cl' = BaSO_4 + 2Na^{\cdot} + 2Cl'.$$

Usually this test alone is sufficient for recognition, as all other ordinary barium salts are soluble in hydrochloric or nitric acid. It is very delicate.

2. When a solution of lead nitrate or acetate is employed, a white precipitate of lead sulphate, $PbSO_4$, is obtained. This is soluble in a solution of ammonium acetate.

3. Grind together in a mortar a knife-pointful of a sulphate, sulphur, or any compound containing it, with 5 to 10 times its bulk of sodium carbonate and about 3 times its bulk of potassium cyanide. Place the mixture in a hole in a piece of charcoal and heat with the blow-pipe flame until it is thoroughly fused. The mass now contains yellowish-brown alkali sulphide (hepar), due to reduction of the sulphate by the hot charcoal and potassium cyanide. The sodium carbonate serves as a *flux*, or fusing material.

Remove the mass, place it upon a silver coin, and moisten it with dilute hydrochloric acid. A black stain of silver sulphide will be formed. This test is of value in the case of insoluble sulphates and sulphides.

The above procedure is known as the *charcoal reduction test*, and is one of the steps taken in systematic qualitative analysis.

**Antidotes.**—Magnesia, sodium carbonate, chalk, and soap, to neutralize the acid.

**Acids of Sulphur.**—While but four oxides of sulphur exist in the separate state, there are a large number of acids containing sulphur, some of which, however, are known only as constituents of the respective salts. The acids are:

| | | | |
|---|---|---|---|
| Hyposulphurous acid, | $H_2S_2O_4$. | Thiosulphuric acid, | $H_2S_2O_3$. |
| Sulphurous acid, | $H_2SO_3$. | Dithionic acid, | $H_2S_2O_6$. |
| Sulphuric acid, | $H_2SO_4$. | Trithionic acid, | $H_2S_3O_6$. |
| Pyrosulphuric acid, | $H_2S_2O_7$. | Tetrathionic acid, | $H_2S_4O_6$. |
| Persulphuric acid, | $H_2S_2O_8$. | Pentathionic acid, | $H_2S_5O_6$. |

Hydrogen sulphide, $H_2S$.

**Pyrosulphuric Acid, $H_2S_2O_7$** (*Disulphuric acid, fuming sulphuric acid, Nordhausen oil of vitriol*).—This acid is made by passing sulphur trioxide (obtained by heating ferrous sulphate) into sulphuric acid, when direct combination takes place:

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

It is a thick, highly corrosive liquid, which gives off dense fumes when exposed to the air, and decomposes readily into sulphur trioxide and sulphuric acid when heated.

**Thiosulphuric Acid,** *formerly* **Hyposulphurous Acid, $H_2S_2O_3$, $SO_2.SH.OH$,** is of interest because some of its salts are used, as, for instance, sodium thiosulphate, $Na_2S_2O_3$, the sodium hyposulphite of commerce. The acid itself is not known in the separate state, since it decomposes into sulphur and sulphurous acid when attempts are made to liberate it from its salts.

Sulphuric is the most stable acid of sulphur, and all the others have a tendency to pass to this acid. It is for this reason that both sulphites and thiosulphates are good reducing agents. A solution of a thiosulphate, when added to an acidified solution of potassium permanganate or dichromate, acts in the same way as a sulphite does. The essential reaction is:

$$Na_2S_2O_3 + 4O + H_2O = Na_2SO_4 + H_2SO_4.$$

Thiosulphates also react with the halogen elements in the manner shown by this reaction:

$$2Na_2S_2O_3 + 2I = Na_2S_4O_6 + 2NaI,$$

forming sodium tetrathionate and sodium iodide. This reaction is used for the quantitative estimation of free iodine and in the preparation of so-called decolorized tincture of iodine. It may also be used for removing iodine stains from the skin or fabrics.

Most of the thiosulphates are soluble in water, those of barium, lead, and silver being only very sparingly soluble. Alkali thiosulphates have a marked solvent action on many salts that are insoluble in water, forming double thiosulphates. All thiosulphates are decomposed by acids.

### Tests for Thiosulphates.

(Use about a 5 per cent. solution of sodium thiosulphate.)

1. The solution, upon addition of dilute sulphuric or hydrochloric acid, liberates sulphur dioxide, while sulphur is precipitated more or less rapidly, according to the concentration and temperature. The formation of these two products is characteristic and the test is sufficient for recognition of a thiosulphate. The precipitate of sulphur distinguishes it from a sulphite.

2. Addition of silver nitrate gives a white precipitate of silver thiosulphate, $Ag_2S_2O_3$, which is immediately dissolved if the sodium thiosulphate is in excess. The precipitate is rather unstable, and decomposes on standing, and more rapidly on heating, giving black silver sulphide and sulphuric acid,

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

Addition of solution of lead nitrate or acetate to thiosulphate solution gives similar results. Most thiosulphates are unstable, like those of silver and lead.

3. Barium chloride solution gives a white precipitate of barium thiosulphate, $BaS_2O_3$. Calcium chloride, however, gives no precipitate, whereas with a sulphite a precipitate is formed.

**Persulphuric acid, $H_2S_2O_8$,** is obtained by passing an electric current through sulphuric acid of a specific gravity 1.3 to 1.5. The reaction is this:

$$2H_2SO_4 = 2H + H_2S_2O_8.$$

The ammonium or potassium salts of this acid are obtained by the electrolysis of saturated solutions of the bisulphates of the metals, thus:

$$2KHSO_4 = K_2S_2O_8 + H_2.$$

Persulphuric acid and its salts act as strong oxidizing agents, liberating, for instance, chlorine from hydrochloric acid or from chlorides.

**Hydrogen Sulphide, $H_2S$** (*Sulphuretted hydrogen*).—This compound has been mentioned as being liberated by the decomposition of organic matter (putrefaction) and as a constituent of some spring waters. It is formed also during the destructive distillation of organic matter containing sulphur. The best mode of obtaining it is the decomposition of metallic sulphides by diluted sulphuric or hydrochloric acid. Ferrous sulphide is usually selected for decomposition:

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

*Experiment* 15.—Use apparatus shown in Fig. 15, page 160. Place about 20 grams of ferrous sulphide in the flask, cover the pieces with water, and add sulphuric or hydrochloric acid. Pass a portion of the washed gas into water, another portion into ammonia water. Use the solutions for the tests mentioned below. Ignite the gas at the delivery tube and notice that sulphur is deposited upon the surface of a cold plate held in the flame. Place the apparatus in the fume chamber during the operation. How much ferrous sulphide is required to liberate a quantity of hydrogen sulphide sufficient to convert 1000 grams of 10 per cent. ammonia water into ammonium sulphide solution? The reaction taking place is this:

$$2NH_3 + H_2S = (NH_4)_2S.$$

Hydrogen sulphide is a colorless gas, having an exceedingly offensive odor and a disgusting taste. Water absorbs about three volumes of the gas, and this solution is feebly acid. It is highly combustible in air, burning with a blue flame, and forming sulphur dioxide and water. It is directly poisonous when inhaled, its action depending chiefly on its power of reducing, and combining with, the blood-coloring matter. Plenty of fresh air, or air containing a very little chlorine, should be used as an antidote.

Hydrogen sulphide can be driven completely from its aqueous solution by heating. It is a rather unstable compound, being easily broken up into its constituents. For this reason it is a good reducing agent. For example, sulphur dioxide is reduced by it to sulphur, but is not affected by free hydrogen gas:

$$2H_2S + SO_2 = 2H_2O + 3S.$$

It is probable that native sulphur found in volcanic regions is produced in this way. Because of the instability of the gas, its sulphur often acts like sulphur in the free state. Thus, the metals from potassium to silver inclusive in the electrochemical series (see page 152) soon become tarnished with a layer of sulphide when exposed to the gas:

$$2Ag + H_2S = Ag_2S + 2H.$$

The solution of hydrogen sulphide is slowly affected by oxygen of the air with precipitation of sulphur, $H_2S + O = H_2O + S$. Hence, it does not keep except in full bottles. In solution it is a dibasic acid of extremely weak character, only 0.07 per cent. of the molecules being dissociated, mainly according to this equation:

$$H_2S \rightleftarrows H^{\cdot} + HS'.$$

The ion $HS'$ also dissociates, but to a less degree even than water:

$$HS' \rightleftarrows H^{\cdot} + S''.$$

Hydrogen sulphide, like any dibasic acid, can give two kinds of salts, acid and normal; for example, sodium hydrosulphide, NaHS, and sodium sulphide, $Na_2S$. The acid salt is obtained in solution, when hydrogen sulphide is passed into a solution of sodium hydroxide to saturation. It has a neutral reaction:

$$NaOH + H_2S = NaHS + H_2O.$$

In solution it dissociates, thus:

$$NaHS \rightleftarrows Na^{\cdot} + HS'.$$

The normal salt, $Na_2S$, does not exist in solution, but can be obtained in the dry state by adding to the acid salt an amount of alkali equal to that used in making the same, and evaporating to dryness:

$$NaHS + NaOH = Na_2S + H_2O.$$

When the dry salt is dissolved in water, it is completely hydrolyzed into the acid salt and free alkali, and, therefore, has a strong alkaline reaction:

$$Na_2S + H_2O = NaHS + NaOH.$$

Hydrogen sulphide gas and its solution in water are frequently used as reagents in analytical chemistry for precipitating and recognizing metals. This use depends on the property of the sulphur to combine with many metals to form insoluble compounds, the color of which frequently is very characteristic:

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

The sulphides that are insoluble in water fall approximately into three groups:

1. Those that are almost completely insoluble in water, such as the sulphides of lead, copper, bismuth, silver, mercury, arsenic, antimony, tin, and a few others. These, moreover, are not dissolved by *dilute* acids, and hence are precipitated from solutions of salts of the metals by passing hydrogen sulphide into them even when a little free acid is present:

$$Pb(NO_3)_2 + H_2S = \underset{\text{Lead sulphide.}}{PbS} + 2HNO_3,$$

or $$Pb^{\cdot\cdot} + 2(NO_3)' + 2H^{\cdot} + S'' = PbS + 2H^{\cdot} + 2(NO_3)'.$$

2. Those that are practically insoluble in water, yet more soluble than the sulphides of group 1, and are dissolved by even very dilute active acids. The metals iron, cobalt, nickel, manganese, zinc, and a few others form such sulphides. Some of these sulphides are so readily soluble in dilute acids that they are prevented from being precipitated by hydrogen sulphide by the acid that would be liberated in the reaction (see equation above). In the case of zinc salts partial precipitation takes place until equilibrium is reached, but if some free acid is present, no precipitation takes place. To form the sulphides of this group, a salt of hydrogen sulphide, such as ammonium or sodium sulphide, is applied to neutral solutions of the salts of the metals, thus:

$$FeSO_4 + (NH_4)_2S = \underset{\text{Iron sulphide.}}{FeS} + (NH_4)_2SO_4,$$

or $$Fe^{\cdot\cdot} + SO_4'' + 2(NH_4)^{\cdot} + S'' = FeS \downarrow + 2(NH_4)^{\cdot} + SO_4''.$$

3. Those that are known only in the dry state, and although they are insoluble as such in water, yet they dissolve because they are hydrolyzed into soluble products, thus:

$$2CaS + 2H_2O = Ca(OH)_2 + Ca(SH)_2.$$

The sulphides of barium, strontium, and calcium belong to this class. They cannot be precipitated, either by hydrogen sulphide or ammonium sulphide. They are generally made from the sulphate by heating with carbon (reduction to sulphide).

Solutions of normal sulphides, as $Na_2S$, and acid sulphides, as NaHS, or $NH_4HS$, when used as reagents in precipitation of insoluble sulphides, give the same results because of the presence of $S''$ ions, which unite with the ions of the other metals.

### Tests for Hydrogen Sulphide or Sulphides.

1. Hydrogen sulphide or soluble sulphides (ammonium sulphide may be used) when added to soluble salts of lead, copper, mercury, etc., give black precipitates of the sulphides of those metals.

2. From insoluble sulphides (ferrous sulphide, FeS, may be used) liberate the gas by dilute sulphuric or hydrochloric acid, and test as above, or suspend a piece of filter-paper, moistened with solution of lead acetate, in the liberated gas, when the paper turns dark. Some sulphides, for instance, those of mercury, gold, platinum, as also $FeS_2$, and a few others, are not decomposed by the acids mentioned, unless zinc be added.

**Carbon Disulphide, $CS_2$ = 76.14.**—This compound is obtained by passing vapors of sulphur over heated charcoal. It is a colorless,

highly refractive, very volatile, and inflammable neutral liquid, having a characteristic odor and a sharp, aromatic taste. It boils at 46° C. (115° F.); it is almost insoluble in water, soluble in alcohol, ether, chloroform, fixed and volatile oils; for the latter two it is an excellent solvent, but dissolves, also, many other substances, such as sulphur, phosphorus, iodine, many alkaloids, etc.

**Selenium, Se, and Tellurium, Te,** are but rarely met with. Both elements show much resemblance to sulphur; both are polymorphous; both combine with hydrogen, forming $H_2Se$ and $H_2Te$, gaseous compounds having an odor more disagreeable even than that of $H_2S$. Like sulphur, they form dioxides, $SeO_2$ and $TeO_2$, which combine with water, forming the acids $H_2SeO_3$ and $H_2TeO_3$, analogous to $H_2SO_3$. The acids $H_2SeO_4$ and $H_2TeO_4$, corresponding to $H_2SO_4$, also are known.

**Ionic mechanism of the solution by acids of salts that are insoluble in water.** The operation of dissolving by the aid of an acid, salts that are insoluble in water is resorted to frequently in general chemical work, and particularly in chemical analysis. It is a matter of observation, too, that a salt will dissolve in some acids, but not in others; also that of salts of the same acid with different metals, some will dissolve in a given acid, while others will not. Thus zinc sulphide is soluble in dilute hydrochloric acid, but not in acetic, and the same is true of calcium oxalate and calcium phosphate. Iron sulphide is soluble in most any dilute acid, but copper sulphide is not appreciably dissolved by the same acids. The student often wonders what the explanation is of such facts as these. The ionic theory gives a physical basis for accounting for them.

Solution is the converse of precipitation. In the discussion of the latter subject (see page 148) it is stated that whenever there are more ions of a substance than a saturated solution of that substance can maintain, the excess of ions unite to molecules, which separate from solution as a precipitate. The more insoluble the substance is the smaller is the concentration of molecules and ions that can be maintained in its saturated solution, and the more complete is the precipitation. Every "insoluble" substance is soluble to some extent in water, even if only minutely. But many of the so-called insoluble salts are slightly soluble in water, which is an important factor in accounting for the solution of salts by acids. Now, water in contact with such a salt becomes saturated, that is, it takes up the maximum number of molecules and ions that it can hold (which, of course, is not large), and these are in equilibrium. If in any way the concentration of the negative (acid radical) ion is diminished, more molecules dissociate to keep up the concentration of that ion, which results in the dissolving of more molecules of the solid salt to keep up saturation and equilibrium. If the negative ions of the salt are of an acid that has a slight dissociating power, their concentration will be diminished when an active (highly dissociating) acid is added to the mixture, thereby furnishing an abundance of $H^{\cdot}$ ions, with which the negative ions of the salt unite to form undissociated molecules of the acid. If the concentration of the negative ions of the salt is greater than that which can be maintained by the corresponding acid, the salt will dissolve by the addition of an active acid, in keeping with the principle of equilibrium as involved in the dissociation con-

stant (see page 146). Even an acid of a moderate degree of dissociation may have its dissociation reversed to such an extent in the presence of an excess of a highly dissociating acid, like hydrochloric, that it becomes equivalent to a slightly dissociating acid, and does not maintain as great a concentration of its negative ion as is maintained by its slightly soluble salts in water. This is illustrated by the solution of calcium oxalate in excess of hydrochloric acid. In the case of highly insoluble salts, like barium sulphate, the amount dissolved, and consequently the concentration of its ions, is so extremely small that addition of active acids has very little effect in reducing the concentration of the negative ion. Hence, extremely little of such a salt is dissolved by acids. Such salts evidently can be precipitated in an acid medium, whereas the salts that are dissolved by a given acid cannot be precipitated in the presence of that acid.

The points just discussed may be given a more concrete form by the consideration of the sulphide of iron and of copper. When dilute hydrochloric acid is added to iron sulphide, hydrogen sulphide is evolved. The ionic representation of the act of solution is the following:

$$\left.\begin{array}{rcl} \text{FeS (slightly soluble)} & \rightleftarrows & \text{Fe}^{\cdot\cdot} + \text{S}'' \\ 2\text{HCl} & \rightleftarrows & 2\text{Cl}' + 2\text{H}^{\cdot} \end{array}\right\} \rightleftarrows \text{H}_2\text{S}.$$

The negative ion $S''$ coming from the slight amount of FeS dissolved in water is also the ion of $H_2S$. Hydrogen sulphide dissociates to a less degree than does FeS; that is, the concentration of $S''$ that can be maintained by $H_2S$ in solution is less than that which can be maintained by FeS in solution. The result is that some $S''$ ions unite with $H^{\cdot}$ ions of the hydrochloric acid to form undissociated molecules of $H_2S$, thus reducing the concentration of $S''$ ion. More FeS dissolves to keep up the equilibrium. This is kept up until all the FeS is dissolved, or until (if FeS is in excess) the HCl is so much exhausted that the little which remains is in equilibrium with the other products. As the $H_2S$ accumulates, the solution becomes saturated and the excess escapes as gas.

In the case of copper sulphide, dilute hydrochloric acid has no action. The ionic reactions would be:

$$\left.\begin{array}{rcl} \text{CuS (very slightly soluble)} & \rightleftarrows & \text{Cu}^{\cdot\cdot} + \text{S}'' \\ 2\text{HCl} & \rightleftarrows & 2\text{Cl}' + 2\text{H}^{\cdot} \end{array}\right\} \rightleftarrows \text{H}_2\text{S}.$$

But the concentration of $S''$ ions maintained by CuS in solution is less than that maintained by $H_2S$ in solution, even in the presence of the excess of $H^{\cdot}$ ions of the dilute hydrochloric acid, which repress to some extent the dissociation of $H_2S$. Hence, not only is there no solution of the copper sulphide, but if $H_2S$ is passed into an acidified solution of a copper salt, CuS is precipitated. Only a rather concentrated solution of hydrochloric acid will so far reduce the concentration of $S''$ ions as to allow the copper sulphide to dissolve.

The subject may be summed up in a general statement, thus: *The difficultly soluble salts of weaker (less ionized) acids are, as a rule, dissolved by solutions of the stronger (more ionized) acids. Exceptions are salts of extreme insolubility of stronger acids, and, in a few cases, even of weaker acids.*

## 15. PHOSPHORUS.

$P^{III \text{ or } V} = 31.04.$

**Occurrence in Nature.**—Phosphorus is found in nature chiefly in the form of phosphates of calcium (*apatite, phosphorite*), iron, and aluminum, which minerals form deposits in some localities, but occur also diffused in small quantities through all soils upon which plants will grow, phosphorus being an essential constituent of the food of most plants. Through the plants it enters the animal system, where it is found either in organic compounds, or—and this in by far the greater quantity—as tricalcium phosphate principally in the bones, which contain about 60 per cent. of it. From the animal system it is eliminated chiefly in the urine.

**Manufacture of Phosphorus.**—Phosphorus was discovered and made first in 1669 by Brandt, of Hamburg, Germany, who obtained it in small quantities by distilling urine previously evaporated and mixed with sand.

The manufacture of phosphorus today depends on the deoxidation of metaphosphoric acid by carbon at a high temperature in retorts.

The acid is obtained by adding to any suitable tricalcium phosphate sulphuric acid in a quantity sufficient to combine with the total amount of calcium present. The first action of sulphuric acid upon the phosphate consists in a removal of only two-thirds of the calcium present, and the formation of an acid phosphate:

$$Ca_3(PO_4)_2 + 3H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4 + H_2SO_4.$$

The nearly insoluble calcium sulphate is separated by filtration, and the solution of acid phosphate containing free sulphuric acid is evaporated to the consistency of a syrup, when more calcium sulphate separates and a solution of nearly pure phosphoric acid is left:

$$CaH_4(PO_4)_2 + H_2SO_4 = CaSO_4 + 2(H_3PO_4).$$

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QUESTIONS.—How is sulphur found in nature? Mention of sulphur: atomic weight, valence, color, odor, taste, solubility, behavior when heated, and allotropic modifications. State the processes for obtaining sublimed, washed, and precipitated sulphur. State composition and mode of preparing sulphur dioxide and sulphurous acid; what are they used for, and what are their properties? Explain the process for the manufacture of sulphuric acid on a large scale. Mention of sulphuric acid: color, specific gravity, its action on water and organic substances. Give tests for sulphates and sulphites, sulphuric and sulphurous acids. What is the difference between sulphates, sulphites, and sulphides? How is hydrogen sulphide formed in nature, and by what process is it obtained artificially? What are its properties, and what is it used for? Mention antidotes in case of poisoning by sulphuric acid and hydrogen sulphide.

This syrupy phosphoric acid is mixed with coal and heated to a temperature sufficiently high to expel water and convert the ortho- into meta-phosphoric acid:

$$2(H_3PO_4) = 2HPO_3 + 2H_2O.$$

The dry solid mixture of this acid and charcoal is now introduced into retorts and heated to a strong red heat, when the following decomposition takes place:

$$2(HPO_3) + 5C = H_2O + 5CO + 2P.$$

The three products formed escape in the form of gases from the retort, and by passing them through cold water phosphorus is converted into a solid. The reaction in the retorts is somewhat more complicated than above stated in the equation, as some gaseous hydrogen phosphide and a few other products are formed in small quantities.

Also phosphorus is now made by subjecting to the action of a strong electric current a mixture of tricalcium phosphate and carbon, when phosphorus is set free, while calcium carbide and carbonic oxide are formed:

$$Ca_3(PO_4)_2 + 14C = 2P + 3CaC_2 + 8CO.$$

**Properties of Phosphorus.**—When recently prepared, phosphorus is a colorless, translucent, solid substance, which has somewhat the appearance and consistency of bleached wax. In the course of time, and especially on exposure to light, it becomes by degrees less translucent, opaque, white, yellow, and finally yellowish-red. At the freezing-point phosphorus is brittle; as the temperature increases it gradually becomes softer, until it fuses at 44° C. (111° F.), forming a yellowish fluid, which at 290° C. (554° F.) (in the absence of oxygen) is converted into a colorless vapor. Specific gravity 1.83 at 10° C. (50° F.).

The most characteristic features of phosphorus are its great affinity for oxygen, and its luminosity, visible in the dark, from which latter property its name, signifying "carrier of light," has been derived. In consequence of its affinity for oxygen, phosphorus has to be kept under water, as it invariably takes fire when exposed to the air, the slow oxidation taking place upon the surface of the phosphorus soon raising it to 50° C. (122° F.), at which temperature it ignites, burning with a bright white flame, and giving off dense, white fumes of phosphoric oxide. The luminosity of phosphorus, due to this slow oxidation, is seen when a piece of it is exposed to the air, and whitish vapors are emitted which are luminous in the dark; at the same time an odor resembling that of garlic is noticed.

Phosphorus is insoluble in water, sparingly soluble in alcohol, ether, fatty and essential oils, very soluble in chloroform and in disulphide of carbon, from which solution it separates in the form of crystals.

Although nitrogen has very weak chemical affinities, while those of phosphorus are extremely strong, yet there is a close resemblance in the chemical properties of these two elements. Both are chiefly either trivalent or quinquivalent; both form compounds correspond-

ing to one another in composition, as also in properties. Thus we know the two gaseous compounds $NH_3$ and $PH_3$; the oxides $N_2O_3$, $N_2O_5$, and $P_2O_3$, $P_2O_5$. There is also metaphosphoric acid, $HPO_3$, corresponding to nitric acid, $HNO_3$. The chlorides $NCl_3$ and $PCl_3$ are known, and many other corresponding features may be pointed out. It will be shown later that nitrogen and phosphorus have a close resemblance to the elements arsenic and antimony.

Phosphorus not only combines directly with oxygen, but also with chlorine, bromine, iodine, sulphur, and with many metals, the latter compounds being known as *phosphides*.

Phosphorus is trivalent in some compounds, as in $PCl_3$, $P_2O_3$; quinquivalent in others, as in $PCl_5$, $P_2O_5$.

The molecules of most elements contain two atoms; phosphorus is an exception to this rule, its molecule containing four atoms. The molecular weight of phosphorus is consequently $4 \times 31.04 = 124.16$.

**Allotropic Modifications.**—Several allotropic modifications of phosphorus are known, of which the *red phosphorus* (frequently called *amorphous phosphorus*) is the most important. This variety is obtained by exposing common phosphorus for some time to a temperature of 260° C. (500° F.), in an atmosphere of carbon dioxide. The change takes place rapidly when a higher temperature is used and pressure is applied. This modified phosphorus is a red powder, which differs widely from common phosphorus. It is not poisonous, not luminous, not soluble in the solvents above mentioned, not combustible until it has been heated to about 280° C. (536° F.), when it is reconverted into common phosphorus.

**Use of Phosphorus.**—By far the largest quantity of all phosphorus (both common and red) is used for matches, which are made by dipping wooden splints into some combustible substance, as melted sulphur or paraffin, and then into a paste made by thoroughly mixing phosphorus with glue in which some oxidizing agent (potassium nitrate or chlorate) has been dissolved. Such matches are poisonous and easily ignited, hence the manufacture of them has been prohibited in most European countries. Workmen in match factories in which yellow phosphorus is used are the victims of chronic poisoning, which results in destruction of bones and tissues, and often death. To avoid these fearful ravages, harmless phosphorus sesquisulphide is now used instead of yellow phosphorus. In this country the Diamond Match Company controlled the sesquisulphide process, but it magnanimously gave up its patent and allowed all match manufacturers to use it. Phosphorus sesquisulphide, $P_2S_3$, is made by heating together the elements in proper proportions, red phosphorus being generally used because of the violence of the action with yellow phosphorus.

The so-called "safety matches" contain a mixture of antimony trisulphide, red lead, and the chlorate and dichromate of potassium. This mixture will not ignite by simple friction, but does so when drawn across a surface upon which is a mixture of red phosphorus and antimony pentasulphide.

Pharmaceutical preparations containing phosphorus in the elementary state are *phosphorated oil, pills of phosphorus,* and *spirit of phosphorus.* The second is official.

Phosphorus is also used for making phosphoric acid and other compounds.

**Poisonous properties of phosphorus; antidotes.** Common phosphorus is extremely poisonous, two kinds of phosphorus-poisoning being distinguished. They are the acute form, consequent upon the ingestion of a poisonous dose, and the chronic form affecting the workmen employed in the manufacture of phosphorus or of lucifer matches.

In cases of poisoning by phosphorus, efforts should be made to eliminate the poison as rapidly as possible by means of stomach-pump, emetics, or cathartics. As antidote a one-tenth per cent. solution of potassium permanganate has been used successfully; it acts by oxidizing the phosphorus, converting it into ortho-phosphoric acid. Oil of turpentine has also been used as an antidote, though its action has not been sufficiently explained. Oil or fatty matter (milk) must not be given, as they act as solvents of the phosphorus, causing its more ready assimilation.

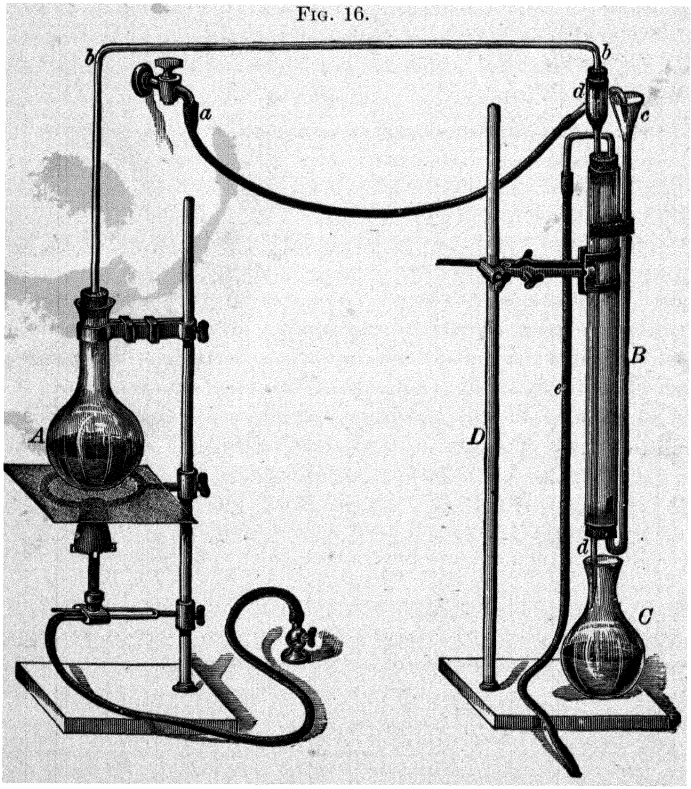
**Detection of phosphorus in cases of poisoning.** Use is made of its luminous properties in detecting phosphorus, when in the elementary state. Organic matter (contents of stomach, food, etc.) containing phosphorus will often show this luminosity when agitated in the dark. If this process fails, in consequence of too small a quantity of the poison, a portion of the matter to be examined is rendered fluid by the addition of water, slightly acidulated with sulphuric acid, and placed in a flask, which is connected with a bent glass tube leading to a Liebig's condenser. The apparatus (Fig. 16) is placed in the dark, and the flask is heated. If phosphorus be present, a luminous ring will be seen where the glass tube, leading from the flask, enters the condenser. The heat should be raised gradually to the boiling-point, the liquid kept boiling for some time, and the products of distillation collected in a glass vessel. Phosphorus volatilizes with the steam, and small globules of it may be found in the collected fluid. If, however, the quantity of phosphorus in the examined matter was very small, it may all have become oxidized during the distillation, and the fluid will then contain phosphorous acid, the tests for which will be stated below

It should be mentioned that the luminosity of phosphorus vapors is diminished, or even prevented, by vapors of essential oils (oil of turpentine, for instance), ether, olefiant gas, and a few other substances.

**Oxides of Phosphorus.**—Four oxides of phosphorus are known. They are *phosphorus monoxide,* $P_4O$, *phosphorus trioxide,* $P_2O_3$, *phosphorus tetroxide,* $P_2O_4$, and *phosphorus pentoxide,* $P_2O_5$. Of these, the pentoxide is the only important one. It is obtained as a white powder when phosphorus is burned in excess of air, $2P + 5O = P_2O_5$. It combines with water with great energy, forming metaphosphoric acid, $P_2O_5 + H_2O = 2HPO_3$. Its intense affinity for water is often utilized in the laboratory for drying gases and for extracting the elements of water from compounds. Vapor density determination shows that its formula is $P_4O_{10}$, but its chemical behavior is just as well accounted for by the simpler formula, $P_2O_5$.

Phosphorus trioxide is formed when phosphorus is burned in a tube in a limited supply of air. It is a white solid which melts at 22.5° C. and boils at 173° C. Because of its low boiling point, it can be separated by distillation from the pentoxide. It unites readily with oxygen, hence its distillation must be conducted out of contact with air. Its vapor density points to the formula, $P_4O_6$, but the simpler one, $P_2O_3$, is often used. It unites very slowly with cold water to form phosphorous acid, $P_2O_3 + 3H_2O = 2H_3PO_3$. With hot water it acts energetically, but the principal products are red phosphorus, phosphine, hypophosphoric and phosphoric acids. When the trioxide is heated to 440° C. it decomposes into the oxide, $P_2O_4$, and red phosphorus.

FIG. 16.




Apparatus for detection of phosphorus in cases of poisoning.

**Acids of Phosphorus.**—There are four different acids representing probably four distinct oxidation stages of phosphorus. Hypophosphorous acid, $H_3PO_2$, of which the corresponding oxide (acid anhydride) is not known, is chiefly of pharmaceutical interest. Phosphorous acid, $H_3PO_3$, derived from the oxide, $P_2O_3$, and hypophosphoric acid, $H_4P_2O_6$, are practically of no importance. The three

acids derived from the same oxide, $P_2O_5$, by different degrees of hydration, namely, orthophosphoric, $H_3PO_4$, pyrophosphoric, $H_4P_2O_7$, and metaphosphoric, $HPO_3$ are most important. They represent the highest stage of oxidation of phosphorus, namely, the pentoxide.

**Hypophosphorous Acid** (*Acidum hypophosphorosum*), $H_3PO_2$, $PO.H_2.OH = 66.06$.—When phosphorus is heated with solution of potassium, sodium, or calcium hydroxide, the hypophosphite of these metals is formed, while gaseous hydrogen phosphide, $PH_3$, is liberated and ignites spontaneously. The action may be represented thus:

$$3KOH + 4P + 3H_2O = 3KPH_2O_2 + PH_3;$$

or

$$3Ca(OH)_2 + 8P + 6H_2O = 3Ca(PH_2O_2)_2 + 2PH_3.$$

From calcium hypophosphite the acid may be obtained by decomposing the salt with oxalic acid, which forms insoluble calcium oxalate, while hypophosphorous acid remains in solution:

$$Ca(PH_2O_2)_2 + H_2C_2O_4 = CaC_2O_4 + 2HPH_2O_2.$$

From potassium hypophosphite the acid may be liberated by the addition of tartaric acid and alcohol, when potassium acid tartrate forms, which is nearly insoluble in dilute alcohol and may be separated by filtration.

Pure hypophosphorous acid is a white crystalline substance, acting energetically as a deoxidizing agent. Although containing three atoms of hydrogen, it is a monobasic acid, only one of the hydrogen atoms being replaceable by metals.

*Hypophosphorous acid* of the U. S. P. contains 30 per cent. and the diluted acid 10 per cent. of the pure acid dissolved in water. Both preparations are colorless acid liquids, which, upon heating, lose water and are afterward decomposed into phosphoric acid and hydrogen phosphide, which ignites:

$$2H_3PO_2 = H_3PO_4 + PH_3.$$

Similar to the case of sulphur, the most stable acid of phosphorus is phosphoric acid, and the others show a tendency to pass to it. These are, therefore, easily oxidized and also easily reduced. Thus, hypophosphorus acid is not only quickly oxidized by the usual oxidizing agents, but even precipitates many metals from their salts. Hypophosphites, when brought into the presence of nascent hydrogen, are reduced to phosphine gas, $PH_3$ (compare with sulphites). All hypophosphites are soluble in water and nearly all are colorless. About six are used in medicine.

### Tests for Hypophosphites.

(Use about a 5 per cent. solution of the sodium salt, $NaPH_2O_2$.)

1. Heat a small quantity of the dry sodium salt in a procelain dish until it ignites. The salt is decomposed into a phosphate and phos-

phine, which burns with a characteristic brilliant light, emitting a white cloud of oxide of phosphorus. Some red phosphorus is also formed.

$$2NaPH_2O_2 = Na_2HPO_4 + PH_3.$$
$$2PH_3 + 8O = P_2O_5 + 3H_2O. \quad 2PH_3 + 3O = 2P + 3H_2O.$$

2. Acidify about 5 c.c. of the solution with dilute hydrochloric acid, and add some mercuric chloride solution. A white precipitate of mercurous chloride is formed. Above 60° C. and with excess of the hypophosphite, further reduction to dark metallic mercury takes place.

$$4HgCl_2 + Na.PH_2O_2 + 2H_2O = 4HgCl + H_3PO_4 + NaCl + 3HCl.$$
$$4HgCl + NaPH_2O_2 + 2H_2O = 4Hg + H_3PO_4 + NaCl + 3HCl.$$

3. Addition of silver nitrate solution causes a dark precipitate of metallic silver. In the first instant, a white precipitate of silver hypophosphite is seen, but this is very unstable.

$$NaPH_2O_2 + 4AgNO_3 + 2H_2O = 4Ag + NaH_2PO_4 + 4HNO_3.$$

4. When the solution is added to acidified potassium permanganate solution, the latter is decolorized. The essential reaction is this,

$$NaPH_2O_2 + O_2 = NaH_2PO_4.$$

Tests 1 and 2 are very distinctive and usually sufficient to recognize the acid or its salts.

**Phosphorous Acid, $H_3PO_3$, PO.H.(OH)$_2$.**—This is a dibasic acid obtained by dissolving phosphorous oxide in water:

$$P_2O_3 + 3H_2O = 2H_3PO_3.$$

or still better by the action of water on phosphorus trichloride:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

It is a colorless acid liquid, which forms salts known as phosphites; it is a strong deoxidizing agent, easily absorbing oxygen, forming phosphoric acid.

**Tests.**—Phosphorous acid and its salts give practically the same reactions as the hypophosphites. The following are the chief distinctions: Phosphites when added to solutions of calcium, barium, and strontium salts give precipitates of phosphites of these metals, whereas hypophosphites do not give a precipitate. Acidified permanganate solution is decolorized only after some time by phosphites, but immediately by hypophosphites.

Phosphites are of very little importance.

**Phosphoric Acids.**—Phosphoric oxide is capable of combining chemically with one, two, or three molecules of water, forming thereby three different acids.

$P_2O_5 + H_2O = H_2P_2O_6 = 2HPO_3$ Metaphosphoric acid.
$P_2O_5 + 2H_2O = H_4P_2O_7$ Pyrophosphoric acid.
$P_2O_5 + 3H_2O = H_6P_2O_8 = 2H_3PO_4$ Orthophosphoric acid.

These three acids show different reactions, act differently upon the animal system, and form different salts.

**Metaphosphoric Acid, $HPO_3$, $PO_2OH$** (*Glacial phosphoric acid*). This acid is always formed when phosphoric oxide is dissolved in water; gradually, and more rapidly on heating with water, it absorbs the latter, forming orthophosphoric acid; by heating the latter to near a red heat metaphosphoric acid is reformed.

Metaphosphoric acid is a monobasic acid which forms colorless, transparent, amorphous masses, readily soluble in water. It coagulates albumin (pyro- and orthophosphoric acids do not) and gives a white precipitate with ammonio-silver nitrate; it is not precipitated by magnesium sulphate in the presence of ammonia and ammonium chloride. It acts as a poison, while common phosphoric acid is comparatively harmless.

**Pyrophosphoric Acid, $H_4P_2O_7$, $P_2O_3(OH)_4$.**—This is a tetrabasic acid which gives a white precipitate with ammonio-silver nitrate, while orthophosphoric acid gives a yellowish precipitate; it is not precipitated by ammonium molybdate, and does not coagulate albumin.

**Phosphoric Acid, Orthophosphoric Acid** (*Acidum phosphoricum*) **$H_3PO_4$, $PO(OH)_3$ = 98.06** (*Common or tribasic phosphoric acid*). Nearly all phosphates found in nature are orthophosphates.

Phosphoric acid may be made by burning phosphorus, dissolving the phosphoric oxide in water, and boiling for a sufficient length of time to convert the meta- into orthophosphoric acid.

*Experiment* 16. Place a piece of phosphorus (about 0.5 gram), after having dried it quickly between filter paper, in a small porcelain dish, standing upon a glass plate; ignite the phosphorus by touching it with a heated wire, and place over the dish an inverted large beaker. The white vapors of phosphoric oxide soon condense into flakes, which fall on the glass plate. Collect the white mass with a glass rod, and dissolve in a few c.c. of water. Use a portion of the solution for tests of metaphosphoric acid; evaporate the remaining quantity in a porcelain dish until it becomes syrupy, dilute with water and use it for making tests for orthophosphoric acid, either as such or after having neutralized with sodium carbonate. How much phosphorus is needed to make 490 grams of the U. S. P. 10 per cent. phosphoric acid?

Phosphoric acid is also made by gently heating pieces of phosphorus with diluted nitric acid, when the phosphorus is oxidized, red fumes of nitrogen tetroxide escaping:

$$3P + 5HNO_3 + 2H_2O = 3H_3PO_4 + 5NO.$$

The liquid is evaporated until the excess of nitric acid has been

expelled, and enough of water added to obtain an acid which contains 85 per cent. of the pure $H_3PO_4$. Specific gravity 1.707 at 25° C.

*Diluted phosphoric acid*, U. S. P., is made by mixing 100 Gm. of the 85 per cent. acid with 750 Gm. of water. It contains 10 per cent. of absolute orthophosphoric acid.

*Phosphoric acid*, U. S. P., is a colorless, odorless, strongly acid liquid, which, on evaporation, forms a thick syrupy liquid. This, on cooling, slowly solidifies in the form of large crystals, which are highly deliquescent. Heated to a sufficiently high temperature the acid loses water, being converted successively into pyrophosphoric and metaphosphoric acid, which is finally volatilized at a low red heat. It is a tribasic acid, forming three series of salts, namely:

$Na_3PO_4$ = Trisodium phosphate.
$Na_2HPO_4$ = Disodium hydrogen phosphate.
$NaH_2PO_4$ = Sodium dihydrogen phosphate.

If the metal be bivalent, the formulas are thus:

$Ca_3(PO_4)_2$ = Tricalcium phosphate.
$Ca_2H_2(PO_4)_2$ = Dicalcium orthophosphate.
$CaH_4(PO_4)_2$ = Monocalcium orthophosphate.

According to the number of hydrogen atoms replaced in the acid, the salts formed are also termed *primary*, *secondary*, and *tertiary* phosphates: $KH_2PO_4$ being, for instance, primary potassium phosphate: $Na_2HPO_4$ secondary sodium phosphate: $Ag_3PO_4$ tertiary silver phosphate. All the alkali phosphates, but only primary phosphates of the other metals, are soluble in water.

All phosphates insoluble in water are dissolved by nitric, hydrochloric, or sulphuric acid; also by acetic acid, except those of lead, aluminum, and ferric iron. All are soluble in phosphoric acid (forming acid phosphates), except those of lead, tin, mercury, and bismuth. Primary alkali phosphates are acid to litmus, but secondary alkali phosphates, although they are acid salts, are alkaline to litmus because of partial hydrolysis by water into primary phosphate and free alkali. Tertiary alkali phosphates are decomposed by water into the secondary salt and free alkali.

Phosphoric acid belongs to the class of weak acids, and the three hydrogen atoms in the molecule show very different degrees of dissociation. It dissociates chiefly according to this equation, $H_3PO_4 \rightleftarrows H^{\cdot} + H_2PO_4'$. The dihydrophosphate ion, $H_2PO_4'$, dissociates to a small degree into $H^{\cdot}$ and $HPO_4''$ ions, as is shown by the fact that monosodium phosphate has a slightly acid reaction to litmus, thus:

$$\begin{array}{lll} NaH_2PO_4 \rightleftarrows Na^{\cdot} & + & H_2PO_4' \\ H_2PO_4' \rightleftarrows H^{\cdot} & + & HPO_4''' \end{array}$$

The ion $HPO_4''$ is practically not dissociated into $H^{\cdot}$ and $PO_4''$ ions, as is evidenced by the slightly alkaline reaction of disodium phosphate, which dissociates thus,

$$Na_2HPO_4 \rightleftarrows 2Na^{\cdot} + HPO_4''.$$

The alkaline reaction is due to the formation of a slight quantity of free alkali by the ions of water (hydrolysis) thus,

$$\left.\begin{matrix} 2Na^{\cdot} + HPO_4'' \\ (OH)' + H^{\cdot} \end{matrix}\right\} \rightleftarrows H_2PO_4',$$

or,

$$Na_2HPO_4 + H_2O = NaOH + NaH_2PO_4,$$

Trisodium phosphate is completely hydrolyzed in solution into disodium phosphate and sodium hydroxide, $Na_3PO_4 + H_2O = Na_2HPO_4 + NaOH$.

Tertiary phosphates are undecomposed by heat, but primary and secondary phosphates, which contain some of the hydrogen of the phosphoric acid molecule, lose this hydrogen as water when heated:

$$NaH_2PO_4 = NaPO_3 + H_2O;$$
$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

Primary sodium phosphate gives sodium metaphosphate and the secondary sodium salt gives sodium pyrophosphate. This in fact is the best method for obtaining these salts. When they are dissolved in water, they slowly take up water and revert to the respective orthophosphates.

When ammonium salts of phosphoric acid are heated, they lose both ammonia and water. Thus, the mixed salt sodium ammonium phosphate (microcosmic salt), $Na.NH_4.HPO_4$, gives sodium metaphosphate, ammonia and water, thus:

$$Na.NH_4.HPO_4 = NaPO_3 + NH_3 + H_2O.$$

The sodium metaphosphate, as a bead on the end of a platinum wire, when fused with traces of certain metallic oxides or salts, assumes various colors, according to the nature of the metal. Copper oxide produces a green color, with formation of a mixed sodium copper orthophosphate, $NaPO_3 + CuO = NaCuPO_4$. Accordingly, microcosmic salt is valuable in qualitative analysis for making the so-called *bead test.*

The insoluble magnesium ammonium phosphate when heated leaves a residue of magnesium pyrophosphate, $2Mg.NH_4.PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$, in which form magnesium is estimated in quantitative analysis.

### Tests for Phosphoric Acid and Phosphates.

(Sodium phosphate, $Na_2HPO_4$, may be used.)

1. Add to phosphoric acid, or to an aqueous solution of a phosphate, a mixture of magnesium sulphate, ammonium chloride, and ammonia water; a white crystalline precipitate falls, which is magnesium ammonium phosphate:

$$H_3PO_4 + MgSO_4 + 3NH_4OH = MgNH_4PO_4 + (NH_4)_2SO_4 + 3H_2O;$$
$$Na_2HPO_4 + MgSO_4 + NH_4OH = MgNH_4PO_4 + Na_2SO_4 + H_2O.$$

2. Add to a solution of disodium phosphate, silver nitrate, a yellow precipitate of silver phosphate is produced, which is soluble both in ammonia and nitric acid:

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$

3. Add to phosphoric acid, or to a phosphate dissolved in water or in nitric acid, an excess of a solution of ammonium molybdate in dilute nitric acid, and heat gently; a yellow precipitate of phosphomolybdate of ammonium $(NH_4)_3PO_4.10MoO_3.2H_2O$, is produced; the precipitate is readily soluble in ammonia water. This test is by far the most delicate, and even traces of phosphoric acid may be recognized by it; moreover, it can be used in an acid solution, while the first two tests cannot. Only a few drops of the solution to be tested should be used.

4. Add to a solution of a phosphate, calcium or barium chloride; a white precipitate of calcium or barium phosphate is produced, which is soluble in acids.

5. Ferric chloride produces a yellowish-white precipitate of ferric phosphate, $FePO_4$, thus:

$$Na_2HPO_4 + FeCl_3 = FePO_4 + 2NaCl + HCl.$$

The liberated hydrochloric acid dissolves some of the precipitate, which may be avoided by adding previously some sodium acetate; the hydrochloric acid combines with the sodium of the acetate, and the acetic acid which is set free has no dissolving action upon the ferric phosphate.

**Hydrogen phosphide, $PH_3$** (*Phosphoretted hydrogen, phosphine*). The formation of this compound has been mentioned in the paragraph on Hypophosphorous acid. It is a colorless, badly smelling, poisonous gas, which, when generated as directed above, is spontaneously inflammable. This last-named property is due to the presence of small quantities of another compound of phosphorus and hydrogen which has the composition $P_2H_4$, and is spontaneously inflammable, while the compound $PH_3$ is not.

Hydrogen phosphide corresponds to the analogous composition of ammonia, $NH_3$. While the latter is readily soluble in water and has strong basic properties, hydrogen phosphide is but sparingly soluble in water and its basic properties are very weak. However, a few salts, such as the phosphonium chloride, $PH_4Cl$, analogous to ammonium chloride, $NH_4Cl$, are known.

There is no scientific evidence whatever for the correctness of the statement, found in some text-books, that hydrogen phosphide is a product of the putrefaction of certain organic compounds.

**Phosphorus trichloride, $PCl_3$.** This is a colorless liquid, heavier than water, boiling at 76° C. Its vapors are very pungent. Water decomposes it very rapidly into phosphorous and hydrochloric acids, thus, $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$. For this reason the liquid gives white fumes in moist air. It can only be obtained by direct union of the elements. This is done by leading chlorine gas over phosphorus in a retort, when the elements unite with

combustion, and the trichloride distils over into a cold receiver. It is purified by redistillation in contact with some phosphorus, which removes any pentachloride present.

**Phosphorus pentachloride, $PCl_5$.** This consists of pale yellow crystals, and is obtained by passing chlorine into phosphorus trichloride. It decomposes at once in water into phosphoric and hydrochloric acids, $PCl_5 + 4H_2O = H_3PO_4 + 5HCl$. It fumes strongly in moist air. At 300° C. it is completely dissociated into trichloride and chlorine. With a small proportion of water it forms phosphorus oxychloride thus, $PCl_5 + H_2O = POCl_3 + 2HCl$. The oxychloride is a colorless liquid that boils at 107.2° C. The pentachloride is often used in organic chemistry to substitute chlorine for hydroxyl (OH) in compounds.

The bromine compounds of phosphorus, $PBr_3$ and $PBr_5$, are very similar to the chlorine compounds, and are made in the same way.

**Dissociation.**—Such decomposition which takes place at high temperature, while at a lower temperature the products recombine to form the original substance, is known as dissociation. Thus, it has been shown experimentally that when phosphorus pentachloride is heated in a closed vessel above 300° C., it decomposes completely into the trichloride and chlorine gas, but as the vessel cools down to ordinary temperature, the pentachloride is reformed. This evidently is a reversible action, and is entirely different from the decomposition of potassium chlorate by heat.

Nitrogen tetroxide, at low temperature, has the formula, $N_2O_4$, but at elevated temperature, the molecule dissociates into two simpler ones of the formula, $NO_2$, to form again $N_2O_4$, when the temperature is decreased.

## 16. THE PERIODIC SYSTEM OF CLASSIFYING THE ELEMENTS.

**Mendelejeff's Periodic Law.**—The relationship between atomic weights and properties has been used for arranging all elements systematically in such a manner that the existing relation is clearly pointed out. Of the various schemes proposed, the one arranged by Mendelejeff may be selected as most suitable to show this relation.

Looking at Mendelejeff's table on page 185 it will be seen that all

QUESTIONS.—In what forms of combination is phosphorus found in nature? Give an outline of the process for manufacturing phosphorus. What are the symbol, valence, atomic, and molecular weights of phosphorus. State the chemical and physical properties both of common and red phosphorus. By what methods may phosphorus be detected in cases of poisoning? What two oxides of phosphorus are known; what is their composition, and what four acids do they form by combining with water? State the official process for making phosphoric acid, and what are its properties? By what tests may the three phosphoric acids be recognized and distinguished from phosphorous acid? What is a phosphide, phosphite, phosphate, and hypophosphite? What is glacial phosphoric acid, and in what respect does its action upon the animal system differ from the action of common phosphoric acid?

the elements are arranged in the order of their atomic weights, and that the latter increase gradually by only a unit or a few units. Moreover, the arrangement is such that nine groups and twelve series are formed. The remarkable features of this classification may thus be stated: Elements which are more or less closely allied in their physical and chemical properties are made to stand together in a group, as may be seen by pointing out a few of the more generally known instances as found in the groups I., II., and VII., the first one containing the alkali metals, the second, the metals of the alkaline earths, the last the halogens.

There is, moreover, to be noticed a periodic repetition in the properties of the elements arranged in the horizontal lines from left to right. Leaving out groups 0 and VIII. for the present, we find that the power of the elements to combine with oxygen atoms increases regularly from the left to the right, while the power of the elements to combine with hydrogen atoms increases from the right to the left, as may be shown by the following instances:

| I. | II. | III. | IV. | V. | VI. | VII. |
|---|---|---|---|---|---|---|
| $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $Cl_2O_7$ |
| Hydrogen compounds unknown | | | $SiH_4$ | $PH_3$ | $SH_2$. | ClH |

The oxides on the left show strongly basic properties, as illustrated by sodium oxide; these basic properties become weaker in the second, and still weaker in the third group; the oxides of the fourth group show either indifferent, or but slightly acid properties, which latter increase gradually in the fifth, sixth, and seventh groups.

While some elements show an exception, it may be stated that most of the elements of group I. are univalent, of II. bivalent, of III. trivalent, of IV. quadrivalent, of V. quinquivalent, of VI. sexivalent, and of VII. septivalent.

Properties other than those above mentioned might be enumerated in order to show the regular gradation which exists between the members of the various series, but what has been pointed out will suffice to prove that there exists a regular gradation in the properties of the elements belonging to the same series, and that the same change is repeated in the other series, or that *the changes in the properties of elements are periodic.* It is for this reason that a series of elements is called a *period* (in reality a small period, in order to distinguish it from a large period, an explanation of which term will be given directly).

The 12 series or periods given in the following table show another highly characteristic feature, which consists in the fact that the corresponding members of the even (2, 4, 6, etc.) periods and of the uneven (3, 5, 7, etc.) periods resemble each other more closely than the members of the even periods resemble those of the uneven periods. Thus the metals calcium, strontium, and barium, of the even periods, 4, 6, and 8, resemble each other more closely than they resemble

## PERIODIC SYSTEM.[1]

| Series. | GROUP 0 — — | GROUP I. — $R_2O$ | GROUP II. — RO | GROUP III. — $R_2O_3$ | GROUP IV. $RH_4$ $RO_2$ | GROUP V. $RH_3$ $R_2O_5$ | GROUP VI. $RH_2$ $RO_3$ | GROUP VII. RH $R_2O_7$ | GROUP VIII. — $RO_4$? |
|---|---|---|---|---|---|---|---|---|---|
| 1 | • — | H, 1 | — | — | — | — | — | — | |
| 2 | He, 4 | Li, 7 | Be, 9 | B, 11 | C, 12 | N, 14 | O, 16 | F, 19 | |
| 3 | Ne, 20 2 | Na, 23 | Mg, 24.3 | Al, 27 | Si, 28 3 | P, 31 | S, 32 1 | Cl, 35 5 | |
| 4 | A, 39 9 | K, 39 | Ca, 40 1 | Sc, 44 | Ti, 48 | V, 51 | Cr, 52 | Mn, 55 | Fe, 55 9 Co, 59. Ni, 58 7. |
| 5 | — | (Cu, 63 6) | Zn, 65 4 | Ga, 70 | Ge, 72 5 | As, 75 | Se, 79.2 | Br, 79 9 | |
| 6 | Kr, 82.9 | Rb, 85.4 | Sr, 87 6 | Yt, 89 | Zr, 90 6 | Cb, 93 5 | Mo, 96 | — | Ru, 101 7. Rh, 102.9. Pd, 106 7. |
| 7 | — | Ag, 107 9 | Cd, 112 4 | In, 114 8 | Sn, 119 | Sb, 120.2 | Te, 127 5 | I, 126 9 | |
| 8 | Xe, 130.2 | Cs, 132 8 | Ba, 137 4 | La, 139 | Ce, 140 2 | Nd, 144 3 | Tb, 159 2 | — | — — — |
| 9 | — | — | — | — | — | Er, 167.7 | — | — | |
| 10 | — | — | — | Yb, 172 | — | Ta, 181 5 | W, 184 | — | Os, 190.9. Ir, 193.1. Pt, 195 2. |
| 11 | — | (Au, 197.2) | Hg, 200 6 | Tl, 204 | Pb, 207 1 | Bi, 208 | — | — | |
| 12 | — | — | Ra, 226 4 | — | Th, 232.4 | — | U, 238.5 | — | — — — |

[1] Mainly approximate figures are used as the atomic weights.

the metals magnesium, zinc, and cadmium, of the uneven periods, 3, 5, and 7, the latter metals again resembling each other greatly in many respects.

It is for this reason that in the table the elements belonging to one group are not placed exactly underneath each other, but are divided into two lines containing the members of even and uneven periods separately, whereby the elements resembling each other most are made to stand together.

In arranging the elements by the method indicated, it was found that the elements mentioned in group VIII. could not be placed in any of the 12 small periods, but that they had to be kept separately in a group by themselves, three of these metals always forming an intermediate series following the even periods 4, 6, and 10.

An uneven and even series, together with an intermediate series, form a *large period*, the number of elements contained in a complete large period being, therefore, $8 + 8 + 3 = 19$.

An *apparently* objectionable feature is the incompleteness of the table, many places being left blank; but it is this very point which renders the table so highly interesting and valuable.

Mendelejeff, in arranging his scheme, claimed that the places left blank belonged to elements not yet discovered, and he predicted not only the existence of these then missing elements, but also described their properties. Fortunately his predictions have, in several cases, been verified, a number of the missing elements having since been discovered. Among them may be mentioned *scandium*, *gallium*, and *germanium*. These elements not only fitted in the previously blank spaces by virtue of their atomic weights, but their general properties also assigned to them the places which they now occupy.

When the table was first arranged it did not show group 0. The elements forming this group have all been discovered since the year 1894, and their discovery necessitated the addition of an extra group. In order to avoid renumbering the previously known groups the new group was designated by zero.

Another graphic representation of the periodic law is obtained by arranging the elements according to the increase in their atomic weights on a spiral line, as shown on the diagram (Fig. 17). From the centre of the spiral extend 20 radii, and in placing the elements on the intersections of the spiral and a radius three important facts are noticed, viz.: 1. The distances of the elements from the centre of the spiral are proportionate (or nearly so) to their atomic weights. 2. From left to right the elements, arranged on the diametric lines, follow one another according to the periodic grouping. 3. The elements belonging to the even series of one of the groups are on one radius, while the elements belonging to the uneven series of the same group find their position on the radius opposite. For example, calcium, strontium, and barium, of the even series 4, 6, and 8 of group II., are on a radius opposite the one on which we find

magnesium, zinc, and cadmium, of the uneven series 3, 5, and 7 of group II.

The periodic system of the elements undoubtedly involves some underlying truth, but it is imperfect, more so now than when first proposed. The elements cannot be arranged strictly according to the increasing atomic weights without having some of them dis-

FIG. 17.

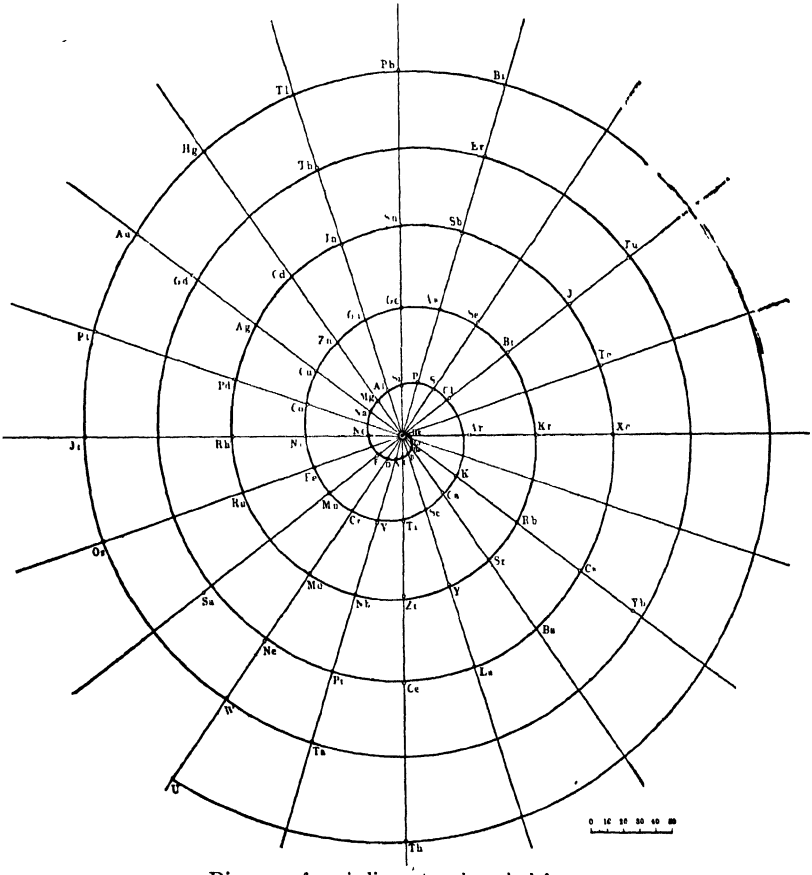



Diagram of periodic system in spiral form.

placed from groups to which they belong by their chemical properties. For example, tellurium properly precedes iodine in the table, although its atomic weight is greater than that of iodine. Likewise, cobalt should follow iron by its chemical behavior, although its atomic weight is greater than that of nickel. The system has been, and still is, a good working hypothesis, it contains much that is true, has been an excellent guiding principle, and has shown a wonderful power of adjustment to new facts.

Another difficulty for the system to grapple with is the existence of about sixteen rare earths, which are very much alike chemically and so different from other substances. It seems impossible to fit them into any vacant places in the table. A still greater problem is the group of about thirty-seven radio-active bodies known at the present time. Each is an element hitherto unknown. The present arrangement of the periodic system has no provision for so many new elements.

## 17. CHLORINE.

$Cl^I = 35.46$.

**Halogens.**—The four elements, fluorine, chlorine, bromine, and iodine, which form a natural group of elements, are known as halogens, the term meaning producers of salt. The relation shown by the atomic weights of these four elements has been mentioned in connection with the consideration of natural groups of elements generally (see chapter 5). In many other respects a resemblance or relation can be discovered. For instance: While the haloids as a general rule act as univalent elements, they all form compounds into which they enter with a valence of either 3, 5, or 7; they combine with hydrogen, forming the acids HF, HCl, HBr, HI, all of which are colorless gases, soluble in water; they combine directly with most metals, forming fluorides, chlorides, bromides, and iodides. The relative combining energy lessens as the atomic weight increases; fluorine with the lowest atomic weight having the greatest, iodine with the highest atomic weight the smallest, affinity for other elements. The first two members of the group are gases, the third (bromine) is a liquid, the last (iodine) a solid, at ordinary temperature. They all show a distinct color in the gaseous state, have a disagreeable odor, and possess disinfecting properties.

**Occurrence in Nature.**—Chlorine is found chiefly as sodium chloride or common salt, NaCl, either dissolved in water (small quantities in almost every spring-water, larger quantities in some mineral waters, and the principal amount in sea-water), or as solid deposits in the interior of the earth as *rock salt*.

Other chlorides, such as those of potassium, magnesium, calcium, also are found in nature. As common salt, chlorine enters the animal system, taking there an active part in many of the physiological and chemical changes.

**Preparation of Chlorine.**—Most methods of liberating chlorine depend on an oxidation of the hydrogen of hydrochloric acid by suitable oxidizing agents, the hydrogen being converted into water, while chlorine is set free.

As oxidizing agents, potassium chlorate, potassium dichromate, potassium permanganate, chromic acid, nitric acid, and many other substances may be used.

The most common and cheapest mode of obtaining chlorine is to heat manganese dioxide, usually called black oxide of manganese, with hydrochloric acid, or a mixture of manganese dioxide and sodium chloride with sulphuric acid:

$$MnO_2 + 2NaCl + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + 2Cl.$$

Chlorine is liberated also by the action of sulphuric or hydrochloric acid on bleaching-powder, which is a mixture of calcium chloride and calcium hypochlorite:

$$CaCl_2.Ca(ClO)_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + 4Cl.$$

Chlorine is now also produced by electrolysis of sodium chloride solution in suitably constructed apparatus.

*Experiment* 17.—Use the apparatus shown in Fig. 10. Conduct operation in a fume-chamber. Place about 50 grams of manganese dioxide in coarse powder in the flask, cover it with hydrochloric acid, shake up well to insure that no dry powder be left at the bottom of the flask, apply heat, and collect the gas in dry bottles by downward displacement. Keep the bottles loosely covered with pieces of stiff paper while filling them. Use the gas for the following experiments:

*a.* Fill a test-tube with chlorine, a second test-tube of same size with hydrogen; place them over one another so that the gases mix by diffusion, then hold them near a flame; a rapid combustion or explosion ensues.

*b.* Hold in one of the bottles filled with chlorine a lighted wax candle, and notice that it continues to burn with liberation of carbon. The hydrogen contained in the wax is in this case the only constituent of the wax which burns, *i. e.*, combines with chlorine.

*c.* Moisten a paper with oil of turpentine, $C_{10}H_{16}$, and drop it into another bottle filled with the gas; combustion ensues spontaneously, a black smoke of carbon being liberated.

*d.* Drop some finely powdered antimony into another bottle, and notice that each particle of the metal burns while passing through the gas, forming white antimonous chloride, $SbCl_3$.

*e.* Pass some chlorine gas into water, and suspend in the chlorine water thus formed colored flowers or pieces of dyed cotton, and notice that the color fades and in many cases disappears completely in a few hours.

**Properties.**—Chlorine is a yellowish-green gas, having a disagreeable taste and an extremely penetrating, suffocating odor, acting energetically upon the air-passages, producing violent coughing and inflammation. It is about two and a half times heavier than air, soluble in water, and convertible into a greenish-yellow liquid by a pressure of about six atmospheres.

Chemically, the properties of chlorine are well marked, and there are but few elements which have as strong an affinity for other elements as chlorine: it unites with all of them directly, except with oxygen, nitrogen, and carbon, but even with these it may be made to combine indirectly. The act of combination between chlorine and other elements is frequently attended by the evolution of so much

heat that light is produced, or, in other words, combustion takes place. Thus, hydrogen, phosphorus, and many metals burn easily in chlorine. The affinity between chlorine and hydrogen is intense, a mixture of the two gases being highly explosive. Such a mixture, kept in the dark, will not undergo chemical change, but when ignited, or when exposed to direct sunlight, combination between the two elements occurs instantly with an explosion. The affinity of chlorine for hydrogen is also demonstrated by its property of decomposing water, ammonia, and many hydrocarbons (compounds of carbon with hydrogen), such as oil of turpentine, $C_{10}H_{16}$, and others:

$$H_2O + 2Cl = 2HCl + O.$$
$$NH_3 + 3Cl = 3HCl + N.$$
$$C_{10}H_{16} + 16Cl = 16HCl + 10C.$$

As shown by these formulas, hydrochloric acid is formed, while the other elements are set free.

Chlorine is a strong disinfecting, deodorizing, and bleaching agent; it acts as such either directly by combining with certain elements of the coloring or odoriferous matter, or, indirectly, by decomposing water with liberation of oxygen, which in the nascent state—that is, at the moment of liberation—has a strong tendency to oxidize other substances.

It should be noted that perfectly dry chlorine has practically no action on other substances when also dried. In the absence of all moisture it has no bleaching action. This inactivity of dry chlorine is exemplified by the fact that it is now sold in steel cylinders. As ordinarily used, however, it acts readily, because of the moisture in the atmosphere, and on objects, even if water is not supplied directly.

**Hydrochloric Acid** (*Acidum Hydrochloricum*), **HCl = 36.46.** *Muriatic Acid*).—This acid occurs in the gastric juice of mammalia, and has been found in some volcanic gases. One volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid.

For all practical purposes the acid is obtained by the decomposition of a chloride by sulphuric acid:

$$NaCl + H_2SO_4 = HCl + NaHSO_4;$$
$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4.$$

*Experiment* 18.—Use the apparatus shown in Fig. 10. Place about 20 grams of sodium chloride into the flask (which should be provided with a funnel-tube) and add about 30 c.c. of concentrated sulphuric acid; mix well, apply heat, and pass the gas into water for absorption. If a pure acid be desired, the gas has to be passed through water contained in a wash-bottle; apparatus shown in Fig. 15 may then be used. Use the acid made for tests mentioned below. How much of the U. S. P. 31.9 per cent. hydrochloric acid can be made from 177 pounds of sodium chloride?

The liberation of the hydrochloric acid from a chloride by sulphuric acid is an

example of reversible reactions that run to completion because of the removal of one of the factors that is necessary to maintain an equilibrium (see page 127). The character of the reaction is like that in the case of the liberation of nitric acid, the ionic features of which are discussed in chapter 13. The ionic reaction is this:

$$\left.\begin{array}{l} NaCl \rightleftarrows Na^{\cdot} + Cl' \\ H_2SO_4 \rightleftarrows HSO_4' + H^{\cdot} \end{array}\right\} \rightleftarrows HCl \rightarrow \begin{array}{l} HCl. \\ \text{gas.} \end{array}$$

dissolved

Hydrochloric acid is a colorless gas, has a sharp, penetrating odor, and is very irritating when inhaled. It is neither combustible nor a supporter of combustion, and has great affinity for water, which property is the cause of the formation of white clouds whenever the gas comes in contact with the vapors of water, or with moist air; the white clouds being formed of minute particles of liquid hydrochloric acid.

While hydrochloric acid is a gas, this name is used also for its solution in water, one volume of which at ordinary temperature takes up over 400 volumes of the gas.

The hydrochloric acid of the U. S. P. is an acid containing 31.9 per cent. of HCl. It is a colorless, fuming liquid, having the odor of the gas, strong acid properties, and a specific gravity of 1.158. The official diluted hydrochloric acid is made by mixing 100 parts by weight of the above acid with 219 parts of water. It contains 10 per cent. of HCl.

The same antidotes may be used as for nitric acid.

A 20.2 per cent. solution of hydrochloric acid distils unchanged at 110° C. (230° F.) under 760 mm. pressure. When a more concentrated solution is heated, it first loses mainly the gas, and a more dilute solution mainly water vapor, until 20.2 per cent. is reached, when the residue in the flask passes over unchanged. Other acids—for example, sulphuric, nitric, hydriodic, hydrobromic—show a similar property.

Neither the dry gas (HCl) nor the liquefied gas has any marked acid character. They do not conduct electricity and have no action on dry litmus-paper or on zinc, but the presence of water causes strong acid properties to be developed. This is explained on the Dissociation Theory, which holds that only hydrogen ions have acid properties. Water is required for the ionization of HCl, and without it the gas lacks acid character. A solution of the gas in liquids like benzene and toluene, which have scarcely any ionizing power, has practically no effect on zinc, which is freely attacked by an aqueous solution of the gas. The same is true of hydrobromic and hydriodic acids (Chapter 13).

Nearly all chlorides are soluble in water. Of those ordinarily met with only two are insoluble in water, namely, silver and mercurous chlorides, and one is difficultly soluble in cold water, but more readily in hot water, namely, lead chloride

**Tests for Hydrochloric Acid and Chlorides.**

(Sodium chloride, NaCl, may be used.)

1. To hydrochloric acid, or to solution of chlorides, add silver nitrate: a white, curdy precipitate is produced, which is soluble in ammonia water, even when very dilute, but insoluble in nitric acid:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$
$$Ag^{\cdot} + NO_3' + Na^{\cdot} + Cl' \rightarrow AgCl + Na^{\cdot} + NO_3'.$$

2. Add solution of mercurous salt (mercurous nitrate): a white precipitate of mercurous chloride (calomel) is produced, which blackens on the addition of ammonia:

$$HgNO_3 + NaCl = HgCl + NaNO_3.$$
$$Hg^{\cdot} + NO_3' + Na^{\cdot} + Cl' \rightarrow HgCl + Na^{\cdot} + NO_3'.$$

3. Add solution of lead acetate: a white precipitate of lead chloride is formed, which is soluble in hot, or in much cold water, and is, therefore, not formed in dilute solutions. Its composition is $PbCl_2$.

$$Pb(C_2H_3O_2)_2 + 2NaCl = PbCl_2 + 2Na(C_2H_3O_2).$$
$$Pb'' + 2(C_2H_3O_2)' + 2Na^{\cdot} + 2Cl' \rightarrow PbCl_2 + 2Na^{\cdot} + 2(C_2H_3O_2)'.$$

4. To a dry chloride add strong sulphuric acid and heat: hydrochloric acid gas is evolved, which may be recognized by the odor, or by its action on silver nitrate, when a drop of the solution on the end of a glass rod is held in the gas. (The insoluble chlorides of silver, lead, and mercury do not give this reaction.)

5. Chlorides treated with sulphuric acid and manganese dioxide evolve chlorine.

Test 1, combined with test 5, is the most decisive proof of hydrochloric acid or chlorides. The others are more corroborative than decisive.

**Nitro-hydrochloric Acid** (*Acidum Nitro-hydrochloricum, Aqua Regia, Nitro-muriatic Acid*).—Obtained by mixing 18 c.c. of nitric acid with 82 c.c. of hydrochloric acid. The two acids act chemically upon each other, forming chloronitrous gas, chlorine, and water:

$$HNO_3 + 3HCl = NOCl + 2H_2O + 2Cl.$$

The dissolving power of this acid upon gold and platinum depends on the action of the free chlorine. The action on platinum is represented by this equation:

$$2HNO_3 + 8HCl + Pt = H_2PtCl_6 + 2NOCl + 4H_2O.$$

Chloroplatinic acid, $H_2PtCl_6$, is in solution. This is used as a test-solution.

The official *diluted nitrohydrochloric acid* is made by mixing 182 c.c. of hydrochloric acid with 40 c.c. of nitric acid and adding, when effervescence has ceased, 782 c.c. of water.

**Compounds of Chlorine with Oxygen.**—There is no method known by which to combine chlorine and oxygen directly, all the compounds formed by the union of these elements being obtained by indirect processes. The oxides of chlorine are the following:

| | |
|---|---|
| Chlorine monoxide or hypochlorous oxide, | $Cl_2O$. |
| Chlorine dioxide, | $ClO_2$. |
| Chlorine heptoxide, | $Cl_2O_7$. |

The first two oxides are yellow or brownish-yellow gases; the third one is a colorless liquid; all combine with water, forming hypochlorous, chlorous and chloric, and perchloric acid, thus:

$$Cl_2O + H_2O = 2HClO.$$
$$2ClO_2 + H_2O = HClO_2 + HClO_3.$$
$$Cl_2O_7 + H_2O = 2HClO_4.$$

The oxide, $Cl_2O_5$, from which chloric acid, $HClO_3$, might be formed, is not known. The chlorine oxides, the acids, and many of their salts are distinguished by the great facility with which they decompose, frequently with violent explosion, for which reason care must be taken in the preparation and handling of these compounds.

### Chlorine acids.

| | | | |
|---|---|---|---|
| Hypochlorous acid, | $HClO$. | Chloric acid, | $HClO_3$. |
| Chlorous acid, | $HClO_2$. | Perchloric acid, | $HClO_4$. |
| | Hydrochloric acid, $HCl$. | | |

With the exception of hydrochloric acid, which has been considered, none of the five acids is of practical interest as such, but many of the salts of hypochlorous and chloric acids, known as hypochlorites and chlorates respectively, are of great and general importance.

The constitution of the chlorine acids may be represented by the following graphic formulas. It is here assumed that chlorine is univalent in hypochlorous, trivalent in chlorous, quinquivalent in chloric, and septivalent in perchloric acid:

$$H-O-Cl, \quad H-O-Cl=O, \quad H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cl}}, \quad H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cl}}=O$$

**Chlorine Monoxide, $Cl_2O$, and Hypochlorous Acid, $HClO$.**—When chlorine is passed over yellow mercuric oxide in a tube, chlorine monoxide is formed, thus,

$$2HgO + 2Cl_2 = HgO.HgCl_2 + Cl_2O.$$

It is a brownish-yellow gas which decomposes with explosion when heated. One volume of water dissolves 200 volumes of the gas, giving a yellow solution of hypochlorous acid which has the strong odor of the chlorine monoxide.

$$Cl_2O + H_2O = 2HClO.$$

Hypochlorous acid is also obtained in solution when chlorine gas is passed into a suspension of mercuric oxide in water, thus,

$$2HgO + 2Cl_2 + H_2O = HgO.HgCl_2 + 2HClO.$$

The compound known as mercury oxychloride is formed and may be removed, being insoluble.

**Properties.**—Hypochlorous acid is a feeble (slightly ionizing) monobasic acid, which unites with active bases, forming hypochlorites. It can be obtained only in solution, and keeps only when dilute and cold. When concentrated it changes gradually to a considerable extent into chloric and hydrochloric acids, thus,

$$3HClO = HClO_3 + 2HCl.$$

Warming a solution of the acid, or exposing it to sunlight, causes a rapid evolution of oxygen,

$$2HClO = 2HCl + 2O.$$

As a result of this action, the acid is a strong oxidizer. This decomposition is interesting, as it explains the oxidizing action of chlorine in the presence of water, and the fact that chlorine water exposed to bright light does not keep, but gives off oxygen and leaves a solution of nothing but hydrochloric acid. When chlorine is dissolved, a reversible action takes place, thus,

$$Cl_2 + H_2O \rightleftarrows HCl + HClO.$$

Only a slight quantity of hypochlorous acid is formed at one time, but its decomposition and constant removal in this way allows the action to go forward to completion. The final result makes it appear that chlorine decomposes water with direct liberation of oxygen, which is usually represented by the equation,

$$Cl_2 + H_2O = 2HCl + O.$$

**Hypochlorites.** For practical purposes solutions of free hypochlorous acid are not made, but the acid is liberated from its salts when wanted. The hypochlorites are formed by the action of chlorine on the hydroxide of potassium, sodium, calcium, etc., at the ordinary temperature. As stated above, chlorine with water forms HCl and HClO, but the action does not go far, because these two acids tend to decompose each other in the reverse direction to produce chlorine. But if they are removed, as by neutralization, action will be complete, thus,

$$\begin{aligned} 2Cl + H_2O &= HCl + HClO \\ HCl + NaOH &= NaCl + H_2O \\ HClO + NaOH &= NaClO + H_2O. \end{aligned}$$

It will be seen that when hypochlorite is made in this manner there is always an equivalent amount of a chloride in the mixture. The reaction is generally written,

$$2Cl + 2NaOH = NaCl + NaClO + H_2O.$$

When a hypochlorite is acidified with an active acid, the reverse of the above reactions takes place, hydrochloric and hypochlorous acids being liberated, which between them evolve chlorine (see bleaching powder). When a hypochlorite is heated, it decomposes into chlorate and chloride, thus,

$$3NaClO = NaClO_3 + 2NaCl.$$

Under some conditions a hypochlorite slowly gives off oxygen, leaving a chloride, but the action may be enormously increased by adding a catalytic agent, for example, a cobalt salt (see under Oxygen).

**Solution of chlorinated soda, Liquor sodæ chlorinatæ** (*Solution of sodium hypochlorite, Labarraque's solution*). This is a solution that yields 2.4 per cent. of available chlorine. It contains chloride and hypochlorite of sodium, and is made by adding sodium carbonate to a solution of bleaching powder (calcium hypochlorite), thus precipitating calcium carbonate:

$$CaCl_2 + Ca(ClO)_2 + 2Na_2CO_3 = 2CaCO_3 + 2NaCl + 2NaClO.$$

It is a clear pale greenish liquid, having a faint chlorine-like odor and strong bleaching properties.

**Chloric Acid, $HClO_3$.**—Chloric acid may be obtained from potassium chlorate by the action of hydrofluosilicic acid; it is, however, an unstable substance which will decompose, frequently with a violent explosion. Chlorates are generally obtained by the action of chlorine on alkali hydroxides at a temperature of about 100° C. (212° F.).

$$6KOH + 6Cl = 5KCl + KClO_3 + 3H_2O.$$

The explanation of this action is that chlorine first forms a hypochlorite, which, as stated above, decomposes by heating into chlorate and chloride. The change will be clearer if written in two steps:

$$6KOH + 6Cl = 3KCl + 3KClO + 3H_2O.$$
$$3KClO = 2KCl + KClO_3.$$

In recent years large quantities of chlorates, especially potassium chlorate, are made by passing an electric current, under proper conditions, through an alkaline solution of potassium chloride.

**Perchloric Acid, $HClO_4$.**—This is a colorless liquid, which, in the pure state, decomposes, and often explodes spontaneously when kept. A 70 per cent. aqueous solution is stable. Although it contains more oxygen than the other acids of chlorine, it is the most stable one of all. It can be prepared by distilling a mixture of potassium perchlorate and concentrated sulphuric acid in a vacuum. It was seen in the chapter on oxygen that potassium chlorate, when heated, gives the perchlorate, chloride, and oxygen. The perchlorate, being difficultly soluble in water, can be separated easily from the far more soluble chloride.

### Tests for Chlorates and Hypochlorites.

(Potass. chlorate, $KClO_3$, and bleaching powder, $Ca(ClO)_2.CaCl_2$, may be used.)

1. Chlorates liberate oxygen when heated by themselves.
2. Chlorates liberate chlorine dioxide, $ClO_2$, a deep yellow explosive gas, on the addition of strong sulphuric acid.

$$2KClO_3 + H_2SO_4 = K_2SO_4 + 2HClO_3.$$
$$3HClO_3 = HClO_4 + H_2O + 2ClO_2.$$

This test should be made only on a quantity about the size of a pea.

3. Chlorates deflagrate when sprinkled on red-hot charcoal.
4. Hypochlorites are strong bleaching agents, and evolve a peculiarly smelling gas (chlorine) on the addition of acid (see page 194).

## 18. BROMINE. IODINE. FLUORINE.

### Bromine, Br = 79.92.

This element is found in sea-water and many mineral waters, chiefly as magnesium, calcium, and sodium bromides, which compounds, however, represent in all these waters a comparatively small percentage of the total quantity of the different salts present. Most of these salts are separated from the water by evaporation and crystallization, and the remaining mother-liquor, containing the bromides, is treated with chlorine, which liberates bromine, the vapors of which are condensed in cooled receivers:

$$MgBr_2 + 2Cl = MgCl_2 + 2Br.$$

Bromine is at common temperature a heavy, dark reddish-brown liquid, giving off yellowish-red fumes of an exceedingly suffocating and irritating odor; it is very volatile, freezes at about −24° C. (−11° F.), and has a specific gravity of 2.99; it is soluble in 33

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QUESTIONS.—State the names and general physical and chemical properties of the four halogens. How is chlorine found in nature, and why does it not occur in a free state? State the general principle for liberating chlorine from hydrochloric acid, and explain the action of the latter on manganese dioxide. Mention of chlorine: its atomic weight, molecular weight, valence, color, odor, action when inhaled, and solubility in water. How does chlorine act chemically upon metals, hydrogen, phosphorus, water, ammonia, hydrocarbons, and coloring matters? Mention two processes for making hydrochloric acid; state its composition, properties, and tests by which it may be recognized. What is aqua regia? State the composition of hypochlorous and chloric acids. What is the difference in the action of chlorine upon a solution of potassium hydroxide at ordinary temperature and at the boiling-point? How many pounds of manganese dioxide, and how many of hydrochloric acid gas are required to liberate 142 pounds of chlorine?

parts of water, more freely in alcohol, abundantly in ether and disulphide of carbon; it is a strong disinfectant, and its aqueous solution is also a bleaching agent; it acts as a corrosive poison.

**Hydrobromic Acid** (*Acidum Hydrobromicum*) **HBr = 80.93.**—This acid cannot well be obtained by the action of concentrated sulphuric acid upon bromides, since the hydrobromic acid first formed becomes readily decomposed with formation of sulphur dioxide and free bromine. Thus:

$$2NaBr + H_2SO_4 = 2HBr + Na_2SO_4;$$
$$2HBr + H_2SO_4 = 2Br + SO_2 + 2H_2O.$$

If, however, dilute sulphuric acid is added to a warm solution of potassium bromide, potassium sulphate is formed, a portion of which crystallizes on cooling. From the remaining portion of the salt, the hydrobromic acid may be separated by distillation.

Hydrobromic acid may also be obtained by the formation of bromide of phosphorus, $PBr_5$ (the two elements combine directly), and its decomposition by water:

$$PBr_5 + 4H_2O = 5HBr + H_3PO_4.$$

In the form of solution this acid may be prepared also by treating bromine under water with hydrogen sulphide until the brown color of bromine has entirely disappeared. The reaction is as follows:

$$10Br + 2H_2S + 4H_2O = 10HBr + H_2SO_4 + S.$$

The liquid is filtered from the sulphur and separated from the sulphuric acid by distillation.

Hydrobromic acid is, like hydrochloric acid, a colorless gas, of strong acid properties, easily soluble in water.

*Diluted hydrobromic acid, Acidum hydrobromicum dilutum,* is a solution of 10 per cent. of hydrobromic acid in water. It is a colorless, odorless, acid liquid of the specific gravity 1.076.

Hydrobromic acid acts in nearly all respects like hydrochloric. It is less stable, and less powerful oxidizing agents will liberate the bromine than are required to liberate chlorine. Nearly all bromides are soluble in water, the insoluble ones being those of silver, mercury (ous), and lead. Bromides are mostly white.

The ionic reactions for bromine compounds are analogous to those for chlorine compounds.

The liberation of bromine from hydrobromic acid by chlorine is accounted for on energy relationships. When gaseous bromine and hydrogen unite to form one molecular weight of hydrobromic acid, 12,100 calories of heat energy are liberated and, conversely, when the elements are separated, the same number of calories are absorbed. When chlorine and hydrogen unite to form one molecular weight of hydrochloric acid, 22,000 calories of heat are set free. Hence in the displacement of bromine by chlorine HBr + Cl = HCl + Br, 9,900 calories of heat (22,000–12,100) are set free. That is, the action is an exothermic one, and hence takes place spontaneously. The same explanation applies to the libera-

tion of bromine from bromides, by chlorine, and to the liberation of iodine from hydriodic acid and iodides by either chlorine or bromine.

**Hypobromous Acid, HBrO; Bromic Acid, $HBrO_3$,** and their salts, the *hypobromites* and *bromates*, are analogous to the corresponding chlorine compounds, and may be obtained by analogous processes. Oxides of bromine are not known.

A solution of bromic acid is obtained when chlorine is passed into water containing bromine, thus:

$$5Cl + 3H_2O + Br = 5HCl + HBrO_3.$$

The solution is colorless and possesses powerful oxidizing properties. For example, it oxidizes iodine to iodic acid:

$$HBrO_3 + I = HIO_3 + Br.$$

Chlorine also converts iodine into iodic acid just as it converts bromine into bromic acid. These transformations indicate that the affinity of the halogen elements for oxygen increases in the order of their atomic weights, or, in other words, that the oxidation of bromine to bromic acid and iodine to iodic acid involve liberation of energy. Iodic acid is the most stable, chloric acid the least stable.

When a mixture of a bromate and bromide in solution is acidified with dilute sulphuric acid, the liberated acids are mutually destroyed, one oxidizing the other, thus:

$$HBrO_3 + 5HBr = 3H_2O + 6Br.$$

This action is analogous to the action between potassium chlorate and hydrochloric acid by which chlorine is liberated, and is used to detect the presence of bromate in the official bromides. A bromide when moistened with dilute sulphuric acid should not at once become colored. If it does, the presence of bromate is concluded.

### Tests for Bromides.

(Potassium bromide, KBr, may be used.)

1. Silver nitrate produces in solutions of bromides a slightly yellowish-white precipitate of silver bromide, insoluble in nitric acid, sparingly soluble in ammonia water.

2. Addition of chlorine water, or heating with nitric acid, liberates bromine, which may be dissolved by shaking with carbon disulphide. Excess of chlorine oxidizes bromine to colorless bromic acid. Hence, it must be added cautiously, else a small quantity of bromine will escape detection. The test is a delicate one.

3. Mucilage of starch added to the liberated bromine is colored yellow. The starch may be held in the vapor on the end of a rod.

4. A solution of mercurous nitrate, or of lead acetate produces a white precipitate of mercurous bromide, or lead bromide, both of which are insoluble in water and dilute acids.

5. Strong sulphuric acid added to a dry bromide liberates hydrobromic acid, HBr, a portion of which decomposes with liberation of yellowish-red vapors of bromine. See explanation above.

Tests 2 and 5 combined with test 1 are decisive and sufficient to recognize hydrobromic acid and its salts, and to distinguish them from chlorides.

**Iodine, Iodum, I = 126.92.**

Iodine is found in nature in combination with sodium and potassium, in some spring-waters and in sea-water, from which latter it is taken up by sea-plants and many aquatic animals. Iodine is derived chiefly from the ashes of sea-weeds known as *kelp*. By washing these ashes with water, the soluble constituents are dissolved, the larger quantities of sodium chloride, sodium and potassium carbonates are removed by evaporation and crystallization, and from the remaining mother-liquor iodine is obtained by treating the liquor with manganese dioxide and hydrochloric (or sulphuric) acid:

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + 2I.$$

The liberated iodine distils, and is collected in cooled receivers. Sodium nitrate found in Chile contains a small quantity of sodium iodate, and the mother-liquors, from which the nitrate has been crystallized, contain enough iodate to be employed for the preparation of iodine.

Iodine is a bluish-black, crystalline substance of a somewhat metallic lustre, a distinctive odor, a sharp and acrid taste, and a neutral reaction. Specific gravity 4.948 at 17° C. (62.6° F.). It fuses at 114° C. (237° F.), and boils at 180° C. (356° F.), being converted into beautiful purple-violet vapors; also, it volatilizes in small quantities at ordinary temperature. It is soluble in about 5000 parts of water, more soluble in water containing salts, for instance, potassium iodide; the official *Liquor iodi compositus* (Lugol's solution) is a preparation based on this property. It contains 5 parts of iodine and 10 parts of potassium iodide in 100 parts of aqueous solution. Iodine is soluble in 10 parts of alcohol, very soluble in ether, disulphide of carbon, and chloroform. The solution of iodine in alcohol or ether has a brown, the solution in disulphide of carbon or in chloroform a violet, color. Iodine stains the skin brown, and when taken internally acts as an irritant poison.

*Tincture of iodine, Tinctura iodi,* is a dark reddish-brown solution of 70 grams of iodine and 50 grams of potassium iodide in enough alcohol to make 1000 c.c. of solution.

The increased solubility of iodine in solutions of iodides, or of hydriodic acid, is due to the formation of definite compounds by a reversible action, thus:

$$KI + 2I \rightleftarrows KI_3.$$

The brown color of solutions of iodine in certain solvents, as alcohol, ether, etc., has been shown to be due to a feeble combination between one molecule of iodine and one molecule of the solvent. In violet-colored solutions there is no combination.

Iodine, unlike chlorine and bromine, does not form a hydrate with water. It shows little tendency to unite directly with hydrogen. It unites directly with some non-metallic elements and with most of the metals. Iodine is displaced from hydriodic acid and the iodides by chlorine and bromine (see explanation under Bromine). In water, it is an oxidizer, but one of much less intensity than chlorine. It oxidizes sulphurous acid and sulphites to sulphuric acid and sulphates, arsenites to arsenates, etc. Use is made of this property in volumetric analysis (see Index).

Iodine is used in the official solution and tincture of iodine, in the manufacture of the various medicinal iodides, in making intermediate products used in the preparation of synthetic organic dyes. Large quantities of potassium iodide are used in the manufacture of iodoform and photographic plates.

Iodine in very small quantity is a constituent of the human body and that of animals. The greatest portion is found in the thyroid gland, as a complex substance known as thyro-iodine, which is of great value in certain diseases, especially cretinism, resulting from deficient development of the thyroid gland. Bauman discovered (1895) iodine in this gland. The thyroid of sheep, which in the dried form is official, contains 0.17 per cent. of iodine.

**Hydriodic Acid** (*Acidum Hydriodicum*) **HI = 127.93.**—This is a colorless gas readily soluble in water; the solution is unstable, being easily decomposed with liberation of iodine.

The direct union of iodine and hydrogen takes place very slowly and is never complete even at elevated temperature. This is because the energy liberated by the union at higher temperature is almost *nil*, and at lower temperature there is actually an absorption of energy, that is, the union is endothermal. This behavior is in marked contrast to that of hydrogen and chlorine, which evolve 22,000 calories of heat when united to form one molecular weight in grams of hydrochloric acid. The endothermal character of hydriodic acid accounts for the fact that it is the least stable of the halogen acids, and that it is an excellent reducing agent. Thus, it is slowly oxidized even by the oxygen of the air, causing a solution of it to become brown on standing, $2HI + O = H_2O + 2I$. When gaseous hydriodic acid is heated to 180° C. it begins visibly to decompose into its elements, and even in solution it readily decomposes when heated, especially when a substance is present that can unite with the liberated hydrogen. Use is frequently made of this reducing property in the field of organic chemistry.

The unstable (endothermal) character of hydriodic acid is shown strikingly when it is attempted to liberate the acid by the action of

concentrated sulphuric acid on an iodide. As the temperature rises by the action, the hydriodic acid reduces the sulphuric acid to a much greater degree than in the case of hydrobromic acid. The primary reactions are:

$$KI + H_2SO_4 = KHSO_4 + HI;$$
$$8HI + H_2SO_4 = H_2S + 4H_2O + 8I.$$

When excess of sulphuric acid is used secondary actions take place, thus:

$$H_2S + H_2SO_4 = 2H_2O + SO_2 + S;$$
$$2H_2S + SO_2 = 2H_2O + 3S.$$

In the case of bromides, the reduction product of sulphuric acid is $SO_2$, but with iodides the lowest reduction product of sulphuric acid is formed, namely, $H_2S$. It is evident that this method cannot be used for preparing hydrobromic and hydriodic acids, as is done in the case of hydrochloric acid.

Hydriodic acid may be obtained by processes analogous to those mentioned for the preparation of hydrobromic acid. When hydrogen sulphide is passed into water containing finely powdered iodine in suspension, action takes place thus:

$$H_2S + 2I = 2HI + S.$$

Although, as was said above, iodine has little tendency to combine with free hydrogen, it decomposes the hydrogen sulphide readily and unites with its hydrogen. This is due to the great amount of heat generated by the solution of the hydriodic acid in the water. The action takes place with appreciable rise of temperature and this in effect is like an exothermal action, and accordingly takes place spontaneously, but only in the presence of water. The precipitated sulphur, after all iodine has been converted into colorless hydriodic acid, is removed by filtration and the solution may be concentrated to 57 per cent. by distilling off the excess of water. The 57 per cent. acid boils constantly at 127° C. under normal atmospheric pressure.

The official method for making diluted hydriodic acid depends on the decomposition of an aqueous solution of potassium iodide by an alcoholic solution of tartaric acid in the presence of a small quantity of potassium hypophosphite, which acts as a preservative. Upon cooling the mixture to the freezing-point, acid potassium tartrate separates, while hydriodic acid remains in solution, which is further diluted until a 10 per cent. acid is obtained. The decomposition taking place is this:

$$KI + H_2C_4H_4O_6 = KHC_4H_4O_6 + HI.$$

While hydriodic acid itself is not of much importance, many of its salts, the iodides, are of great interest.

At 0° C. an aqueous solution can be obtained containing as much as 90 per cent. HI. Nearly all iodides are soluble in water. The insoluble ones are of silver, mercury, copper (ous). Lead iodide is sparingly soluble.

The ionic reactions for iodine compounds are analogous to those for chlorine compounds.

**Tests for Iodine and Iodides.**

(Any soluble iodide may be used.)

1. Add to solution of an iodide, solution of silver nitrate: a pale-yellow precipitate of silver iodide, AgI, falls, which is insoluble in nitric acid, very sparingly soluble in ammonia water, but soluble in solution of sodium thiosulphate or potassium cyanide. (See Photography in chapter 31, under Silver.)

2. Add lead acetate to a solution of an iodide: a yellow precipitate of lead iodide, $PbI_2$, is produced. When the precipitate is dissolved in a large volume (200 c.c.) of boiling water, and the solution is cooled slowly, beautiful golden spangles are formed.

3. Add mercuric chloride solution to a solution of an iodide: a red precipitate of mercuric iodide, $HgI_2$, is produced, which is soluble in solutions of mercuric chloride and potassium iodide. Note that the corresponding chloride and bromide of mercury are soluble and white.

Also make the test with solution of mercurous nitrate. A greenish-yellow precipitate of mercurous iodide, HgI, is obtained. The corresponding chloride and bromide are white and also insoluble.

4. To the solution of an iodide add some chlorine water, or a few drops of concentrated nitric acid; iodine is liberated, which, with strongly diluted starch solution, gives a blue color. Iodine in combination has no action on starch. Excess of chlorine oxidizes iodine to colorless iodic acid; hence, the same precaution must be used as given in test 2 for bromides.

Traces of iodine may be detected readily by the fine violet color given to chloroform or carbon disulphide when the liquid is shaken with them.

5. Add a little concentrated sulphuric acid to a few granules of an iodide and warm gently. Colorless hydriodic acid gas is liberated, which causes white fumes with the moisture of the air; also free iodine, which may be recognized by its violet vapor.

Tests 3 and 4 are usually sufficient to identify iodides or hydriodic acid.

**Iodic Acid, $HIO_3$.**—When iodine is dissolved in strong nitric acid, this solution being then evaporated to dryness and heated to about 200° C. (392° F.) a white residue remains, which is iodine pentoxide:

$$6I + 10HNO_3 = 10NO + 5H_2O + 3I_2O_5.$$

By dissolving this oxide in water, iodic acid is obtained:

$$I_2O_5 + H_2O = 2HIO_3.$$

Iodic acid is a white crystalline substance, very soluble in water. From iodic acid or from iodates, sulphurous acid and many other reducing agents liberate iodine. Iodic acid instantly decomposes hydriodic acid, with liberation of iodine, thus:

$$HIO_3 + 5HI = 3H_2O + 6I.$$

This action is exactly like that between bromic acid and hydrobromic acid, and is used as a test for iodate in an iodide. A mixture of these salts which are compatible in a neutral medium, turns brown when moistened with dilute sulphuric or hydrochloric acid, due to liberation of iodine.

Potassium and sodium iodate are found to some extent in Chile saltpeter (sodium nitrate). They may be made in the same manner as are the chlorates and bromates, namely, by adding powdered iodine to a hot solution of potassium or sodium hydroxide:

$$6KOH + 6I = KIO_3 + 5KI + 3H_2O.$$

Iodide of potassium or sodium is formed at the same time. Because of the much greater solubility of the iodide, the iodate can be separated from it by crystallization. At 18° C., 100 c.c. of water dissolves 7.6 grams of potassium iodate, or 8.3 grams of sodium iodate.

Hypoiodous acid and its salts are not known. Periodic acid and its salts can be obtained. These oxygen compounds, in marked contrast to those of chlorine, are stable. Iodine pentoxide is the only oxide of the element known.

**Sulphur Iodide, $S_2I_2$.**—When the two elements, sulphur and iodine, are mixed together in the proportion of their atomic weights, and this mixture is heated, direct combination takes place. The fused mass is grayish-black, brittle, has a crystalline fracture and a metallic lustre. It is almost insoluble in water, but soluble in glycerin and in carbon disulphide.

**Compounds of Iodine with Bromine and Chlorine.**—While the affinity between the halogens is feeble, yet a few compounds formed by their union are known; all of them are unstable, decomposing readily on heating and some also in contact with water. Of some interest is *iodine trichloride*, $ICl_3$, obtainable as an orange, crystalline substance by passing dry chlorine gas over iodine, when at first iodine monochloride, ICl, and then the trichloride is formed. The latter has been used as a disinfectant.

**Compounds of nitrogen with the halogens.** When chlorine or iodine acts on ammonia the hydrogen of the latter combines with the halogens, while nitrogen is either set free or also enters into combination with the halogens, thus:

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

or

$$NH_3 + 6Cl = 3HCl + NCl_3.$$

The compounds $NH_2Cl$ and $NHCl_2$, as also the corresponding iodine compounds, are known. All these bodies are very unstable; nitrogen trichloride, an oily liquid, is one of the most explosive substances known; nitrogen iodide, a black powder, also explodes readily.

**Thermochemical Considerations.**—It has been stated before that reactions which take place spontaneously are accompanied by a conversion of chemical energy into some other form of energy which is liberated, and usually appears as heat. The vigor with which chemical actions take place is proportional to the total amount of energy liberated. In the case of oxidation by the use of an oxidizing compound, the energy liberated is the sum of the energy produced by the union of oxygen with the substance oxidized and the energy liberated by the decomposition of the oxidizer. In many cases this is much greater than the energy liberated by the action of free oxygen gas. This difference explains the fact that oxygen gas either does not oxidize, or only slowly oxidizes, many substances, whereas these same substances are readily oxidized by the compounds which furnish oxygen with the simultaneous liberation of considerable energy. Thus indigo is not affected by the atmosphere, but is very quickly oxidized to a colorless compound by hypochlorous acid.

The various oxygen compounds of chlorine, bromine and iodine have markedly different activities as oxidizing agents, because of the different quantities of energy liberated when they decompose. A fair idea of the relative activities of the principal oxygen acids of the halogens is given by the following table, which shows the amount of heat liberated by the decomposition of one molecular weight of the respective acids in aqueous solution:

| | | | For each atomic weight of oxygen. |
|---|---|---|---|
| $HClO$ | $= HCl + O +$ | 9,300 calories, or | 9,300 calories. |
| $HClO_3$ | $= HCl + 3O +$ | 15,300 " " | 5,100 " |
| $HClO_4$ | $= HCl + 4O +$ | 700 " " | 175 " |
| $HBrO_3$ | $= HBr + 3O +$ | 15,000 " " | 5,000 " |
| $HIO_3$ | $= HI + 3O -$ | 42,900 " " | −14,300 " |
| $HIO_4$ | $= HI + 4O -$ | 34,500 " " | − 8,625 " |

It will be seen that hypochlorous acid is the most energetic oxidizer, while iodic and periodic acids are the least energetic. The latter acids actually absorb energy when decomposing, and accordingly are the most stable of the oxygen compounds of the halogens.

## Fluorine, F = 19.

This element is found in nature, chiefly as fluorspar, calcium fluoride, $CaF_2$; traces of fluorine occur in many minerals, in some waters, and also in the enamel of teeth, and in the bones of mammals. Fluorine was, until 1887, scarcely known in the elementary state, because all attempts to isolate it were frustrated by the powerful affinities which this element possesses, and which render it difficult to obtain any material (from which a vessel may be made) which is not chemically acted upon, and, therefore, destroyed, by fluorine. The method used now for liberating fluorine depends upon the decomposition of hydrofluoric acid by a strong current of electricity in an apparatus constructed of platinum with stoppers of fluorspar. To prevent too rapid corrosion of the platinum vessels, the decomposition is accomplished at a temperature below the freezing-point. Fluorine is a gas of yellowish color, having a highly irritating and suffocating odor, and possessing affinities stronger than those of

any other element. As a supporter of combustion, fluorine leaves oxygen far behind; it combines spontaneously even in the dark and at low temperature with hydrogen; sulphur, phosphorus, lampblack, and also many metals ignite readily in fluorine; even the noble metals, gold, platinum, and mercury, are converted into fluorides; from sodium chloride the chlorine is liberated with the formation of sodium fluoride; organic substances, such as oil of turpentine, alcohol, ether, and even cork ignite spontaneously when brought in contact with this remarkable element.

**Hydrofluoric Acid, HF.**—A colorless gas, very irritating, soluble in water. It is obtained by the action of sulphuric acid on fluorspar:

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

Hydrofluoric acid, either in the gaseous state or its solution in water, is used for etching on glass. This effect is due to the action of the acid upon the silica of the glass, which is converted into either silicon fluoride, $SiF_4$: or into hydrofluosilicic acid, $H_2SiF_6$,

Hydrofluoric acid, or strong solutions of it, are powerful antiseptics. In small quantities the acid is used as an admixture to fermenting liquids, as it has been found that it does not act upon the principal ferment of yeast, which causes the decomposition of sugar into alcohol and carbon dioxide, while it readily destroys a number of objectionable ferments. The yield of alcohol is thus considerably increased.

*Experiment* 19. Prepare a glass plate by heating it slightly and covering its surface with a thin layer of wax or paraffin; after cooling, scratch some letters or figures through the wax, thus exposing the glass. Set the plate over a dish (one made of lead or platinum answers best), in which a few grams of powdered fluorspar have been mixed with about an equal weight of sulphuric acid, and set in the open air for a few hours (heating slightly facilitates the action); upon removing the wax or paraffin, the glass will be found to be *etched* where its surface was exposed to the vapors of the acid. This experiment serves also as the best *test for fluorides.* (See under Silicon.)

## 19. DETERMINATION OF ATOMIC AND MOLECULAR WEIGHTS.

### Determination of Atomic Weights.

As was said in chapter 10 in the discussion of the atomic theory and atomic weights, it is impossible to determine the absolute weight

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QUESTIONS.—How is bromine found in nature? State the physical and chemical properties of bromine. What is hydrobromic acid, and how can it be made? By what tests may bromine and bromides be recognized? What is the chief source of iodine? What are the chemical and physical properties of iodine? What is tincture of iodine, what is its color, and how does it stain the skin? Mention reactions by which iodine and iodides may be recognized. By what element may bromine and iodine be liberated from their compounds? How is hydrofluoric acid made, and what is it used for?

of an atom, and fortunately that is not necessary. It is possible, however, to determine with a great degree of accuracy the relative weights of atoms, that is, how many times heavier one atom is than another atom. These relative weights or ratios are called atomic weights, and the problem for the chemist in determining the atomic weight of any element is to find how many times heavier the atom of that element is than the atom which is taken as the standard of comparison. Formerly this standard was the hydrogen atom, being the lightest of all atoms, and its weight was taken as unity. On this standard the atomic weight of oxygen is 15.88, that is, its atom weighs 15.88 times as much as the atom of hydrogen. For reasons given in chapter 10, chemists prefer to call the atomic weight of oxygen 16, on which standard the relative weight of hydrogen is 1.008. On this oxygen standard, the figures assigned to the other elements as atomic weights mean that the amount of matter in one atom of the respective elements and in one atom of oxygen are to each other as the atomic weight of the elements is to the atomic weight of oxygen, 16.

It was comparatively easy to establish the atomic weight of some of the most important elements. For instance, the molecule of hydrochloric acid is in all probability composed of one atom of each constituent element, and as there is nothing known concerning hydrochloric acid that contradicts this view, the formula HCl is accepted. By careful quantitative analysis of this acid, it is found to contain 2.76 per cent. of hydrogen and 97.24. per cent. of chlorine; therefore, since there are always the same number of atoms of hydrogen and chlorine in the acid, it follows that the weights of the atom of hydrogen and chlorine must be to each other as 2.76 : 97.24. In other words, the atom of chlorine must be 35.2 (97.24 ÷ 2.76) times as heavy as the atom of hydrogen, or if the atomic weight of hydrogen is taken as 1, then the atomic weight of chlorine is 35.2. If the molecule of hydrochloric acid is correctly represented by HCl, then it follows by Gay-Lussac's law of volumes and Avogadro's law, as shown in chapter 10, that the molecule of hydrogen consists of 2 atoms, and also that the molecule of oxygen consists of at least two atoms. The physical and chemical study of water leads to the conclusion that its molecule consists of 2 atoms of hydrogen and 1 atom of oxygen as represented by the formula $H_2O$. By accepting this formula as correct, it follows that the molecule of oxygen contains just 2 atoms. The determination of the parts by weight in which hydrogen and oxygen unite to form water has been done with the greatest exactness, the result being 1 part by weight of hydrogen to 7.94 parts by weight of oxygen. Reasoning as above in the case of hydrochloric acid, these figures mean that 1 atom of oxygen weighs 7.94 times as much as 2 atoms of hydrogen, or 15.88 times as much as 1 atom of hydrogen. If we call the weight of 1 atom of oxygen 16, then in proportion an atom of hydrogen weighs 1.008, and this is called the atomic weight of hydrogen on the oxygen = 16 basis.

The determination of atomic weights in all cases ultimately rests upon accurate quantitative analysis, by which the proportions in which the element whose atomic weight is desired, unites with one or more elements whose atomic weight is known, or displaces an element of known atomic weight from a compound. But in most cases, the true atomic weight cannot be deduced from the results of analysis directly; other facts and considerations must be utilized to arrive at a proper solution. This is made clear from the following examples: Accurate analysis shows a substance to contain iron and oxygen in the proportions of 55.84 parts of the former to 16 parts of the latter. If in this iron compound the elements are united atom for atom, then the atomic weight of iron is 55.84. But there might be two atoms of iron to one of oxygen, in which case the atomic weight would be 27.92, or there might be one atom of iron to two of oxygen, when the atomic weight of iron would be 111.68. As the analysis gives no clue whatever to the number of atoms of iron and oxygen in the molecule of the compound, it is impossible to decide without further help which of the above figures is the correct atomic weight of iron. It is evident, however, that it will be either the smallest figure, or some simple multiple of it.

Another example illustrating the displacement of one element by another may be taken. Metallic zinc displaces hydrogen from dilute hydrochloric acid. By carefully weighing the zinc and collecting the hydrogen and calculating its weight, it is found that 64.9 grams of zinc displace 2 grams of hydrogen, or 32.45 grams of zinc displace 1 gram of hydrogen. If 1 atom of zinc displaces 1 atom of hydrogen, then the atomic weight of zinc would be 32.45 on the hydrogen basis. But here, again, analysis gives no information as to the atomic relationship involved, and therefore it is impossible to decide on the real atomic weight of zinc, but we know that it must bear a simple relationship to 32.45.

We will now consider some of the other facts that are used to enable one to choose the correct atomic weight from the number of possibilities as the result of analysis. The first of these will be the consideration of molecular weights.

## Determination of Molecular Weights.

In the case of all substances that are gases by nature or can be vaporized by heat without decomposition, we have a ready means of determining the relative heaviness of molecules by using Avogadro's law. Since equal volumes of all gases at the same temperature and pressure contain the same number of molecules, the weights of equal volumes of gases must bear the same ratio to one another as the weights of the individual molecules. But the weights of molecules are in the same ratio as the molecular weights. Hence we deduce the following rule from Avogadro's law: *Densities of gases at the same temperature and pressure are to each other as their molecular*

*weights.* If we know the molecular weight of any gas and its density, by comparing any other gas with it we can determine its molecular weight. In view of the fact that it is now practically a universal custom to express atomic and molecular weights on the oxygen basis, oxygen is the logical standard for comparing densities of gases. Formerly hydrogen or air was used. The determination of the densities of gases or vapors is a routine laboratory experiment, and for the various methods by which it is done the student must be referred to works on physics, or large text-books on chemistry.

The density of oxygen has been very carefully determined to be 1.429 grams per liter at 0° C. and 760 mm. pressure. Suppose it is desired to know the molecular weight of carbon dioxide gas, the density of which has been found to be 1.977 grams per liter at 0° C. and 760 mm. pressure. We would make the proportion:

| Density of oxygen. | | Density of carbon dioxide. | :: | Molec. wt. of oxygen. | : | Molec wt. of carbon dioxide. |
|---|---|---|---|---|---|---|
| 1.429 | : | 1.977 | :: | 32 | : | $x$. |

$$x = \frac{1.977}{1.429} \times 32 = 44.2.$$

If a substance is not gaseous at ordinary temperature but requires heat to maintain it in a gaseous state, the density as determined at elevated temperature must be reduced by the use of Charles' law to the imaginary density that the substance would have at 0° C., before making the comparison with oxygen in a proportion like the one above.

The molecular weights determined as outlined above are not absolutely correct, because Avogadro's law is not an absolute law. It expresses what would be true, if all gases and vapors were ideal or perfect gases. The weights obtained by the use of the law are close approximations to the correct molecular weights, the differences being so small that we can use the values obtained for deciding what figures resulting from the analysis of compounds are the correct atomic weights.

For substances that cannot be vaporized, another method that is used for determining molecular weights is that of Raoult. This is based upon the fact that the freezing-point of a liquid is lowered to the same extent by dissolving in it compounds in quantities proportional to their molecular weights. For example: Water begins to solidify at 0° C. (32° F.), but by dissolving in it say 4 per cent. of its weight of a salt (the molecular weight of which is known) the freezing-point is lowered, say 1° C. If, then, another salt (the molecular weight of which is not known) be dissolved in water, and it be found that to reduce the freezing-point 1° C. there must be dissolved a quantity equal to 7 per cent. of the weight of the water used, then the molecular weights of the two salts are to each other as 4 to 7, provided neither salt has undergone dissociation in solution. If the latter be true, the percentage of dissociation can be

determined by the conductivity method and appropriate correction made in the molecular weight found by the freezing-point method.

Molecular weights may also be found by the analogous boiling-point method. These two methods are discussed in chapter 8 on Solution, but for details as to the execution of the methods in the laboratory and description of the apparatus employed, the student must refer to works on Physical Chemistry.

When a substance cannot be vaporized and is insoluble in the usual solvents, its molecular weight cannot be determined with certainty. Its percentage composition may be determined by analysis and a formula constructed as described in chapter 4. For example, the formula $CaCO_3$ for calcium carbonate corresponds to its percentage composition, but so does $Ca_2C_2O_6$, or $Ca_3C_3O_9$, or any multiple of $CaCO_3$. There is no way of determining the actual number of atoms in the molecule of calcium carbonate, but the relative number of atoms of each element is known. In all such cases it is customary to adopt the simplest formula that expresses the percentage composition of the substances.

**Atomic Weights Determined by the Help of Molecular Weights.**

Having discussed the methods of finding molecular weights, let us see how these may be used in aiding us to fix upon the correct atomic weights of elements. It was pointed out above that, since analysis gives no clue as to the number of atoms that unite to form a molecule of a compound, it is impossible to fix upon the exact atomic weight by that method. We can deduce a set of figures, one of which is the atomic weight, but we do not know which one.

The method of procedure may be illustrated in the case of carbon. A number of typical compounds of this element that can be volatilized, are selected, accurately analyzed for the percentage composition, and molecular weights determined. Then from the percentage composition, the parts by weight of carbon that is present in amounts of the respective compounds represented by the molecular weights are calculated. The figures thus obtained will represent the proportion of carbon helping to make up the molecules of the respective compounds. The smallest figure in such a series is taken as corresponding to 1 atom of carbon in a molecule, and hence is the atomic weight of carbon. The calculations may be made clear by a concrete example. Careful analysis of carbon dioxide gives 27.27 per cent. of carbon and 72.73 per cent. of oxygen. Molecular weight determination gives about 44.2. The amount of carbon in 44.2 parts of the gas is found by the proportion:

$$100 : 27.27 :: 44.2 : x,$$

$$x = \frac{27.27 \times 44.2}{100} = 12.05.$$

The following table gives the results of the above calculation applied to eight well-known carbon compounds. Small decimals are omitted:

| | Molecular weight. | Parts of carbon in amount of substances represented by mol. wt. |
|---|---|---|
| Carbon monoxide | 28 | 12 |
| Carbon dioxide | 44 | 12 |
| Carbon disulphide | 76 | 12 |
| Methane | 16 | 12 |
| Ethylene | 28 | 24 |
| Ether | 74 | 48 |
| Acetylene | 26 | 24 |
| Acetic acid | 60 | 24 |

In none of the compounds is the proportion of carbon in the molecular weight less than 12, which, therefore, is accepted as the atomic weight of carbon. When once the approximate atomic weights of elements are thus determined, the number of atoms in the molecule of any substance analyzed is easily determined, and from this knowledge, the exact atomic weights are worked out by the most refined analysis. Thus, the formula of carbon dioxide is $CO_2$, 1 atom of carbon united to 2 of oxygen in the molecule. Exact analysis shows that this gas contains 12 parts of carbon to every 32 parts of oxygen, hence the atomic weight of carbon is exactly 12, that of oxygen being 16.

### Determination of Atomic Weights by Specific Heat.

Specific heat has been stated to be the quantity of heat required to raise the temperature of a given weight of any substance a given number of degrees, as compared with the quantity of heat required to raise the temperature of the same weight of water the same number of degrees.

In comparing atomic weights with the numbers expressing the specific heats, it is found that the higher the atomic weight, the lower the specific heat, and the lower the atomic weight, the higher the specific heat. This simple relation may be thus expressed: Atomic weights are inversely proportional to the specific heats; or the product of the atomic weight multiplied by the specific heat is a constant quantity for the elements examined.

| Elements. | Specific heats. (Water = 1.) | Atomic weights. | Product of specific heat × atomic weight. |
|---|---|---|---|
| Lithium, | 0.9408 | 6.94 | 6.53 |
| Sodium, | 0.2934 | 23.0 | 6.75 |
| Sulphur, | 0.2026 | 32.07 | 6.50 |
| Zinc, | 0.0956 | 65.37 | 6.25 |
| Bromine (solid), | 0.0843 | 79.92 | 6.74 |
| Silver, | 0.0570 | 107.88 | 6.15 |
| Bismuth, | 0.0308 | 208.0 | 6.41 |

An examination of this table will show this relation between atomic weight and specific heat, and also that the product of atomic weight multiplied by specific heat is equal to about 6.5. The variations noticed in this constant quantity of about 6.5 may be due to errors made in the determinations of the specific heats, and subsequent determinations may cause a more absolute agreement.

However, the agreement is sufficiently close to justify the deduction of a law which says: *The atoms of all elements have exactly the same capacity for heat.* This law was first recognized by Dulong and Petit in 1819, and is simply a generalization of the facts stated.

To show more clearly what is meant by saying that all atoms have the same capacity for heat, we will select three elements to illustrate this law.

If we take 6.94 grams of lithium, 32.07 grams of sulphur, 107.88 grams of silver, we have of course in these quantities equal numbers of atoms, because 6.94, 32.07, and 107.88 represent the atomic weights of these elements. If we expose these stated quantities of the three elements to the same action of heat, we shall find that the temperature increases equally for all three substances—that is to say, the same heat will be required to raise 6.94 grams of lithium 1°, which is necessary to raise either 32.07 grams of sulphur or 107.88 grams of silver 1°.

The quantity of heat necessary to raise the atom of any element a certain number of degrees is, consequently, the same. As heat is the consequence of motion, the result of the facts stated may also be expressed by saying: It requires the same energy to cause different atoms to vibrate with such a velocity as to acquire the same temperature, no matter whether these atoms be light or heavy.

It is evident that these facts give us another means of determining atomic weights, by simply dividing 6.5 by the specific heat of the element. The specific heat of sulphur, for instance, has been found to be 0.2026. 6.5 divided by this number is 31.6, or nearly 32. Originally the atomic weight of sulphur had been determined by chemical methods to be 16, but its specific heat, as well as other properties, has shown this number to be but one-half of the weight, 32 (or exactly 32.07), now adopted.

It may be mentioned that elements possess essentially the same specific heat whether they exist in a free state or are in combination; this fact will, in many cases, be of use in the determination of atomic weights.

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QUESTIONS.—How are atomic weights determined? Why cannot atomic weights be determined by chemical analysis alone? How are molecular weights determined? If the weight of a liter of a pure gas under normal conditions is 1.2507 grams, what is its molecular weight? What relation exists between atomic weight and specific heat (Dulong and Petit's law)? If the specific heat of an element is 0.1138, what is its atomic weight approximately? 53.94 grams of an element replaced 0.504 grams of hydrogen from 18.23 grams of hydrochloric acid; what is the atomic weight of the element, if its specific heat is 0.057?

# METALS AND THEIR COMBINATIONS.

## 20. GENERAL REMARKS REGARDING METALS.

Of the sixty odd metallic elements only about one-half are of sufficient general interest and importance to deserve consideration in this book. Those in the following list will receive extended or brief consideration.

### Derivation of Names, Symbols, and Atomic Weights.

| | | | |
|---|---|---|---|
| Aluminum, | Al | = 27.1. | From *alum*, a salt containing it. |
| Antimony, (Stibium) | Sb | = 120.2. | From the Greek *ἀντὶ* (anti) against, and *moine*, a French word for monk, from the fact that some monks were poisoned by compounds of antimony. Stibium, from the Greek, *στίβι* (stibi), the name for the native sulphide of antimony. |
| Arsenic, | As | = 74.96. | From the Greek *ἀρσενικὸν* (arsenicon), the name for the native sulphide of arsenic. |
| Barium, | Ba | = 137.37. | From the Greek *βαρὺς* (barys), heavy, in allusion to the high specific gravity of barium sulphate, or heavy-spar. |
| Bismuth, | Bi | = 208. | From the German *wismuth*, an expression used long ago by the miners in allusion to the variegated tints of the metal when freshly broken. |
| Cadmium, | Cd | = 112.4. | From the Greek *καδμεία* (kadmeia) the old name for calamine (zinc carbonate), with which cadmium is frequently associated. |
| Cæsium, | Cs | = 132.81. | From the Latin *cæsius*, sky-blue, in allusion to the blue line in its spectrum. |
| Calcium, | Ca | = 40.07. | From the Latin *calx*, lime, the oxide of calcium. |
| Chromium, | Cr | = 52.0. | From the Greek *χρῶμα* (chroma), color, in allusion to the beautiful colors of all its compounds. |
| Cobalt, | Co | = 58.97. | From the German *Kobold*, which means a demon inhabiting the mines. |
| Copper, | Cu | = 63.57. | From the Latin *cuprum*, copper, and this from the Island of Cyprus, where copper was first obtained by the ancients. |
| Gold, (Aurum) | Au | = 197.2. | Gold means bright yellow in several old languages. The Latin *aurum* signifies the color of fire. |

| | | | | |
|---|---|---|---|---|
| Iridium, | Ir | = | 193.1. | From iris, rainbow, in allusion to the varying tints of its salt solutions. |
| Iron, | Fe | = | 55.84. | Iron probably means metal; the derivation of the Latin *ferrum* is not definitely known. |
| Lead, (Plumbum) | Pb | = | 207.1. | Both words signify something heavy. |
| Lithium, | Li | = | 6.94. | From the Greek λίθειος (litheios), stony. |
| Magnesium, | Mg | = | 24.32. | From Magnesia, a town in Asia Minor, where magnesium carbonate was found as a mineral. |
| Manganese, | Mn | = | 54.93. | Probably from magnesium, with the compounds of which it was long confounded. |
| Mercury, (Hydrargyrum) | Hg | = | 200.6. | From Mercury, the messenger of the Greek gods. Hydrargyrum means liquid silver. |
| Molybdenum, | Mo | = | 96.0. | From the Greek μόλυβδος (molybdos), lead. |
| Nickel, | Ni | = | 58.68. | From the old German word *nickel*, which means worthless. |
| Platinum, | Pt | = | 195.2. | Platina is the diminutive of the Spanish word *plata*, silver. |
| Potassium, (Kalium) | K | = | 39.1. | From pot-ash; potassium carbonate being the chief constituent of the lye of wood-ashes. Kali is the Arabic word for ashes. |
| Radium, | Ra | = | 226.4. | Named from the fact that it emits invisible rays that affect a photographic plate, etc. |
| Rubidium, | Rb | = | 85.45. | From Latin *rubidus*, red, in reference to the red lines in its spectrum. |
| Silver, | Ag | = | 107.88. | Silver and *argentum* signify white. |
| Sodium, (Natrium) | Na | = | 23 0. | From soda-ash, or sod-ash, the ashes of marine plants which are rich in sodium carbonate. Natron is an old name for natural deposits of sodium carbonate. |
| Strontium, | Sr | = | 87.63. | From Strontian, a village in Scotland, where strontium carbonate is found. |
| Tin, (Stannum) | Sn | = | 119.0. | Both words most likely signify stone. |
| Uranium, | U | = | 238.5. | From *uranus*, the name of a planet. |
| Zinc, | Zn | = | 65.37. | Most likely from the German *zinn* or *tin*, the metals having been confounded with each other. |

## Melting-points of Metals.

| | | C. | F. |
|---|---|---|---|
| Fusible below the boiling-point of water, | Mercury | —40° | — 40° |
| | Potassium | +62 | +144 |
| | Sodium | 97 | 207 |
| Fusible below red heat, | Lithium | 180 | 356 |
| | Tin | 228 | 443 |
| | Cadmium | 310 | 590 |
| | Bismuth | 260 | 500 |
| | Lead | 325 | 617 |
| | Zinc | 412 | 773 |
| | Magnesium | 700 | 1292 |
| | Antimony | 425 | 797 |
| | Aluminum | 700 | 1292 |

| | | | |
|---|---|---|---|
| Fusible at red heat, | Barium. | | |
| | Calcium. | | |
| | Strontium. | | |
| | Silver | 1020 | 1868 |
| | Copper | 1100 | 2012 |
| | Gold | 1200 | 2192 |
| | Cast iron | 1150 | 2102 |
| Infusible below a red heat. | Pure iron, Nickel, Cobalt, Manganese, | Highest heat of forge. | |
| | Molybdenum, Chromium, | Agglomerate, but do not melt in forge. | |
| | Platinum, Iridium, | Fusible in the oxyhydrogen blowpipe flame. | |

Arsenic does not fuse, but volatilizes at a low red heat.

## Specific Gravities of Metals at 15.5° C.

| | | | |
|---|---|---|---|
| Lithium | 0.593 | Manganese | 8.00 |
| Potassium | 0.865 | Molybdenum | 8.63 |
| Sodium | 0.972 | Cadmium | 8.70 |
| Calcium | 1.57 | Nickel | 8.70 |
| Magnesium | 1.75 | Cobalt | 8.95 |
| Strontium | 2.54 | Copper | 8.96 |
| Aluminum | 2.67 | Bismuth | 9.90 |
| Barium | 4.00 | Silver | 10.50 |
| Arsenic | 5.88 | Lead | 11.36 |
| Antimony | 6.72 | Mercury | 13.59 |
| Zinc | 6.90 | Gold | 19.36 |
| Tin | 7.29 | Platinum | 21.50 |
| Iron | 7.79 | Iridium | 22.42 |

## Time of Discovery of the Metals.

| | |
|---|---|
| Gold, Silver, Mercury, Copper, Zinc, Tin, Iron, Lead, | These metals were known to the ancients, because either they are found in a metallic state, or can be obtained by comparatively simple processes from the oxides. |
| Antimony, Bismuth, | Latter part of the fifteenth century. |
| Arsenic, | 1694, by Schröder. |
| Cobalt, | 1733, by Brandt. |
| Platinum, | 1741, by Wood. |
| Nickel, | 1751, by Cronstedt. |
| Manganese, | 1774, by Galm. |
| Molybdenum, | 1782, by Hjelm. |

Chromium, 1797, by Vauquelin.
Iridium, 1804, by Smithson Tennant.
Potassium, Sodium, Barium, Calcium, Strontium, Magnesium, 1807–1808 — H. Davy discovered methods for the separation of these metals from their oxides.
Cadmium, 1817, by Stromeyer.
Lithium, 1817, by Arfvedson.
Aluminum, 1828, by Wohler

## Valence of metals.[1]

| *Univalent.* | *Bi, tri, or sexivalent.* |
|---|---|
| Lithium, | Chromium, |
| Potassium, | Cobalt, |
| Sodium, | Iron, |
| Silver. | Manganese, |
| | Nickel, |
| | Molybdenum. |
| *Bivalent.* | *Bi- and quadrivalent.* |
| Barium, | Iridium, |
| Calcium, | Platinum, |
| Strontium, | Tin. |
| Magnesium, | |
| Cadmium, | |
| Zinc, | *Tri- and quinquivalent.* |
| Copper, | Antimony, |
| Mercury. | Arsenic, |
| | Bismuth. |
| *Trivalent.* | *Uni- or trivalent.* |
| Aluminum, | Gold. |

## Occurrence in nature.

*a. In a free or combined state.*

Gold, Iridium, Platinum, } Almost exclusively in the metallic state.
Silver, Mercury, } As metals or sulphides.
Bismuth, generally metallic, also as oxide and sulphide.
Copper, rarely metallic; chiefly as sulphide, oxide, and carbonate.

*b. In combination only.*

Potassium, Sodium, Lithium, } Chiefly as chlorides or silicates.

[1] The valence here given is the one *chiefly* exerted by the elements, but several compounds are known in which some of the metals exhibit a yet different valence; thus copper and mercury seem to be univalent in certain compounds, while some metals exhibiting a valence of six (iron, chromium, etc.) are also bi- and trivalent.

Barium, as sulphate.
Calcium, Strontium, Magnesium, } As carbonates, sulphates, silicates.
Aluminum, in silicates.
Iron, Zinc, Cadmium, } As oxides, carbonates, sulphides.
Arsenic, Antimony, Lead, Cobalt, Nickel, Molybdenum, } Chiefly as sulphides.
Chromium, Manganese, Tin, } Chiefly as oxides.

## Classification of Metals.

For the purpose of study, metals may be differently arranged into groups according to the selection of those properties which are made the basis for comparison. Thus, the valence alone may serve for classification, and in that case the arrangement will also largely correspond to the periodic system. The scheme adopted below is based more especially on the analytical behavior of the metals. While this classification brings together in many cases those metals belonging to one group of the periodic system, in a few cases the elements of one periodic group are separated, as, for instance, in the case of magnesium, zinc, and cadmium. These elements resemble one another closely in many respects, and are found together in group II. of the periodic system, while in a classification based chiefly on analytical properties these metals are found in different groups.

*Light metals.*
Sp. gr. from 0.6 to 4.
Sulphides soluble in water.

*Heavy metals.*
Sp. gr. from 6 to 22.4.
Sulphides insoluble in water

*Light metals.*

*Earth metals.*
Al, and many rare metals
Oxides insoluble

*Alkaline earth metals.*
Ba, Ca, Sr, (Mg).
Oxides soluble;
Carbonates insoluble

*Alkali metals*
K, Na, Li, ($NH_4$).
Oxides, carbonates, and most salts soluble.

*Heavy metals.*

*Arsenic group.*
As, Sb, Sn, Au, Pt, Mo.

*Lead group.*
Pb, Cu, Bi, Ag, Hg, Cd

*Iron group.*
Fe, Co, Ni, Mn, Zn, Cr.
Sulphides soluble in dilute acids.

Sulphides insoluble in dilute acids.

Sulphides soluble in ammonium sulphide.

Sulphides insoluble in ammonium sulphide.

**Properties of Metals.**—All metals have a peculiar lustre known as metallic lustre, and all are more or less good conductors of heat and electricity. The color of most metals is white, grayish, or bluish-white, or dark gray; a few metals show a distinct color, as, for instance, gold (yellow) and copper (red).

At ordinary temperatures metals are solids with the exception of mercury, all are fusible, and some are so volatile that they may be distilled. Most, probably all, metals may be obtained in a crystallized condition.

Metals show a wide difference in the properties of *malleability*, *ductility*, and *tenacity*. Gold is both the most malleable and most ductile metal, while lead possesses comparatively little of these qualities. In many cases heat increases or develops malleability and ductility, but diminishes tenacity; however, the tenacity of iron, which surpasses that of any other metal, is not lessened by heating.

The term *annealing* denotes the process of restoring the malleability and ductility of some metals after these properties have been diminished, by causing a change in the molecular structure of the metals through hammering, rolling, or sudden cooling. Annealing consists in heating the metal and permitting it to cool slowly (in a few cases quickly) in order to allow the cohesive force to produce the most stable arrangement of the molecules.

*Tempering*, which term at times is used analogously with annealing, consists in heating the metal and chilling it suddenly. The result of annealing is the highest development of softness and in case of some metals the restoration of cohesiveness; the object of tempering is the attainment of a certain degree of hardness and elasticity.

*Elasticity, i. e.*, the power of recovering original form when twisted or bent, and *sonorousness, i. e.*, the property of yielding a musical sound when struck, are possessed only by the harder metals, and to a high degree by certain mixtures of metals.

All metals expand when heated, but the *rate of expansion* of the different metals differs. Within certain limits of temperature the expansion of a metal occurs uniformly in direct ratio to the increase in temperature. The great expansibility of zinc is an important property of the metal when used as a die in dental prosthesis.

Molten metals, as a rule, dissolve in one another. Their mixtures (alloys) still exhibit the metallic nature in their general physical characters. It is different, however, when metals combine with non-metals; in this case the metallic characters are lost almost invariably. All metals combine with chlorine, fluorine, and oxygen; most metals also with sulphur, bromine, and iodine; many also with carbon and phosphorus, forming the respective chlorides, fluorides, oxides, sulphides, bromides, iodides, carbides, and phosphides. Metals replace hydrogen in acids, forming salts.

The intensity with which metals combine with non-metals or with acids differs widely. Selecting the combinations with oxygen as a typical instance, we find that the affinity between the alkali metals and the alkaline earth

metals is so intense that these metals cannot be exposed to the atmosphere for even a few hours without undergoing complete oxidation. It is for this reason that these metals cannot be used in the metallic state for purposes requiring constant exposure to air. Other metals, such as iron, will oxidize (rust) slowly at ordinary temperature or will burn when heated sufficiently high. Yet other metals retain their metallic lustre in dry or moist air at low or high temperature. Indeed, the oxides of these metals are decomposed into oxygen and the respective metal by the mere application of heat. The metals showing this behavior are often called *noble metals*, while all others are designated as *base metals*. The noble metals are gold, silver, mercury, platinum, iridium, and a few other metals related to platinum. (See also page 152.)

The general chemical characteristics of metals have been pointed out in chapters 10 and 13. *A striking difference between metals and non-metals* is shown in the behavior of their halogen compounds toward water. We have seen that the phosphorus halides, silicon fluoride, etc., are rapidly and completely decomposed (hydrolyzed) in water after the following plan:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

A halogen acid and an acid of the other element are formed. The halogen compounds of the elements classed as metals are either not at all hydrolyzed by water, or only partially. Most of the metallic halides are not perceptibly hydrolyzed, in other words, they are neutral in solution; some are slightly decomposed, giving a slightly acid solution, as, for example, iron and copper chloride. There are a few extreme cases, the halides of antimony and bismuth, in which the decomposition is considerable, but not complete, thus:

$$SbCl_3 + H_2O \rightleftarrows SbOCl + 2HCl;$$
$$BiCl_3 + H_2O \rightleftarrows BiOCl + 2HCl.$$

The metals are found in an insoluble compound which still contains chlorine and is known as an oxy-salt or basic salt, while the liquid becomes decidedly acid. These basic salts dissolve in an excess of the halogen acid and become normal salts. The point is that the action between water and the halides of metals is reversible, while in the case of non-metals it is not. For instance, no amount of hydrochloric acid in water would prevent phosphorus halides from being decomposed completely.

The halogen acids are decidedly active acids, hence if hydrolysis of halides takes place, the reason for it must reside in the other element in combination. It is on this account that the halogen compounds are chosen to bring out the difference between metals and non-metals as indicated above.

**Manufacture of Metals.**—Most metals may be obtained from their oxides by heating the latter with charcoal, the carbon combining with the oxygen of the oxide, while the metal is liberated:

$$MO + C = CO + M;$$
$$2MO + C = CO_2 + 2M.$$

Also hydrogen may be used in some cases as the deoxidizing agent:

$$MO + 2H = H_2O + M.$$

Some metals are found in nature chiefly as sulphides, which usually are converted into oxides (before the metal can be obtained) by roasting. The term *roasting*, when used in metallurgy, means heating strongly in an oxidizing atmosphere, when the sulphides are converted into sulphates or oxides, thus:

$$MS + 4O = MSO_4; \text{ or } MS + 3O = MO + SO_2.$$

A few metals are obtained by heating the chloride with metallic sodium, when sodium chloride is formed, while the other metal is set free. Electrolysis is also one of the means for obtaining metals from their compounds.

Recently a generally applicable method of obtaining metals has been devised, which consists in the action of aluminum powder on the oxides of the metals, especially of those that have a high fusing-point and form difficultly reducible oxides. So much heat is developed in these reductions that the method may be used for welding, for example, the joints between rails.

**Alloys.**—Alloys are combinations or, more correctly speaking, mixtures of two or more metals. Whenever mercury is a constituent of an alloy it is called *amalgam*. All alloys exhibit metallic nature in their physical properties—*i. e.*, they have metallic lustre and are more or less good conductors of heat and electricity.

While alloys are generally looked upon as molecular mixtures, and not as definite chemical compounds, yet there are many alloys the properties of which are not intermediate between those of the elements entering into these alloys, as we should expect if they were mechanical mixtures. For this reason it is assumed that, in at least some cases, compounds are formed which, however, are generally dissolved in, or mixed with, an excess of one of the constituent metals.

On the other hand, there are cases where there is an utter lack of affinity between the component parts of an alloy. Thus, alloys of copper and lead, usually termed *pot-metal alloys*, show particles of the two metals side by side, when the fractured surface is examined with the microscope.

**Manufacture of Alloys.**—Alloys are generally obtained by fusing the metals together; but in order to do it successfully such properties of the components as fusibility, specific gravity, proneness to oxidize, etc., should be considered. As a general rule the metal having the slightest fusing-point is melted first, and to it are added the other metals in the diminishing order of their fusing-points. Loss or deterioration by oxidation should be guarded against by covering the surface of the liquid mass with charcoal or with such fluxes as borax, sodium chloride, or ammonium chloride. The heat should at no time be higher than is necessary for the liquefaction.

**Properties of Alloys.**—Alloys generally are harder and more brittle, but less ductile and malleable than the constituent metals possessing these qualities

in the highest degree. The union even of two ductile metals may destroy that property more or less completely, as is shown by the absence of ductility in an alloy of gold and a small portion of lead. The combination of a brittle and a ductile metal always yields a brittle alloy.

Tenacity is generally increased. Thus, copper alloyed with 12 per cent. of tin has its tenacity trippled; gold, when alloyed with copper, silver, or platinum, has its tensile resistance nearly doubled; aluminum bronze, an alloy of copper and aluminum, has a greater tenacity than that of either of the constituent metals.

Certain metals impart to alloys specific properties. Thus, bismuth and cadmium increase fusibility; tin and lead, both of which are soft metals, impart hardness and tenacity; arsenic and antimony produce brittle alloys.

The fusibility of an alloy is invariably greater than that of its least fusible constituent, and may be greater than that of its most fusible constituent. Thus an alloy of 2 parts of tin, 3 of lead, and 5 of bismuth fuses at 91° C., while tin alone melts at 228°, lead at 325°, and bismuth at 260° C.

The conductivity of alloys for heat and electricity is less than that of the pure metals. The color of alloys is generally a modification of the predominating ingredient, but instances are known where the color of alloys has no relation to its constituents. For instance, German silver is perfectly white, although it contains a considerable portion of red copper.

## 21. POTASSIUM (KALIUM).

$K^i = 39.1.$

**General Remarks Regarding Alkali-metals.**—The metals potassium, sodium, lithium (rubidium and cæsium) form the group of the alkali-metals, which, in many respects, show a great resemblance to each other in chemical and physical properties. For reasons to be explained hereafter, the compound radical ammonium is usually classed among the alkali-metals.

The alkali-metals are all univalent: they decompose water at the ordinary temperature, with liberation of hydrogen; they combine spontaneously with oxygen and chlorine; their hydroxides, sulphates, nitrates, phosphates, carbonates, sulphides, chlorides, iodides, and nearly all other of their salts are soluble in water; all these compounds are white, solid substances, most of which are fusible at a

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QUESTIONS.—How many metals are known, and about how many are of general interest? Mention some metals having very low and some having very high fusing-points. What range of specific gravities do we find among the metals? Mention some univalent and some bivalent metals; also some which show a different valence under different conditions. Mention some metals which are found in nature in an uncombined state; some which are found as oxides, sulphides, chlorides, and carbonates, respectively. Into what two groups are the metals divided? State the three groups of light metals. What is a metal? What is an alloy, and what is an amalgam? By what process can most metals be obtained from their oxides?

red heat. Of all metals, those of the alkalies are the only ones forming hydroxides and carbonates which are not decomposed by heat.

In a natural family of elements there is always a gradation of properties, either in the direct order of the atomic weights or inversely. This is well illustrated in the following table, which gives some of the physical properties of the alkali metals:

| | Atomic weight. | Specific gravity | Melting point. | Boiling point. |
|---|---|---|---|---|
| Lithium | 6.94 | 0.59 | 186.0° C. | Above red heat. |
| Sodium | 23.0 | 0.97 | 95.6° C. | 742° C. |
| Potassium | 39.1 | 0.87 | 62.5° C. | 667° C. |
| Rubidium | 85.45 | 1.52 | 38.5° C. | — |
| Cæsium | 132.81 | 1.88 | 26.5° C. | 270° C. |

As the atomic weights increase the specific gravities increase, but the melting-points and boiling-points decrease. Sodium shows a little irregularity in specific gravity. The activity increases with the atomic weights, cæsium being the most active of the group, and also of all metals. The same is true of the hydroxides. Lithium hydroxide is much less soluble than the other alkali hydroxides, and the carbonate and phosphate are difficultly soluble, in which respects the metal differs from the others of the family, and resembles magnesium.

The metals themselves are of a silver-white color, and extremely soft; on account of their tendency to combine with oxygen they must be kept in a liquid, such as coal-oil, which is not acted on by them, or in an atmosphere of hydrogen.

The metals may be obtained by heating their carbonates with carbon in iron retorts, the escaping vapors being passed under coal-oil for condensation of the metal:

$$K_2CO_3 + 2C = 3CO + 2K.$$

At present most of the alkali metals are obtained by the electrolysis of the fused hydroxides, the metal and hydrogen being liberated at the negative, oxygen at the positive pole:

$$KOH = K + H + O.$$

**Occurrence in Nature.**—Potassium is found in nature chiefly as a double silicate of potassium and aluminum (granite rocks, feldspar, and other minerals), or as chloride and nitrate. By the gradual disintegration of the different granite rocks containing potassium silicate, this has entered into the soil, whence it is taken up by plants as one of the necessary constituents of their food.

In the plant potassium enters largely into the combination of organic compounds, and when the plant is burned ashes are left containing the potassium, now in the form of carbonate. By extracting such ashes with water, the potassium carbonate, along with small quantities of chlorides and sulphates of potassium and sodium,

is obtained in solution, by the evaporation of which to dryness an impure article is obtained, known as *crude potash.* Formerly this was the chief source of potassium compounds, but about the year 1850 the inexhaustible salt mines of Stassfurt, Germany, were discovered. The salt there mined contains, besides the chlorides and sulphates of sodium, magnesium, calcium, and other salts, considerable quantities of potassium chloride, and the Stassfurt mines at present are practically the source of all potassium compounds.

The most important minerals containing potassium in the Stassfurt beds are:

Kainite, $KCl.MgSO_4.3H_2O$.
Carnallite, $KCl.MgCl_2.6H_2O$.
Polyhalite, $K_2SO_4.MgSO_4.2CaSO_4.2H_2O$.
Sylvite, $KCl$.
Picromerite, $K_2SO_4.MgSO_4.6H_2O$.

The German potash industry includes about 200 mines in operation and about 50 in course of construction. Only the more favorable locations have been developed. The United States use about one-fourth of the total production of the potash mines. The total amount of material mined annually is about 11,000,000 tons.

**Potassium Hydroxide** (*Potassii Hydroxidum*) **KOH = 56.11** (*Caustic potash*).—This may be obtained by the action of the metal on water:

$$K + H_2O = H + KOH.$$

The action is violent and must be carried out with care, using small pieces of the metal. Glass or porcelain vessels should not be used, as they are affected by the alkali. A silver vessel is the best to use. Such alkali is free from impurities and is sometimes made by this method for analytical purposes when a pure substance is wanted.

The usual process for making potassium hydroxide is to boil together a dilute solution of potassium carbonate or bicarbonate and calcium hydroxide:

$$K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2KOH.$$

The action is the same in principle as the precipitation of calcium carbonate from the chloride by sodium carbonate. Calcium carbonate is far less soluble than calcium hydroxide, and, although the latter is only slightly soluble in water, yet its removal from solution by precipitation enables what is in suspension to dissolve progressively until all of the potassium carbonate is converted into hydroxide. The amount of alkali must not exceed 10 per cent., otherwise the reverse action sets in and it is impossible to convert all of the potassium carbonate.

Large quantities of high-grade potassium hydroxide are now manufactured directly from the chloride by electrolysis.

*Experiment* 20.—Add gradually 5 grams of calcium hydroxide (slaked lime) to a boiling solution of about 5 grams of potassium carbonate in 50 c.c. of water, and continue to boil until the conversion of potassium carbonate into hydroxide is complete. This can be shown by filtering off a few drops of the liquid, and supersaturating with dilute hydrochloric acid, which should not cause effervescence. Set aside to cool, and when all solids have subsided, pour off the clear solution of potassium hydroxide, which may be used for Experiment 21. What quantities of $K_2CO_3$ and $Ca(OH)_2$ are required to make 1 kilo. of a 5 per cent. solution of potassium hydroxide?

Potassium hydroxide is a white, hard, highly deliquescent substance, soluble in 0.5 part of water and 2 parts of alcohol; it fuses at a low red heat, forming an oily liquid, which may be poured into suitable moulds to form pencils; at a strong red heat it is slowly volatilized without decomposition; it is strongly alkaline and a powerful base, readily combining with all acids; it rapidly destroys organic tissues, and when taken internally acts as a powerful corrosive, and most likely otherwise as a poison.

The commercial article always contains impurities, which may be removed by dissolving the alkali in alcohol in which the impurities are insoluble, decanting the clear solution, and evaporating the alcohol.

*Antidotes:* dilute acids, vinegar, to form salts; or fat, oil, or milk, to form soap.

*Liquor potassi hydroxidi* is a 5 per cent. solution of potassium hydroxide in water.

**Potassium Oxide, $K_2O$.**—This compound can be obtained by heating potassium nitrate with potassium in a vessel with exclusion of air.

$$5K + KNO_3 = 3K_2O + N.$$

It acts violently on water, forming the hydroxide. Exposed to air it combines spontaneously with oxygen, forming $K_2O_4$. The latter compound is formed as a yellow solid substance when potassium is burned in oxygen. It acts on water with great energy, forming potassium hydroxide and liberating the excess of oxygen. It is a strong oxidizing agent.

**Potassium Carbonate** (*Potassii Carbonas*) **$K_2CO_3$ = 138.2,** is obtained from wood-ashes in an impure state, as described above, or from the native chloride by the so-called Leblanc process, which will be described in connection with sodium carbonate. It is also made by passing carbon dioxide into solution of potassium hydroxide, obtained by the electrolytic process.

Pure potassium carbonate is obtained by heating the bicarbonate, which is decomposed as follows:

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2.$$

Potassium carbonate is deliquescent, is soluble in about an equal weight of water, insoluble in alcohol, and has strong basic and alkaline properties.

The strong alkaline reaction of potassium and sodium carbonate in solution is due to hydrolysis of the salts into bicarbonate, which is neutral to litmus and free alkali. (See page 155.)

$$K_2CO_3 + H_2O = KHCO_3 + KOH.$$

**Potassium Bicarbonate** (*Potassii Bicarbonas*) **$KHCO_3$ = 100.1.** Obtained by passing carbon dioxide through a strong solution of potassium carbonate, when the less soluble bicarbonate forms and separates into crystals:

$$K_2CO_3 + H_2O + CO_2 = 2KHCO_3.$$

It is colorless, odorless, permanent in air, and has a saline and slightly alkaline, but not a caustic taste. It is soluble in 3 parts of water at 25° C., 1.9 parts at 50° C., and almost insoluble in alcohol. A solution of the pure salt has at first a neutral reaction to litmus or phenolphthalein indicator, but soon becomes feebly alkaline by the conversion of a small amount of the bicarbonate into carbonate. This conversion is facilitated by violent agitation of the solution. When the solution is heated at the boiling-point, it loses carbon dioxide rapidly and completely, and then contains carbonate. The above behavior is likewise shown by sodium bicarbonate.

A solution of pure potassium bicarbonate is not visibly affected by the addition of a solution of magnesium sulphate or of mercuric chloride, but the presence of carbonate is shown at once by a white precipitate of magnesium carbonate, or a red precipitate of basic mercuric carbonate. The same is true of a solution of sodium bicarbonate.

**Potassium Percarbonate, $K_2C_2O_6$,** also exists as a bluish-white powder, which liberates oxygen when heated, and in dilute acid solution gives off hydrogen dioxide. It is obtained by electrolysis of a concentrated solution of potassium carbonate at about −10° C. (14° F.). It is a good oxidizer.

**Potassium Nitrate** (*Potassii Nitras*) **$KNO_3$ = 101.11** (*Niter, Saltpeter*).—Potassium and sodium nitrate are found as an incrustation upon and throughout the soil of certain localities in dry and hot countries, as, for instance, in Peru, Chile, and India. The formation of these nitrates is to be explained by the absorption of ammonia by the soil, where it gradually is oxidized and converted into nitric acid. This nitrification, *i. e.*, the conversion of ammonia into nitric acid, seems to be due largely to the action of microörganisms, termed the nitrifying ferment. The acid after being formed combines with the strongest base present in the soil. If this base be potash, potassium nitrate will be formed; if soda, sodium nitrate; if lime, calcium nitrate.

Upon the same principle is based the manufacture of niter on a large scale, which is accomplished by mixing animal refuse matter with earth and lime, and placing the mixture in heaps under a roof to prevent lixiviation by rain. By decomposition (putrefaction) of the animal matter ammonia is formed, which, by oxidation, is converted into nitric acid, which then combines with the calcium of the lime, forming calcium nitrate. This is dissolved in water, and to the solution potassium carbonate (or chloride) is added, when calcium carbonate (or chloride) and potassium nitrate are formed:

$$Ca(NO_3)_2 + K_2CO_3 = 2KNO_3 + CaCO_3.$$

Large quantities of potassium nitrate are made also by heating sodium nitrate (Chile saltpeter) and potassium chloride with very little water. The reaction taking place is: $KCl + NaNO_3 = KNO_3 + NaCl$. It is a reversible action, and while all the substances concerned are soluble in water, nevertheless in effect it is like a case of precipitation. This is due to the great differences of solubilities of the four compounds involved. Sodium chloride is not much more soluble in boiling water than in water at ordinary temperature, and in the boiling mixture in this process it is by far the least soluble of the four salts, and, consequently, a large proportion of the sodium of sodium nitrate is found in the sediment of sodium chloride which is formed. Another factor helping the reaction is the fact that potassium nitrate at the boiling temperature is by far the most soluble of the four salts. The hot liquid is drained from the sediment of sodium chloride and cooled. As the solubility of potassium nitrate at low temperature is rather small, being 13 grams in 100 c.c. of water at 0° C., most of it crystallizes out and is contaminated with only a little sodium chloride. It is purified by recrystallization.

Potassium nitrate crystallizes in six-sided prisms; it is soluble in about 3.8 parts of cold, and 0.4 part of boiling water. It has a cooling, saline, and pungent taste, and a neutral reaction. When heated with deoxidizing agents or combustible substances these are readily oxidized.

It is this oxidizing power which is made use of in the manufacture of *gunpowder*—an intimate mixture of potassium nitrate, sulphur, and carbon. Upon heating or igniting the gunpowder, the sulphur and carbon are oxidized, a considerable quantity of various gases (CO, $CO_2$, N, $SO_2$, etc.) being formed, the sudden generation and expansion of which cause the explosion.

**Potassium Chlorate** (*Potassii Chloras*), **$KClO_3$ = 122.56** (*Chlorate of Potash*).—This salt may be obtained by the action of chlorine on a boiling solution of potassium hydroxide, as explained on page 195.

A cheaper process for its manufacture is the action of chlorine upon a boiling solution of potassium carbonate, to which calcium hydroxide has been added:

$$K_2CO_3 + 6Ca(OH)_2 + 12Cl = 2KClO_3 + CaCO_3 + 5CaCl_2 + 6H_2O.$$

Practically all potassium chlorate is manufactured now by electrolysis of solutions of potassium chloride under proper conditions.

Potassium chlorate crystallizes in white plates of a pearly lustre; it is soluble in 16.7 parts of cold, and 1.7 parts of boiling water. It is even a stronger oxidizing agent than potassium nitrate, for which reason care must be taken in mixing it with organic matter or other deoxidizing agents, or with strong acids, which will liberate chloric acid. When heated by itself, it is decomposed into potassium chloride and oxygen.

**Potassium Sulphate, $K_2SO_4$ = 174.27.**—Obtained by the decomposition of potassium chloride, nitrate, or carbonate, by sulphuric acid:

$$2KCl + H_2SO_4 = 2HCl + K_2SO_4;$$
$$K_2CO_3 + H_2SO_4 = H_2O + CO_2 + K_2SO_4.$$

Potassium sulphate exists in small quantities in plants, and in nearly all animal tissues and fluids, more abundantly in urine.

*Potassium hydrogen sulphate, bisulphate, or potassium acid sulphate*, may be obtained by the action of one molecule of potassium chloride upon one molecule of sulphuric acid:

$$KCl + H_2SO_4 = HCl + KHSO_4.$$

**Potassium Sulphite.**—Obtained by the decomposition of potassium carbonate by sulphurous acid:

$$K_2CO_3 + H_2SO_3 = H_2O + CO_2 + K_2SO_3.$$

**Potassium Hypophosphite** (*Potassii Hypophosphis*), **$KPH_2O_2$ = 104.15,** may be obtained by decomposing a solution of calcium hypophosphite by potassium carbonate:

$$Ca(PH_2O_2)_2 + K_2CO_3 = 2KPH_2O_2 + CaCO_3$$

The filtered solution is evaporated at a very gentle heat, stirring constantly from the time it begins to thicken until a dry, granular salt is obtained, which is soluble in 0.5 part of cold and 0.3 part of boiling water.

**Potassium Iodide** (*Potassii Iodidum*), **KI = 166.02,** is made by the addition of iodine to a solution of potassium hydroxide until the dark brown color no longer disappears:

$$6KOH + 6I = 5KI + KIO_3 + 3H_2O.$$

Iodide and iodate of potassium are formed, and may be separated by crystallization. A better method, however, is to boil to dryness the liquid containing both salts, and to heat the mass after having mixed it with some charcoal, in a crucible, when the iodate is converted into iodide:

$$KIO_3 + 3C = KI + 3CO.$$

*Experiment* 21.—Add to a solution of about 3 grams of potassium hydroxide in about 25 c.c. of water (or to the solution obtained by making Experiment 20) iodine until the brown color no longer disappears. (How much iodine will be needed for 3 grams of KOH?) Evaporate the resulting solution (What does this solution contain now?) to dryness, mix the powdered mass with about 10 per cent. of powdered charcoal and heat the mixture in a crucible until slight deflagration has taken place. Dissolve the cold mass in hot water, filter and set aside for crystallization; if too much water has been used for dissolving, the liquid must be concentrated by evaporation.

Potassium iodide forms colorless, cubical crystals, which are soluble in 0.5 part of boiling and 0.8 part of cold water, also soluble in 12 parts of alcohol, and 2.5 parts of glycerin. When heated it fuses, and at a bright red heat is volatilized without decomposition.

**Potassium Bromide** (*Potassii Bromidum*), **KBr = 119.02,** may be obtained in a manner analogous to that given for potassium iodide, by the action of bromine upon potassium hydroxide, etc.

Or it may be made by the decomposition of a solution of ferrous bromide by potassium carbonate:

$$FeBr_2 + K_2CO_3 = 2KBr + FeCO_3.$$

Ferrous carbonate is precipitated, while potassium bromide remains in solution, from which it is obtained by crystallization.

**Sulphurated Potassa** (*Potassa Sulphurata*) (*Liver of Sulphur*), is a mixture composed chiefly of polysulphides and thiosulphate of potassium, containing not less than 12.8 per cent. of sulphur combined as sulphides. It is obtained by heating a mixture of potassium carbonate and sulphur, at first gently until all carbon dioxide is given off and effervescence ceases, finally to low red heat. It occurs in pieces which are liver-brown when fresh but become greenish-yellow and finally gray by exposure to the air through absorption of moisture, oxygen, and carbon dioxide. It has an odor of hydrogen sulphide and a bitter acrid taste. Its aqueous solution is brown and strongly alkaline, effervesces upon addition of dilute acids, with evolution of hydrogen sulphide and precipitation of sulphur.

*Potassium salts of interest*, which have not yet been mentioned, will be considered under the head of their respective acids. Some of these salts are potassium chromate and permanganate, and the salts formed from organic acids, such as potassium tartrate, acetate, etc.

### Tests for Potassium.

(Potassium chloride, KCl, or nitrate, $KNO_3$, may be used.)

1. To a solution of any potassium salt add some solution of chloroplatinic acid. A yellow crystalline precipitate of potassium chloroplatinate is obtained:

$$2KNO_3 + H_2PtCl_6 = K_2PtCl_6 + 2HNO_3;$$

or

$$2K^{\cdot} + 2NO_3' + 2H^{\cdot} + PtCl_6'' = K_2PtCl_6 + 2H^{\cdot} + 2NO_3'.$$

This test is not very delicate, as 1 part of the precipitate is soluble in about 100 parts of water. It is much less soluble in alcohol, which is usually added to facilitate precipitation.

2. To a neutral or slightly acid solution of a potassium salt add solution of sodium cobaltic nitrite: a yellow precipitate of potassium cobaltic nitrite $(KNO_2)_6.Co_2(NO_2)_6 + H_2O$ is produced. (The reaction is not influenced by the presence of alkaline earths, earths, or metals of the iron group, but is not suitable in case of potassium iodide, since iodine is liberated by the nitrous acid of the cobalt solution, and interferes with the test.)

3. Add to a concentrated solution of a neutral potassium salt a freshly prepared strong solution of tartaric acid: a white precipitate of potassium acid tartrate, $KHC_4H_4O_6$, is slowly formed. Addition of alcohol facilitates precipitation.

Tartaric acid, $H_2.C_4H_4O_6$, is dibasic and dissociates chiefly into $H^{\cdot}$ and $HC_4H_4O_6'$ ions. Potassium ions, $K^{\cdot}$, and $HC_4H_4O_6'$ unite to form the difficultly soluble acid tartrate:

$$K^{\cdot} + NO_3' + H^{\cdot} + HC_4H_4O_6' = KHC_4H_4O_6 + H^{\cdot} + NO_3'.$$

One part of the salt is soluble in about 200 parts of water, but practically insoluble in alcohol, even when diluted.

4. Potassium compounds color violet the flame of a Bunsen burner or of alcohol. The presence of sodium, which colors the flame intensely yellow, interferes with this test, as it masks the violet caused by potassium. The difficulty may be overcome by observing the flame through a blue glass or through a thin vessel filled with a solution of indigo. The yellow light is absorbed by the blue medium, while the violet light passes through and can be recognized.[1]

[1] The *flame reaction* for metals is one of the steps taken in qualitative analysis. For this purpose the platinum wire should be kept immersed in hydrochloric acid in a test-tube. When needed, it is cleaned by alternately holding it in the flame and dipping it in the acid, until no color is given to the flame. The salt best adapted for flame tests is a chloride; hence the substance to be tested should be moistened in a dish with hydrochloric acid before introducing it into the flame on the loop of the wire. Chlorides are readily volatilized. Unless the substance is volatile, there will be no flame reaction.

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QUESTIONS.—How is potassium found in nature, and from what sources is the chief supply of potassium salts obtained? What color have the salts of the alkali metals, and which are insoluble? Mention two processes for making potassium hydroxide, and what are its properties? Show by symbols the conversion of carbonate into bicarbonate of potassium. Explain the principle of the manufacture of potassium nitrate, and what is the office of the latter in gunpowder? How is potassium chlorate made, and what are its properties? Give the processes for manufacturing iodide and bromide of potassium, both in words and symbols. State the composition of potassium sulphate and sulphite. How can they be obtained? Mention tests for potassium compounds. How much iodine is contained in 33 grams of potassium iodide?

With few exceptions, potassium compounds are white, soluble in water, and not volatile at a low red heat. Of the above tests, the second is the most delicate. Some other difficultly soluble salts of potassium are the picrate, perchlorate and fluosilicate. With the exception of the acid tartrate (cream of tartar) and the picrate, the other difficultly soluble salts of potassium are of a kind not usually met with.

## 22. SODIUM. LITHIUM. CÆSIUM. RUBIDIUM.

$Na^i = 23$. $Li^i = 6.94$. $Cs^i = 132.81$. $Rb^i = 85.45$.

**Occurrence in Nature.**—Sodium is found very widely diffused in small quantities through all soils. It occurs in large quantities in combination with chlorine, as rock-salt, or common salt, which forms considerable deposits in some regions, or is dissolved in spring-waters and is by them carried to the rivers, and finally to the ocean, which contains immense quantities of sodium chloride. It is found, also, as nitrate, and in double silicates.

**Sodium Chloride** (*Sodii Chloridum*), **NaCl = 58.46** (*Common salt*). This is the most important of all sodium compounds, and also is the material from which the other compounds are directly or indirectly obtained. Common table-salt frequently contains small quantities of calcium and magnesium chlorides, the presence of which causes absorption of moisture, as these compounds are hygroscopic, while pure sodium chloride is not.

In the animal system, sodium chloride is found in all parts, it being of great importance in aiding the absorption of albuminoid substances and the phenomena of osmose; also by furnishing, through decomposition, the hydrochloric acid of the gastric juice.

Sodium chloride is soluble in 2.8 parts of cold water, and in 2.5 parts of boiling water; almost insoluble in alcohol; it crystallizes in cubes and has a neutral reaction.

**Physiological Salt Solution** (*Normal Salt Solution*) (*Liquor Sodii Chloridi Physiologicus*), contains 8.5 grams of sodium chloride in 1000 c.c. Freshly distilled water is used, and the solution, after filtering, is sterilized either in an autoclave, under steam pressure, at 115° to 120° C. for fifteen minutes, or by boiling for at least one hour. The solution should not be used after it has been made forty-eight hours.

**Sodium Hydroxide** (*Sodii Hydroxidum*), **NaOH = 40** (*Caustic Soda*), may be obtained by the processes mentioned for potassium hydroxide, which compound it closely resembles in its chemical and most of its physical properties.

*Experiment* 22.—Examine the consistency and lustre of sodium metal by cutting a piece the size of a pea. (Do not get water on it while handling it. Why?) Throw *small* chips of the metal into a little water in a porcelain dish. When all the metal has disappeared, taste the solution and test its action on red

litmus. Add dilute hydrochloric acid to slight acid reaction and evaporate to dryness. Taste the residue. What is it? Explain all that took place and write reactions.

**Sodium Peroxide, $Na_2O_2$,** is now extensively used as a bleaching and oxidizing agent. It is a white or yellowish-white powder, readily decomposed by water into sodium hydroxide and oxygen; when dissolved in a dilute acid, hydrogen peroxide is formed. It is made by heating sodium in a current of oxygen. When it is brought in contact with water or dilute acids, great care must be taken to have a low temperature, else violent action will take place, with evolution of oxygen.

**Sodium Carbonate, $Na_2CO_3.10H_2O$** (*Washing Soda, Sal sodæ*).—This compound is, of all alkaline substances, the one manufactured in the largest quantities, being used in the manufacture of many highly important articles, as, for instance, soap, glass, etc.

Sodium carbonate is made, according to Leblanc's process, from the chloride by first converting it into sulphate (salt-cake) by the action of sulphuric acid:

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

The escaping vapors of hydrochloric acid are absorbed in water, and this liquid acid is used largely in the manufacture of bleaching-powder. The sodium sulphate is mixed with coal and limestone (calcium carbonate) and the mixture heated in reverberatory furnaces, when decomposition takes place, calcium sulphide, sodium carbonate, and carbonic oxide being formed:

$$Na_2SO_4 + 4C + CaCO_3 = CaS + Na_2CO_3 + 4CO.$$

The resulting mass, known as *black-ash*, is washed with water, which dissolves the sodium carbonate, while calcium sulphide enters into combination with calcium oxide, thus forming an insoluble compound of oxysulphide of calcium.

The liquid obtained by washing the black-ash, when evaporated to dryness, yields *crude sodium carbonate*, or "soda ash;" when this is dissolved and crystallized it takes up ten molecules of water, forming the ordinary washing soda.

Sodium carbonate is manufactured also by the so-called ammonia process, or the Solvay process. This depends on the decomposition of sodium chloride by ammonium bicarbonate under pressure, when sodium bicarbonate and ammonium chloride are formed, thus:

$$NaCl + NH_4HCO_3 = NH_4Cl + NaHCO_3.$$

The sodium acid carbonate thus obtained is converted into carbonate by heating:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The carbon dioxide obtained by this action is caused to act upon ammonia, liberated from the ammonium chloride, obtained as one of

the products in the first reaction. Ammonium bicarbonate is thus regenerated and used in a subsequent operation for the decomposition of common salt.

The success of this process, as in the case of making potassium nitrate from sodium nitrate, depends on differences of solubility. Sodium bicarbonate is much less soluble than sodium or ammonium chloride, or ammonium bicarbonate. Hence if the solution is saturated in the beginning with sodium chloride, the excess of sodium over what corresponds to the solubility of sodium bicarbonate in the mixture, will separate from the solution as sodium bicarbonate. This process, like so many others, is an illustration of the fact that the trend of a chemical change is far more often determined by physical properties and conditions than by chemical affinity (see Reversible Actions and Chemical Equilibrium).

Crystallized sodium carbonate is soluble in 1.6 parts of cold water, 0.09 part of water at 38° C., and 0.2 part of boiling water. The salt is efflorescent, losing nine molecules of water when exposed to the air. The last molecule of water can be expelled below 100° C. At 35.2° C. the crystals melt and form a solution, which, if evaporated at a little higher temperature to dryness, leaves a residue of monohydrated sodium carbonate. The solubility of the decahydrated salt increases up to 35.2° C. Above this point the monohydrate is the only stable salt, which has the same solubility at 35.2° C. as the decahydrate. Above this point the solubility decreases as the temperature rises. Anhydrous sodium carbonate is soluble in about 3 parts of cold water. The solution has a harsh alkaline taste and strong alkaline properties, due to the partial hydrolysis of the carbonate by water:

$$Na_2CO_3 + H_2O = NaHCO_3 + NaOH.$$

**Monohydrated Sodium Carbonate** (*Sodii Carbonas Monohydras*), **$Na_2CO_3.H_2O$ = 124,** is official. It has been adopted by the pharmacopœia to displace the decahydrated and anhydrous sodium carbonate, because it is stable in air at ordinary temperature, whereas the decahydrate loses water and the anhydrous salt absorbs moisture.

It is obtained by crystallizing a solution of sodium carbonate above 35° C. It is a white crystalline granular powder and should contain not less than 85 per cent. of anhydrous sodium carbonate. It is soluble in 2.9 parts of water at 25° C., 1.8 parts of boiling water, and in about 1 part of glycerin.

**Sodium Bicarbonate** (*Sodii Bicarbonas*) **$NaHCO_3$ = 84.01** (*Baking-soda*).—Obtained, as stated in the previous paragraph, by the ammonia-soda process. It can also be made by passing carbon dioxide over monohydrated sodium carbonate.

$$Na_2CO_3.H_2O + CO_2 = 2NaHCO_3.$$

It is a white powder, having a cooling, mildly saline taste, and a slightly alkaline reaction. Soluble in 12 parts of cold water and insoluble in alcohol. It is decomposed by heat or by hot water into sodium carbonate, water, and carbon dioxide (see Potassium Bicarbonate).

Sodium bicarbonate is a constituent of the various *baking-powders*, the action of which depends on the gradual liberation of carbon dioxide in the dough. This is brought about through a second constituent, generally an acid salt such as potassium bitartrate or calcium acid phosphate, which decomposes the bicarbonate.

**Sodium Sulphate** (*Sodii Sulphas*) **$Na_2SO_4.10H_2O$ = 322.23** (*Glauber's Salt*).—Made, as mentioned above, by the action of sulphuric acid on sodium chloride, dissolving the salt thus obtained in water, and crystallizing. Large, colorless, transparent crystals, rapidly efflorescing on exposure to air. Soluble in 2.8 parts of water at 15° C. (50° F.), in 0.25 part at 34° C. (93° F.), and in 0.47 part of boiling water.

*Experiment* 23.—Dissolve about 10 grams of crystallized sodium carbonate in 10 c.c. of hot water, add to this solution dilute sulphuric acid until all effervescence ceases and the reaction on litmus-paper is exactly neutral. Evaporate to about 20 c.c., and set aside for crystallization. Explain the action taking place, and state how much $H_2SO_4$, and how much of the diluted sulphuric acid, U. S. P., are needed for the decomposition of 10 grams of crystallized sodium carbonate.

**Sodium Sulphite** (*Sodii Sulphis*) **$Na_2SO_3.7H_2O$ = 252.18. Sodium Bisulphite, $NaHSO_3$ = 104.08.**—By saturating a cold solution of sodium carbonate with sulphur dioxide, sodium bisulphite is formed, and separates in opaque crystals:

$$Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2.$$

If to the sodium bisulphite thus obtained a quantity of sodium carbonate be added, equal to that first employed, the normal salt is formed:

$$2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + H_2O + CO_2.$$

**Sodium Thiosulphate, Sodium Hyposulphite** (*Sodii Thiosulphas*), **$Na_2S_2O_3.5H_2O$ = 248.22.**—Made by digesting a solution of sodium sulphite with powdered sulphur, when combination slowly takes place:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

It may also be obtained by boiling a solution of sodium hydroxide with sulphur (see Precipitated Sulphur), and crystallizing out the thiosulphate, $6NaOH + 4S = Na_2S_2O_3 + 2Na_2S + 3H_2O$. The $Na_2S$ also combines with sulphur to form yellow colored polysulphides.

The thiosulphate forms large transparent crystals, very soluble in water. The solution slowly decomposes on standing, rapidly on

boiling. When heated dry, the salt first loses water, then decomposes into sodium sulphate and yellow sodium pentasulphide, $4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5$. If heated high enough, the pentasulphide decomposes and ignites, four of the five atoms of sulphur being converted into sulphur dioxide.

The salt is used under the name of "hypo" in photography as a fixing bath, to dissolve from the plate unaffected chloride, bromide or iodide of silver. Also, in bleaching industries, to remove chlorine from fabrics, thus:

$$Na_2S_2O_3 + 8Cl + 5H_2O = Na_2SO_4 + H_2SO_4 + 8HCl.$$

It is known in these industries as *antichlor*.

**Sodium Phosphate** (*Sodii Phosphas*) $\mathbf{Na_2HPO_4.12H_2O = 358.24}$, is made from calcium phosphate by the action of sulphuric acid, which removes two-thirds of the calcium, forming calcium sulphate, while acid phosphate of calcium is formed and remains in solution:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH(PO_4)_2.$$

The solution is filtered and sodium carbonate added, when calcium phosphate is precipitated, sodium phosphate, carbon dioxide, and water being formed:

$$CaH_4(PO_4)_2 + Na_2CO_3 = CaHPO_4 + H_2O + CO_2 + Na_2HPO_4.$$

The filtered and evaporated solution yields crystals of sodium phosphate, which have a slightly alkaline reaction to litmus, but NOT to phenolphthalein.

By exposure of the crystallized sodium phosphate to warm air its water of crystallization is expelled and the dry salt is *Exsiccated sodium phosphate, Sodii phosphas exsiccatus*. This salt, when mixed with the proper quantities of sodium bicarbonate and tartaric and citric acids, is official under the name of *Effervescent sodium phosphate, Sodii phosphas effervescens*.

*Experiment* 24.—Mix thoroughly 30 grams of bone-ash with 10 c.c. of sulphuric acid, let stand for some hours, add 20 c.c. of water, and again set aside for some hours. Mix with 40 c.c. of water, heat to the boiling-point, and filter. The residue on the filter is chiefly calcium sulphate. To the hot filtrate of calcium acid phosphate add concentrated solution of sodium carbonate until a precipitate ceases to form and the liquid is faintly alkaline, filter, evaporate, and let crystallize.

**Sodium Pyrophosphate, $\mathbf{Na_4P_2O_7.10H_2O}$ = 446.24.**—When exsiccated sodium phosphate is heated to a low red heat it loses water, and is converted into pyrophosphate, which dissolves in hot water and deposits beautiful crystals. The chemical change taking place is this:

$$2(Na_2HPO_4) = Na_4P_2O_7 + H_2O.$$

The normal sodium phosphate, $Na_3PO_4$, is known also, but it is not a very stable compound, being acted upon even by the moisture and carbon dioxide

of the air, with the formation of sodium carbonate and disodium hydrogen phosphate, thus:

$$2Na_3PO_4 + H_2O + CO_2 = 2Na_2HPO_4 + Na_2CO_3.$$

**Sodium Nitrate, $NaNO_3$ = 85.01** (*Chile Saltpeter, Cubic Niter*).—Found in nature, and is purified by crystallization. The crystals are transparent, deliquescent, and readily soluble.

*Sodium nitrite, Sodii nitris*, $NaNO_2$ = 69.01, is formed by heating the nitrate to a sufficiently high temperature to expel one-third of the oxygen; or, better, by treating the fused nitrate with metallic lead, which latter is converted into oxide. The sodium nitrite which is formed is dissolved and purified by crystallization.

**Sodium Borate** (*Sodii Boras*), **$Na_2.B_4O_7.10H_2O$ = 382.16** (*Borax*).—This salt occurs in Clear Lake, Nevada, and in several lakes in Asia. It is manufactured by adding sodium carbonate to the boric acid found in Tuscany, Italy. In Germany, boracite ($MgCl_2.2Mg_3B_8O_{15}$) found in the Stassfurt salt beds is first decomposed by hydrochloric acid, with liberation of boric acid. The latter is redissolved in hot water and neutralized with sodium carbonate, forming borax. In California, colemanite ($Ca_2B_6O_{11}.5H_2O$) is boiled with sodium carbonate solution, and from the resulting solution borax is obtained by crystallization. It forms colorless, transparent crystals, but is sold mostly in the form of a white powder. It is slightly efflorescent, is soluble in 16 parts of cold, and in 0.5 part of boiling water; insoluble in alcohol, but soluble in one part of glycerin at 80° C. (176° F.). When heated, borax puffs up, loses water of crystallization, and at red heat it melts, forming a colorless liquid which, on cooling, solidifies to a transparent mass, known as *fused borax*, or *borax glass*. Molten borax has the power to combine with metallic oxides, forming double borates, some of which have a characteristic color, for which reason borax is used in blow-pipe analysis. Borax has antiseptic properties, preventing the decomposition of some organic substances.

A solution of borax is alkaline and has no action on carbonates or bicarbonates, but if an equal volume of glycerin is added to the solution, it becomes strongly acid and decomposes carbonates and bicarbonates with effervescence. This behavior is involved in the preparation of Dobell's solution. On diluting the glycerin mixture strongly with water, the alkaline reaction returns.

**Sodium Perborate** (*Sodii Perboras*), **$NaBO_3.4H_2O$.**—When a mixture of 248 grams of boric acid and 78 grams of sodium peroxide is gradually added to 2 liters of cold water a crystallized compound is obtained. When the latter in solution is treated with the proper proportion of an acid, sodium perborate separates. It is very stable when dry, but in solution it has all the properties of a solution of hydrogen dioxide. It is a good antiseptic and deodorant, and may be applied as a dusting-powder or in solution. It should contain not less than 9 per cent. of available oxygen, corresponding to 86.5 per cent. of perborate.

Other sodium salts which are official are *sodium hypophosphite*, $NaPH_2O_2 + H_2O$; *bromide*, NaBr; *iodide*, NaI. These salts may be obtained by processes analogous to those given for the corresponding potassium compounds.

Sodium compounds are nearly all white and are not volatile at or below a red heat.

### Tests for Sodium.

(Sodium chloride, NaCl, may be used.)

1. As all salts of sodium are soluble in water, we cannot precipitate this metal in the form of a compound by any of the common reagents. (Potassium antimoniate precipitates neutral solution of sodium salts, but this test is not reliable.)

2. The chief reaction for sodium is the flame-test, compounds of sodium imparting to a colorless flame a yellow color, which is very intense. A crystal of potassium dichromate appears colorless, and a paper coated with red mercuric iodide appears white when illuminated by the yellow sodium flame. (The spectroscope shows a characteristic yellow line.)

As practically all substances contain a trace of some sodium compound, and give a momentary sodium flame, the yellow flame can only be used to judge the presence of an actual sodium compound when it persists for a long time.

**Lithium, Li = 6.94.** Found in nature in combination with silicic acid in a few rare minerals or as a chloride in some spring waters. Of inorganic salts, *lithium bromide* and *carbonate* are official. Hydroxide, carbonate, and phosphate of lithium are much less soluble than the corresponding compounds of potassium and sodium. Sodium phosphate added to a strong solution of a lithium salt produces, on boiling, a white precipitate of lithium phosphate, $Li_3PO_4$. Lithium compounds color the flame a beautiful crimson or carmine-red.

LiOH is soluble in 14.5 parts of water at 20° C., $Li_2CO_3$ in 75 parts at 20° C., and 140 parts of boiling water, $Li_3PO_4$ in 2540 parts of plain water and 3920 parts of ammoniacal water.

**Cæsium**, Cs, and **Rubidium**, Rb, occur widely distributed, but only in small quantities, and generally in company with potassium, which they resem-

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QUESTIONS.—What is the composition of common salt; how is it found in nature, and what is it used for? Describe Leblanc's and the Solvay process for manufacturing sodium carbonate on a large scale. How much water is in 100 pounds of the crystallized sodium carbonate? What is Glauber salt, and how is it made? State the composition of disodium hydrogen phosphate, and how is it prepared from calcium phosphate? What difference exists between sodium carbonate and bicarbonate both in regard to physical and chemical properties? Give the composition of sodium thiosulphate; what is it used for? Which sodium salts are soluble, and which are insoluble? How does sodium and how does lithium color the flame? Which lithium salts are official?

ble closely. Rubidium occurs in *carnallite* of the Stassfurt beds, and is obtained as rubidium alum, from the mother-liquors after the potassium chloride is crystallized out. Cæsium takes fire in air at the ordinary temperature, and it is the most electropositive of all metals. Rubidium takes fire in air and decomposes water with greater energy than does potassium, the hydroxide formed, Rb(OH). having even stronger basic properties than potassium hydroxide. Both rubidium and cæsium have a marked power of forming double salts. All the salts are white and soluble in water. Probably the one most often used medicinally is *cæsium-rubidium-ammonium bromide*, $(CsRb)Br_2.3NH_4Br$. Rubidium bromide, RbBr, and iodide, RbI, have been recommended as substitutes for the corresponding potassium salts. Cæsium bromide, CsBr, has also been used.

## 23. AMMONIUM.

$NH_4^1 = 18.04.$

**General Remarks.**—The salts of ammonium show so much resemblance, both in their physical and chemical properties, to those of the alkali-metals, that they may be studied most conveniently at this place.

The compound radical $NH_4$ acts in these ammonium salts very much like one atom of an alkali-metal, and, therefore, frequently has been looked upon as a compound metal. The physical metallic properties (lustre, etc.) of ammonium cannot be fully demonstrated, as it is not capable of existing in a separate or free state. There is known, however, an alloy of ammonium and mercury, which may be obtained by dissolving potassium in mercury, and adding to the potassium-amalgam thus formed, a strong solution of ammonium chloride, when potassium chloride and ammonium-amalgam are formed. The latter is a soft, spongy, metallic-looking substance, which readily decomposes into mercury, ammonia, and hydrogen:

$$HgK + NH_4Cl = KCl + NH_4Hg;$$
$$NH_4Hg = NH_3 + H + Hg.$$

Ammonium-amalgam has only a temporary existence, but there is a closely related substance which is much more stable. Numerous compounds are known in organic chemistry in which radicals take the place of hydrogen in ammonia or the ammonium group. Thus, tetramethyl ammonium chloride is very well known, is stable, has the formula $N(CH_3)_4Cl$ and corresponds exactly with ammonium chloride, $NH_4Cl$. When a solution of it in absolute alcohol is electrolyzed at —10° C. with a mercury cathode and platinum anode, shiny, silvery, metallic-looking crystals of an amalgam form upon the mercury, having the composition, $N(CH_3)_4.Hg$. Below 10° C. the crystals do not become inflated as does the ammonium-amalgam. They are moderately stable in alcohol, but act violently with water. The evidence for the existence of the ammonium radical is pretty conclusive.

The existence of the ammonium radical is accounted for by the fact that the valence of nitrogen changes from 3 to 5. The direct union of ammonia gas and hydrochloric acid gas is strong evidence of this increase in valence.

The source of all ammonium compounds is ammonia $NH_3$, or ammonium hydroxide, $NH_4OH$, both of which have been considered heretofore.

A solution of ammonia has much weaker basic properties than a solution of sodium or potassium hydroxide has. In a normal solution (about 1.7 per cent.) only about 0.4 per cent. of the ammonia molecules are dissociated into $NH_4^{\cdot}$ and $(OH)'$ ions. There is much free $NH_3$, besides the $NH_4OH$ which results from union of $NH_3$ with water. It is only the ionized portion of the $NH_4OH$ which shows basic properties.

The ionic equation for the neutralization of ammonia water with an acid is this:

$$NH_4^{\cdot} + OH' + H^{\cdot} + Cl' \rightarrow NH_4^{\cdot} + Cl' + H_2O.$$

As fast as $(OH)'$ and $H^{\cdot}$ ions unite to form water, more $NH_4OH$ dissociates and more $NH_3$ unites with water to form $NH_4OH$ until the reaction is complete. All ammonium salts are highly dissociated in dilute solutions.

The reverse of the above action, namely, the liberation of ammonia from its salts by an alkali, is discussed from the ionic point of view on page 149.

**Ammonium Chloride** (*Ammonii Chloridum*), **$NH_4Cl$ = 53.50** (*Sal-ammoniac*).—Obtained by saturating the "ammoniacal liquor" of the gas-works with hydrochloric acid, evaporating to dryness, and purifying the crude article by sublimation.

Pure ammonium chloride either is a white, crystalline powder, or occurs in the form of long, fibrous crystals, which are tough and flexible; it has a cooling, saline taste; is soluble in 2 parts of cold, and in 1 part of boiling water; and, like all ammonium compounds, is completely volatilized by heat.

**Carbamic acid, $CO.NH_2.OH$.** This acid may be looked upon as carbonic acid, $CO.(OH)_2$, in which one of the hydroxyl groups is replaced by $NH_2$. The ammonium salt of this acid, $CO.NH_2.ONH_4$, is formed when dry ammonia gas and dry carbon dioxide are brought together, direct combination taking place, thus:

$$CO_2 + 2NH_3 = CO\begin{matrix}\diagup NH_2 \\ \diagdown ONH_4\end{matrix}.$$

**Ammonium Carbonate** (*Ammonii Carbonas*) **$NH_4HCO_3.NH_4NH_2CO_2$ = 157.11** (*Ammonium Sesquicarbonate, Sal Volatile, Preston Salt*).—Commercial ammonium carbonate is not the normal salt, but, as shown by the above formula, a combination of acid ammonium carbonate with ammonium carbamate. It is obtained by sublimation of a mixture of ammonium chloride and calcium carbonate, when calcium chloride is formed, ammonia gas and water escape, and ammonium carbonate condenses in the cooler part of the apparatus:

$$2CaCO_3 + 4NH_4Cl = NH_4HCO_3.NH_4NH_2CO_2 + 2CaCl_2 + H_2O + NH_3.$$

Ammonium carbonate thus obtained forms white, translucent masses, losing

both ammonia and carbon dioxide on exposure to the air, becoming opaque, and finally converted into a white powder of acid ammonium carbonate.

$$NH_4HCO_3\,NH_4NH_2CO_2 = NH_4HCO_3 + 2NH_3 + CO_2.$$

When commercial ammonium carbonate is dissolved in water the carbamate unites with one molecule of water, forming normal ammonium carbonate.

$$NH_4NH_2CO_2 + H_2O = (NH_4)_2CO_3.$$

A solution of the common ammonium carbonate in water is, consequently, a liquid containing both acid and normal carbonate of ammonium; by the addition of some ammonia water the acid carbonate is converted into the normal salt. The solution thus obtained is used frequently as a reagent.

The *Aromatic spirit of ammonia* is a solution of normal ammonium carbonate in diluted alcohol to which some essential oils have been added.

**Ammonium Sulphate $(NH_4)_2SO_4$, Ammonium Nitrate, $NH_4NO_3$,** and **Ammonium Phosphate $(NH_4)_2HPO_4$,** may be obtained by the addition of the respective acids to ammonia water or ammonium carbonate:

$$H_2SO_4 + 2NH_4OH = (NH_4)_2SO_4 + 2H_2O.$$
$$HNO_3 + NH_4OH = NH_4NO_3 + H_2O.$$
$$H_3PO_4 + 2NH_4OH = (NH_4)_2HPO_4 + 2H_2O.$$
$$H_2SO_4 + (NH_4)_2CO_3 = (NH_4)_2SO_4 + H_2O + CO_2.$$

**Ammonium Iodide** (*Ammonii Iodidum*) **$NH_4I$,** and **Ammonium Bromide** (*Ammonii Bromidum*) **$NH_4Br$,** may be obtained by mixing together strong solutions of potassium iodide (or bromide) and ammonium sulphate, and adding alcohol, which precipitates the potassium sulphate formed; by evaporation of the solution the ammonium iodide (or bromide) is obtained:

$$2KI + (NH_4)_2SO_4 = 2NH_4I + K_2SO_4;$$
$$2KBr + (NH_4)_2SO_4 = 2NH_4Br + K_2SO_4.$$

Another mode of preparing these compounds is by the decomposition of ferrous bromide (or iodide) by ammonium hydroxide:

$$FeBr_2 + 2NH_4OH = 2NH_4Br + Fe(OH)_2.$$

Ammonium iodide is the principal constituent of the *decolorized tincture of iodine.*

**Ammonium Hydrogen Sulphide, $NH_4SH$** (*Ammonium Hydrosulphide, Ammonium Sulphydrate*).—Obtained by passing hydrogen sulphide through ammonia water until this is saturated:

$$H_2S + NH_4OH = NH_4SH + H_2O.$$

The solution thus obtained is, when recently prepared, a colorless liquid, having the odor of both ammonia and of hydrogen sulphide; when exposed to the air it soon assumes a yellow color. This behavior

is characteristic of the soluble hydrosulphides in general, and is due to the liberation of sulphur by oxidation, thus:

$$NH_4SH + O = NH_4OH + S.$$

The sulphur combines with undecomposed hydrosulphide, forming polysulphides, which are yellow. The normal sulphide $(NH_4)_2S$, can be obtained in the solid state, but it quickly loses half of its ammonia and forms hydrosulphide. In solution it is almost completely hydrolyzed, thus:

$$(NH_4)_2S + H_2O \rightleftarrows NH_4OH + NH_4SH.$$

A mixture corresponding to the normal sulphide is obtained by adding to a solution of the hydrosulphide, prepared as above, an equivalent amount of ammonia water.

These solutions can easily be freed from the sulphide by boiling. Both substances, the ammonium hydrogen sulphide and ammonium sulphide, are valuable reagents, frequently used for precipitation of certain heavy metals, or for dissolving certain metallic sulphides. (See under Hydrogen Sulphide.)

### Tests for Ammonium Compounds.

(Ammonium chloride, $NH_4Cl$, may be used.)

1. Ammonium salts give the same form of precipitates as potassium with solution of chloroplatinic acid, sodium cobaltic nitrite, and tartaric acid (see tests for potassium).

2. All compounds of ammonium are volatilized below or at a low red heat, either with or without decomposition (see preparation of nitrogen and nitrogen monoxide in chapter on Nitrogen). If the acid constituent of the salt is volatile and not decomposed by heat, the salt volatilizes without decomposition.

Heat with a small flame a little ammonium chloride in a covered porcelain crucible. The salt sublimes upon the sides and cover of the crucible.

3. The best test, and one which is sufficient for recognition of any ammonium compound, is to heat a mixture of it and slaked lime or

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QUESTIONS.—What is ammonium, and why is it classed with the alkali-metals? Is ammonium known in a separate state? What is ammonium-amalgam, how is it obtained, and what are its properties? What is the source of ammonium compounds? State the composition, mode of preparation, and properties of sal ammoniac. How is ammonium carbonate manufactured, and what difference exists between the solid article and its solution? State the composition of ammonium sulphide and of ammonium hydrogen sulphide; how are they made, and what are they used for? By what process may ammonium sulphate, nitrate, and phosphate be obtained from ammonium hydroxide or ammonium carbonate, and what chemical change takes place? How does heat act upon ammonium compounds? Give analytical reactions for ammonium salts.

strong alkali in a tube. Ammonia gas is liberated, which may be recognized by its odor and action on red litmus-paper, and by causing dense white fumes when a rod, moistened with strong hydrochloric acid, is held in the mouth of the tube.

All commonly occurring ammonium salts are colorless, soluble in water, and odorless, with the exception of the carbonate and sulphide. Traces of ammonium compounds are detected by Nessler's solution (see Index), which causes a reddish-brown precipitate or coloration. (See under Water Analysis, end of chapter 38.)

**Summary of Analytical Characters of the Alkali-metals.**

| | *Potassium.* | *Sodium* | *Lithium* | *Ammonium.* |
|---|---|---|---|---|
| Sodium cobaltic nitrite . . | Yellow precipitate. | ..... | ..... | Yellow precipitate. |
| Platinic chloride . . . . | Yellow precipitate. | ..... | ..... | Yellow precipitate. |
| Sodium bitartrate . . . | White precipitate. | ..... | ..... | White precipitate. |
| Sodium phosphate . . . | ..... | ..... | White precipitate in conc solution on boiling. | ..... |
| Sodium hydroxide . . . | ..... | ..... | ..... | Ammonia gas. |
| Action of heat . . . . | Fusible. | Fusible. | Fusible. | Volatile. |
| Flame color . . . . . | Violet. | Yellow. | Crimson. | ..... |

## 24. MAGNESIUM.

$Mg^{ii} = 24.32.$

**General Remarks.**—Magnesium falls in group II of the periodic table of elements. This group is subdivided into the alkaline-earth family of metals consisting of calcium, strontium, barium and radium, and the family composed of glucinum, magnesium, zinc, cadmium and mercury. In the latter family of metals, the sulphates are soluble, the hydroxides easily lose water by heating and form oxides, the chlorides are fairly volatile by heat, and the metals do not rust rapidly in the air and act very slightly on water, even at elevated temperature. Magnesium resembles zinc very closely and should be studied with it. Because of its behavior toward the analytical reagents, it is left in the so-called alkali group of metals in analysis, for which reason it is taken up for consideration in this place. Magnesium resembles the alkaline-earth metals and differs from zinc in the following respects: The sulphide is hydrolyzed by water, the oxide cannot be reduced by heating with carbon, and it does not form complex combinations with ammonia.

Air Contains Oboa

The compounds of the family of metals to which magnesium belongs give no color to a borax bead.

**Occurrence in Nature.**—Magnesium is widely diffused in nature, and several of its compounds are found in large quantities. It occurs as chloride and sulphate in many spring-waters and in the salt-mines at Stassfurt; as carbonate in the mineral *magnesite;* as double carbonate of magnesium and calcium in the mineral *dolomite* (magnesian limestone), which forms entire mountains; as silicate of magnesium in the minerals *serpentine, meerschaum, talc, asbestos, soapstone,* etc.

**Metallic Magnesium.**—Metallic magnesium may be obtained by the decomposition of magnesium chloride by sodium; but is now made in large quantities by electrolysis of the molten double chloride of magnesium and potassium, $MgCl_2.KCl$. The furnace used for the operation is shown in Fig. 7.

Magnesium is an almost silver-white metal, losing its lustre rapidly in moist air by oxidation of the surface. It decomposes hot water with liberation of hydrogen; and when heated to a red heat burns with a brilliant bluish-white light, which is extensively used for photographic purposes. The ash left by burning magnesium is a mixture of the oxide MgO, and the nitride, $Mg_3N_2$. The presence of the latter is shown by the odor of ammonia given off when the ash is boiled with water. The metal is less active chemically than calcium, strontium or barium. It is readily attacked by nearly all dilute acids.

**Magnesium Chloride, $MgCl_2.6H_2O$.**—This may be obtained by dissolving magnesium, its oxide or carbonate in hydrochloric acid and evaporating to crystallization. It occurs in salt deposits, also associated with potassium chloride in the mineral carnallite, $MgCl_2.KCl.6H_2O$. Magnesium chloride is a white, very deliquescent salt. When heated it is partially decomposed, giving off hydrochloric acid, thus:

$$MgCl_2 + H_2O = MgO + 2HCl.$$

Because of this tendency to liberate hydrochloric acid, sea-water, which contains magnesium chloride, cannot be used in boilers. Anhydrous magnesium chloride can be prepared by heating the double ammonium salt, $MgCl_2.NH_4Cl.6H_2O$, which is isomorphous with carnallite; both water and ammonium chloride are driven off, leaving undecomposed $MgCl_2$.

**Magnesium Carbonate** (*Magnesii Carbonas*).—Approximately: $(MgCO_3)_4.Mg(OH)_2.5H_2O$ = **485.70** (*Magnesia Alba*).—The normal magnesium carbonate, $MgCO_3$, is found in nature, but the official preparation contains carbonate, hydroxide, and water. It is obtained by boiling a solution of magnesium sulphate with solution of sodium carbonate, when the carbonate is precipitated, some carbon dioxide evolved, and sodium sulphate remains in solution:

$$5MgSO_4 + 5Na_2CO_3 + 6H_2O = (MgCO_3)_4Mg(OH)_2 5H_2O + 5Na_2SO_4 + CO_2.$$

By filtering, washing, and drying the precipitate, it is obtained in the form of a white, light powder.

*Experiment* 25.—Dissolve 10 grams of magnesium sulphate in hot water and add a concentrated solution of sodium carbonate until no more precipitate is formed. Collect the precipitated magnesium carbonate on a filter and dry it at a low temperature. (How much crystallized sodium carbonate is needed for the decomposition of 10 grams of crystallized magnesium sulphate?) Notice that the dried precipitate evolves carbon dioxide when heated with acids.

**Magnesium Oxide** (*Magnesii Oxidum*) **MgO = 40.32** (*Calcined Magnesia*), is obtained by heating light magnesium carbonate in a crucible to a full red heat, when all carbon dioxide and water are expelled:

$$(MgCO_3)_4Mg(OH)_2.5H_2O = 5MgO + 4CO_2 + 6H_2O.$$

It is a very light, amorphous, white, almost tasteless powder, which absorbs moisture and carbon dioxide gradually from the air: in contact with water it forms the hydroxide $Mg(OH)_2$, which is almost insoluble in water, requiring of the latter over 50,000 parts for solution. Milk of magnesia is the hydroxide suspended in water (1 part in about 15).

*Heavy magnesium oxide, magnesii oxidum ponderosum*, differs from the common or light magnesia, not in its chemical composition, but merely in its physical condition, being denser and heavier.

*Experiment* 26.—Place 1 gram of magnesium carbonate, obtained in performing Experiment 25, into a weighed crucible and heat to redness, or until by further heating no more loss in weight ensues. Treat the residue with dilute hydrochloric acid and notice that no evolution of carbon dioxide takes place. What is the calculated loss in weight of magnesium carbonate when converted into oxide, and how does this correspond with the actual loss determined by the experiment?

**Magnesium Sulphate** (*Magnesii Sulphas*) **$MgSO_4.7H_2O$ = 246.50** (*Epsom Salt*), is obtained from spring-waters, from the mineral Kieserite, $MgSO_4.H_2O$, and by decomposition of the native carbonate by sulphuric acid:

$$MgCO_3 + H_2SO_4 = MgSO_4 + CO_2 + H_2O.$$

It forms colorless crystals, which have a cooling, saline, and bitter taste, a neutral reaction, and are easily soluble in water.

**Magnesium Nitride, $Mg_3N_2$,** is obtained as a yellow, porous mass by heating magnesium to red heat in nitrogen. With water it forms magnesium hydroxide and ammonia, thus:

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3.$$

**Remarks on Tests for Metals.**—Many of the tests for magnesium and the metals to follow have already been before us when discuss-

ing the acids. They involve reactions of double decomposition, resulting in the formation of an insoluble product. The solubilities of the different classes of salts, such as chlorides, carbonates, sulphates, etc., have been stated under the various acids, and the student, by keeping these facts in mind, will be able to anticipate many of the tests enumerated under the metals. Some of these are not distinctive at all, but simply corroborative, because two or more metals may respond to the same test. For example, to obtain a white precipitate on adding a solution of sodium carbonate or phosphate to a solution of a substance is no more a test for magnesium than for calcium, strontium, barium, or any other metal whose carbonate or phosphate is white and insoluble in water. In cases where distinctive tests are lacking, a systematic procedure of elimination is followed. This is known as qualitative analysis.

The solubilities of the classes of salts and the different methods of producing salts have been mentioned, and something has been said in this respect about the two classes of compounds of metals known as oxides and hydroxides. In regard to solubility in water, the oxides and hydroxides are very much alike; that is, if a hydroxide is soluble, the corresponding oxide is also soluble, and *vice versa*. The hydroxides of the common metals that are soluble in water are those of potassium, sodium, lithium, barium, strontium, and the hypothetical metal, ammonium. Calcium hydroxide is slightly soluble, less than calcium sulphate, but sufficiently soluble to be employed as a reagent. Hydroxides of the other metals are either insoluble or so little soluble as to be classed insoluble. These are obtained as precipitates by adding a soluble hydroxide (usually of sodium, potassium, or ammonium) to a salt of the metals whose hydroxides are insoluble. The principle involved here is the same as in the case of precipitation of insoluble carbonates, namely, bringing together in solution constituents which by their union can form insoluble products and thus be eliminated from the solution, thereby allowing the reaction to go on to completion. This reaction is given as a test under many of the metals.

Ammonium hydroxide acts, in general, like the alkalies, but toward certain metals it shows a marked difference. For example, calcium hydroxide is precipitated from fairly concentrated solutions of calcium salts by the alkalies, but not by ammonia water. This is explained by the ionic or dissociation theory by the fact that ammonium hydroxide is only slightly dissociated. According to this theory, practically all reactions in aqueous solutions take place between ions (see page 149). The alkalies are largely dissociated into metal ions and (OH) ions, which latter unite with the metal ions of the other metals to form the slightly ionized and insoluble hydroxides. Now ammonium hydroxide is only slightly ionized—in fact, to a less extent than calcium hydroxide—so that only a small amount of calcium hydroxide is formed, which remains in

solution, because somewhat soluble. The presence of this calcium hydroxide in solution prevents further ionization of the ammonium hydroxide to such an extent that it ceases to act as an alkali or soluble hydroxide. In fact, the slight ionization of ammonium hydroxide accounts for the reverse action, namely, the liberation of ammonia from its salts by the action of calcium hydroxide.

In the presence of ammonium salts, ammonium hydroxide ionizes only to a very slight extent, so that it loses almost all the character of a hydroxide as far as precipitating other metallic hydroxides is concerned, only the extremely insoluble ones being precipitated. This accounts for the fact that magnesium hydroxide is not precipitated by ammonia water when ammonium salts are present. The magnesium hydroxide, although being nearly insoluble, is sufficiently soluble and ionizable not to be precipitated by ammonia water under these conditions. Alkalies, on the other hand, precipitate magnesium hydroxide copiously, because they are almost completely ionized in dilute solutions, and thus act as strong bases, as we say. Ammonium carbonate behaves very much like ammonia water toward magnesium and some other metals.

Hydroxides of nearly all metals, when heated sufficiently, lose water and give the oxide. Many oxides are prepared in this way. Only a few oxides unite with water to form a hydroxide. One of the best examples of this is the process of slaking lime. Oxides may also be obtained by heating carbonates or nitrates, or directly from the metals. The method followed in any particular case is determined by the properties of the metal, the question of economy, etc.

### Tests for Magnesium.

(Use the reagent solution of magnesium sulphate.)

1. The addition of an alkali carbonate solution causes a white precipitate of basic magnesium carbonate (see Experiment 25).

2. Add to the solution some caustic alkali: a white precipitate of magnesium hydroxide, $Mg(OH)_2$, is formed, insoluble in excess of alkali.

$$Mg^{\cdot\cdot} + SO_4'' + 2Na^{\cdot} + 2(OH)' = Mg(OH)_2 + 2Na^{\cdot} + SO_4''.$$

3. Add to the solution ammonia water or ammonium carbonate: part of the magnesium is precipitated as hydroxide or carbonate. The latter is increased on heating. If an equal volume of ammonium chloride solution is previously added, no precipitate is obtained (for explanation, see Remarks on Tests above).

4. To the solution add an equal volume of solution of ammonium chloride and some ammonia water. The mixture should be clear. Then add sodium phosphate solution: a white, finely crystalline precipitate of the double salt, ammonium magnesium phosphate, is produced, which increases by shaking (see reactions under test 1 for

phosphoric acid). This is a delicate and decisive test for magnesium, when other metals which resemble it are eliminated. This is easily done by adding to a solution some chloride, sulphide, and carbonate of ammonium, which will remove by precipitation all metals except magnesium and alkali metals.

**25. CALCIUM. STRONTIUM. BARIUM. RADIUM.**

$Ca^{II} = 40.07$. $Sr^{II} = 87.63$. $Ba^{II} = 137.37$. $Ra^{II} = 226.4$.

**General Remarks Regarding the Metals of the Alkaline Earths.**

The three metals, calcium, barium, and strontium, form the second group of light metals. Similar to the alkali-metals, they decompose water at the ordinary temperature with liberation of hydrogen; their separation in the elementary state is even more difficult than that of the alkali-metals.

They differ from the latter by forming insoluble carbonates and phosphates (those of the alkalies are soluble), from the earths by their soluble hydroxides (those of the earths are insoluble), and from all heavy metals by the solubility of their sulphides (those of heavy metals are insoluble). The sulphates are either insoluble (barium) or sparingly soluble (strontium and calcium). The hydroxides and carbonates are decomposed by heat, water or carbon dioxide being expelled and the oxides formed. In case of calcium carbonate this decomposition takes place easily, while the carbonates of barium and strontium require a much higher temperature. They are bivalent elements.

**Occurrence in Nature.**—Calcium is one of the most abundantly occurring elements. As carbonate ($CaCO_3$) it is found in the form of calc-spar, limestone, chalk, marble, shells of eggs and mollusks etc., or, as acid carbonate, dissolved in water. The sulphate is found as *gypsum* or *alabaster*, $CaSO_4 2H_2O$; the phosphate, $Ca_3(PO_4)_2$, in the different phosphatic rocks (apatite, etc.); the fluoride, $CaF_2$, as fluor-spar; the chloride, $CaCl_2$, in some waters, and the silicate in many rocks. It enters the vegetable and animal system in various forms of combination, chiefly, however, as phosphate and sulphate.

**Preparation.**—Unlike the alkali-metals, the alkaline-earth metals cannot be prepared by heating their carbonates with carbon. They are usually obtained by electrolysis of the molten chlorides, which

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QUESTIONS.—How is magnesium found in nature? By what process is metallic magnesium obtained? Give the physical and chemical properties of magnesium. State two methods by which magnesium oxide can be obtained. What is calcined magnesia? State the composition and properties of the official magnesium carbonate, and how it is made. What is Epsom salt, and how is it obtained? Which compounds of magnesium are insoluble? Give tests for magnesium compounds. How can the presence of magnesium be demonstrated in a mixture of magnesium sulphate and sodium sulphate?

are kept in the molten state by the heat produced by the resistance to the current.

**Properties.**—Calcium is silvery white, crystalline, melts at 760° C., and has the specific gravity 1.85. It can be cut with a knife, though not easily. When heated (but not when cold) it combines actively with oxygen, hydrogen, nitrogen, and the halogens. When burned in the air, the residue is a mixture of oxide, and nitride, $Ca_3N_2$, which latter is decomposed by water into calcium hydroxide and ammonia.

**Calcium Oxide, Lime, Calx, CaO = 56.07** (*Quick-lime, Burned lime*), is obtained on a large scale by the common process of lime burning, which is the heating of limestone or any other calcium carbonate to about 800° C. (1472° F.), in furnaces termed lime-kilns. On a small scale decomposition may be accomplished in a suitable crucible over a blowpipe flame:

$$CaCO_3 = CaO + CO_2.$$

The pieces of oxide thus formed retain the shape and size of the carbonate used for decomposition.

Lime is a white, odorless, amorphous, infusible substance, of alkaline taste and reaction; exposed to the air it gradually absorbs moisture and carbon dioxide and becomes "air-slaked" lime. It occupies among the basic substances the same position of importance as sulphuric acid does among acids, and is used directly or indirectly in many branches of chemical manufacture. Lime does not melt in the oxyhydrogen flame, but it can be made to boil in the electric arc.

**Calcium Hydroxide, Calcium Hydrate, $Ca(OH)_2$** (*Slaked Lime*).—When water is sprinkled upon pieces of calcium oxide, the two substances combine chemically, liberating much heat; the pieces swell up, and are converted gradually into a dry, white powder, which is the *slaked lime*. When this is mixed with water, the so-called *milk of lime* is formed. Pure lime slakes readily and is known as *fat* lime, while that made from material containing magnesium carbonate or clay is called *poor* lime and slakes slowly and incompletely. When made into mortar, the latter does not harden satisfactorily. Calcium hydroxide is about twice as soluble in water at 18° C. as it is in boiling water. At 18° C. about 600 parts of water are required to dissolve 1 part of the hydroxide.

Freshly slaked lime made into a thin paste with water and mixed with 3 or 4 times as much sand as lime used, forms the ordinary *mortar*, employed for building purposes. The hardening of mortar is due first to loss of water, followed by a gradual conversion of calcium hydroxide into carbonate. In the course of years calcium silicate is also formed.

**Lime-water** (*Liquor Calcis*) (*Solution of Lime*).—This is a saturated solution of calcium hydroxide in water: 10,000 parts of the

latter dissolving about 15 to 17 parts of hydroxide. In making lime-water, 1 part of calcium oxide is slaked and agitated occasionally during half an hour with 30 parts of water. The mixture is then allowed to settle, and the liquid, containing besides calcium hydroxide the salts of the alkali-metals which may have been present in the lime, is decanted and thrown away. To the calcium hydroxide left, and thus purified, 300 parts of water are added and occasionally shaken in a well-stoppered bottle, from which the clear liquid may be poured off for use.

Lime-water is a colorless, odorless liquid, having a feebly caustic taste and an alkaline reaction. When heated to boiling it becomes turbid by precipitation of calcium hydroxide which redissolves when the liquid is cooled. Carbon dioxide causes a precipitation of calcium carbonate, soluble in an excess of carbonic acid.

*Experiment* 27.—Make lime-water according to directions given above.

**Calcium Carbonate** (*Calcii Carbonas Præcipitatus*) $CaCO_3$ = **100.07.**—Precipitated calcium carbonate is obtained as a white, tasteless, neutral, impalpable powder by mixing solutions of calcium chloride and sodium carbonate:

$$CaCl_2 + Na_2CO_3 = 2NaCl + CaCO_3.$$

It requires about 100,000 parts of cold water, but more of boiling water, to dissolve 1 part of the carbonate. The bicarbonate or acid carbonate, $Ca(HCO_3)_2$, is about thirty times more soluble, but requires the presence of an excess of carbon dioxide to overcome the tendency of the acid carbonate to lose some of its carbonic acid and form the normal carbonate. Heat decomposes the acid calcium carbonate into normal carbonate and carbonic acid, which latter, together with the excess present in the solution, is driven out.

Water containing calcium or magnesium salts is known as *hard water*, because it converts soap into insoluble calcium or magnesium soap, thus preventing the formation of lather until all the calcium or magnesium is precipitated. Hardness due to acid carbonates in solution is called *temporary*, because it can be removed by boiling the water, or adding sufficient slaked lime to convert all carbonic acid into insoluble carbonate. Hardness due to dissolved sulphate of calcium or magnesium, or chloride of the same, is called *permanent*, because it cannot be removed by boiling. Such hardness can be removed by adding sodium carbonate to the water. After the disturbing salts have been removed, the water is said to be *soft*.

Hard waters are responsible for the deposits in boilers known as boiler scales, and in caves known as stalagmites and stalactites.

*Experiment* 28.—Add to about 10 grams of marble (calcium carbonate), in small pieces, hydrochloric acid as long as effervescence takes place; filter the solution of calcium chloride thus obtained and add to it solution of sodium carbonate as long as a precipitate is formed, collect the precipitate on a filter, wash and dry it.

**Dried Calcium Sulphate, $CaSO_4$ = 136.14** (*Dried Gypsum, Plaster of Paris, Calcined Plaster*).—It has been mentioned above that the mineral *gypsum* is native calcium sulphate in combination with 2 molecules of water of crystallization. By heating to about 115° C. (239° F.) about three-fourths of this water is expelled, and a nearly anhydrous sulphate formed. This article readily recombines with water, becoming a hard mass, for which reason it is used for making moulds and casts, and in surgery. If the gypsum is heated to a higher temperature than the one mentioned, all water is expelled, and the product thus obtained combines with water but very slowly.

**Calcium Phosphate, $Ca_3(PO_4)_2$ = 310.29** (*Phosphate of Lime*).—By dissolving bone-ash (bone from which all organic matter has been expelled by heat) in hydrochloric acid, and precipitating the solution with ammonia water there is obtained calcium phosphate, which contains traces of calcium fluoride and magnesium phosphate.

A pure article is made by precipitating a solution of calcium chloride by sodium phosphate and ammonia:

$$2Na_2HPO_4 + 3CaCl_2 + 2NH_4OH = Ca_3(PO_4)_2 + 4NaCl + 2NH_4Cl + 2H_2O.$$

It is a white, tasteless, amorphous powder, insoluble in cold water, soluble in hydrochloric or nitric acids.

**Superphosphate, or acid phosphate of lime.** Among the inorganic substances which serve as plant-food, calcium phosphate is a highly important one. As this compound is found usually in very small quantities as a constituent of the soil, and as this small quantity is soon removed by the various crops taken from a cultivated soil, it becomes necessary to replace it in order to enable the plant to grow and to form seeds.

For this purpose the various phosphatic rocks (chiefly calcium phosphate) are converted into commercial fertilizers, which is accomplished by the addition of sulphuric acid to the ground rock. The sulphuric acid removes from the tricalcium phosphate one or two atoms of calcium, forming mono- or dicalcium phosphate and calcium sulphate. The mixture of these substances, containing also the impurities originally present in the phosphatic rocks, is sold as acid phosphate or superphosphate.

**Bone-black and Bone-ash.**—Phosphates enter the animal system in the various kinds of food, and are to be found in every tissue and fluid, but most abundantly in the bones and teeth. Bones contain about 30 per cent. of organic and 70 per cent. of inorganic matter, most of which is tricalcium phosphate. When bones are burned until all the organic matter has been destroyed and volatilized, the resulting product is known as *bone-ash*. If, however, the bones are subjected to the process of destructive distillation (heating with exclusion of air), the organic matter suffers decomposition, many volatile products escape, and most of the non-volatile carbon remains mixed with the inorganic portion of the bones, which substance is known as *bone-black* or *animal charcoal, carbo animalis*. It contains

about 85 per cent. of inorganic matter, the balance being chiefly carbon.

**Composition of Bone and Teeth.**—Different bones (and even different parts of the same bone) of the same person differ somewhat in composition; moreover, the bones of a child contain somewhat more of organic matter than those of a grown person, as may be shown by the following analyses of the corresponding bone in children and a grown person:

| | Child one year. Per cent. | Child five years. Per cent. | Man twenty-five years. Per cent |
|---|---|---|---|
| Organic matter | 43.42 | 32.29 | 31.17 |
| Tricalcium phosphate | 48.55 | 59.74 | 58.95 |
| Magnesium phosphate | 1.00 | 1.34 | 1.30 |
| Calcium carbonate | 5.79 | 6.00 | 7.08 |
| Soluble salts | 1.24 | 0.63 | 1.50 |
| Ferric phosphate | Traces. | Traces. | Traces. |

Frequently human bones contain calcium fluoride, which substance, to the amount of 1 to 2 per cent., is a normal constituent of the bones of many animals. The organic matter of bone is *ossein*, a collagen, yielding gelatin on boiling with dilute hydrochloric acid.

Teeth consist of three distinct tissues, viz., *dentine*, forming the chief mass, in its interior being the pulp cavity; *enamel*, investing the crown and extending some distance down the neck; and *cement*, covering the fangs. The composition of *cement* is almost the same as that of bone, its organic and inorganic constituents having the relative proportions of 30 : 70.

*Dentine* contains less water than bone and is also poorer in organic matter. The following table gives the composition of the dentine of an adult woman and man respectively:

| | Woman | Man |
|---|---|---|
| Organic matter—ossein and vessels | 27.61 | 20.42 |
| Calcium phosphate | 66.72 | 67.54 |
| Calcium carbonate | 3.36 | 7.97 |
| Magnesium phosphate | 1.08 | 2.49 |
| Soluble salts, chiefly sodium chloride | 0.83 | 1.00 |
| Fat | 0.40 | 0.58 |

*Enamel* is distinguished by the very small proportion of water and organic matter contained in it. Its average composition may be thus stated:

| | |
|---|---|
| Water and organic matter | 3.6 |
| Calcium phosphate and traces of fluoride | 86.9 |
| Magnesium phosphate | 1.5 |
| Calcium carbonate | 8.0 |

*Tartar* is the name given to the substance which deposits from alkaline saliva on the teeth. It is of a grayish, yellowish, or brownish color, and consists chiefly of calcium phosphate, with a little carbonate, but contains also bacteria and other organic matter, salts of the alkalies, and silica.

**Calcium Hypophosphite** (*Calcii Hypophosphis*) $Ca(PH_2O_2)_2$ = **170.18.**—Obtained by heating pieces of phosphorus with milk of lime

until hydrogen phosphide ceases to escape. From the filtered liquid the excess of lime is removed by carbon dioxide, and the clear liquid evaporated to dryness. (Great care must be taken during the whole of the operation, which is somewhat dangerous on account of the inflammable and explosive nature of the compounds.)

$$8P + 6H_2O + 3Ca(OH)_2 = 3Ca(PH_2O_2)_2 + 2PH_3.$$

Calcium hypophosphite is generally met with as a white, crystalline powder with a pearly lustre; it is soluble in 6 parts of water and has a neutral reaction to litmus.

**Calcium Chloride** (*Calcii Chloridum*) **$CaCl_2$ = 110.99,** and **Calcium Bromide** (*Calcii Bromidum*) **$CaBr_2$ = 199.91,** may both be obtained by dissolving calcium carbonate in hydrochloric acid or hydrobromic acid, until the acids are neutralized. Both salts are highly deliquescent.

Calcium chloride crystallizes at ordinary temperature with 6 molecules of water in large deliquescent prisms. These crystals mixed with snow or ice cause a fall of temperature to —48° C. When heated to about 200° C., the crystals lose nearly all their water and yield a porous mass, which is used in the laboratory as a drying agent for gases and liquids. It is less efficient, however, than concentrated sulphuric acid or phosphorus pentoxide. As it combines with ammonia and with alcohol, it cannot be used for removing water from them; for this purpose, unslaked lime may be used.

**Chlorinated Lime** (*Calx Chlorinata*) (*Bleaching-powder*, incorrectly called *Chloride of Lime*).—This is chiefly a mixture (according to some, a compound) of calcium chloride with calcium hypochlorite, and is manufactured on a very large scale by the action of chlorine upon calcium hydroxide:

$$\underset{\text{Calcium hydroxide.}}{2Ca(OH)_2} + 4Cl = 2H_2O + \underbrace{Ca(ClO)_2 + CaCl_2}_{\text{Chlorinated lime}}.$$

Bleaching-powder is a white powder, having a feeble chlorine-like odor; exposed to the air it becomes damp from absorption of moisture, undergoing decomposition at the same time; with dilute acids it evolves chlorine, of which it should contain not less than 30 per cent. in available form. The action of hydrochloric acid takes place thus:

$$Ca(ClO)_2 + 2HCl = CaCl_2 + 2HClO;$$
$$2HClO + 2HCl = 2H_2O + 4Cl.$$

Bleaching-powder is a powerful disinfecting and bleaching agent.

**Crude Calcium Sulphide** (*Calcii sulphidum crudum*) is a mixture of calcium sulphide and sulphate, obtained by heating to redness in a crucible a mixture of dried calcium sulphate, starch, and charcoal until the contents have lost their black color. By the deoxidizing action of the coal and starch the larger portion of the calcium sulphate is converted into sulphide.

Calcium Carbide, $C_2Ca$, is manufactured on a large scale by heating in an electric furnace a mixture of lime and coal, or coal-tar. The combined action of the high temperature and of the electric current causes this decomposition to take place:

$$CaO + 3C = CaC_2 + CO.$$

Calcium carbide thus made is not pure; it forms gray or brown masses of extreme hardness; it is used extensively for generating acetylene gas, $C_2H_2$, which is evolved when calcium carbide acts on water:

$$C_2Ca + H_2O = C_2H_2 + CaO.$$

## Tests for Calcium.

(The reagent solution of calcium chloride, $CaCl_2$, may be used.)

1. Add to solution of a calcium salt, the carbonate of either potassium, sodium, or ammonium: a white precipitate of calcium carbonate, $CaCO_3$, is produced. Try the test also on solution of calcium sulphate and lime-water.

2. Add sodium phosphate to neutral solution of a calcium salt: a white precipitate of calcium phosphate, $CaHPO_4$, is produced.

3. Add ammonium (or potassium) oxalate to solution of a calcium salt: a white precipitate of calcium oxalate, $CaC_2O_4$, is produced, which is insoluble in acetic, soluble in hydrochloric acid. Try the test also on solution of calcium sulphate and lime-water.

4. Sulphuric acid or soluble sulphates produce a white precipitate of calcium sulphate, $CaSO_4$, in concentrated, but not in dilute solutions of a calcium salt. Try the test also on lime-water.

5. Add potassium or sodium hydroxide: a white precipitate of calcium hydroxide, $Ca(OH)_2$, is produced in concentrated, but not in diluted solutions. Ammonia-water gives no precipitate. (See Remarks on Tests, page 243.)

6. Volatile compounds of calcium impart a reddish-yellow color to the Bunsen flame. Non-volatile compounds, as the oxide, carbonate, phosphate, etc., have scarcely any effect on the flame. (Try it.) These should first be moistened with strong hydrochloric acid to convert them to the volatile chloride before introducing into the flame. (See note to test 4 for potassium.)

Test 3, done in dilute solution, combined with tests 4 and 6, is decisive for recognizing calcium compounds. The oxide, carbonate and phosphate may be dissolved by dilute hydrochloric acid for tests. The phosphate solution cannot be neutralized without precipitation, but if left weakly acid and considerably diluted test 3 can be applied.

The above tests are examples of more or less complete reactions, due to the formation of insoluble or sparingly soluble substances, and their removal from the field of action by precipitation (see pages 129 and 148). The ionic equations in the tests are as follows:

Test 1. $Ca^{\cdot\cdot} + 2Cl' + 2Na^{\cdot} + CO_3'' = CaCO_3 + 2Na^{\cdot} + 2Cl'$;
$Ca^{\cdot\cdot} + SO_4'' + 2Na^{\cdot} + CO_3'' = CaCO_3 + 2Na^{\cdot} + SO_4''$;
$Ca^{\cdot\cdot} + 2(OH)' + 2Na^{\cdot} + CO_3'' = CaCO_3 + 2Na^{\cdot} + 2(OH)'$.

Test 2. $Ca^{\cdot\cdot} + 2Cl' + 2Na^{\cdot} + HPO_4'' = CaHPO_4 + 2Na^{\cdot} + 2Cl'$;

Test 3. $Ca^{\cdot\cdot} + 2Cl' + 2NH_4^{\cdot} + C_2O_4'' = CaC_2O_4 + 2NH_4^{\cdot} + 2Cl'$.

The equations for sulphate and hydroxide of calcium are similar (see test 1).

Test 4. $Ca^{\cdot\cdot} + 2Cl' + 2H^{\cdot} + SO_4'' = CaSO_4 + 2H^{\cdot} + 2Cl'$;

Test 5. $Ca^{\cdot\cdot} + 2Cl' + 2Na^{\cdot} + 2(OH)' = Ca(OH)_2 + 2Na^{\cdot} + 2Cl'$.

The ionic equations in the tests for strontium and barium are like those for calcium.

## Strontium, $Sr^{ii} = 87.63$.

Found in a few localities in the minerals *strontianite*, $SrCO_3$, and *celestite*, $SrSO_4$. Its compounds resemble those of calcium and barium. The *oxide*, SrO, cannot be obtained easily by heating the carbonate, as this is much more stable than calcium carbonate. It may, however, be readily prepared by heating the nitrate. The *hydroxide*, $Sr(OH)_2$, is formed when the oxide is brought in contact with water; it is more soluble than calcium hydroxide.

*Strontium nitrate*, $Sr(NO_3)_2$, *Strontium chloride*, $SrCl_2$, *Strontium bromide*, $SrBr_2$, and *Strontium iodide*, $SrI_2$, may be obtained by dissolving the carbonate in the respective acids. The nitrate is used extensively for pyrotechnic purposes, as strontium imparts a beautiful red color to flames; the bromide and iodide are official.

### Tests for Strontium.

(Use about a 5 per cent. solution of strontium nitrate.)

1. The reactions of strontium with soluble carbonates, oxalates, and phosphates are analogous to those of calcium.

2. Add calcium sulphate solution: a white precipitate of strontium sulphate, $SrSO_4$, is formed after a few minutes. This test shows that the sulphate is less soluble than calcium sulphate.

3. Add dilute sulphuric acid or a solution of a sulphate: a white precipitate forms at once in concentrated, after a while in dilute, solutions.

4. Add potassium chromate solution: a pale yellow precipitate of strontium chromate, $SrCrO_4$, is formed, which is soluble in acetic acid and in hydrochloric acid. (Potassium dichromate causes no precipitation.)

5. Volatile strontium compounds color the Bunsen flame crimson (see remarks in test 6 for calcium.) The color appears at the moment when the substance is first introduced into the flame, whereby the color can be seen, even in the presence of barium. Lithium is the only other metal which gives a similar flame, but strontium may be distinguished from it by test 3 applied in somewhat dilute solution.

Tests 2 and 3 combined with 5 give conclusive proof of strontium compounds. Insoluble compounds are treated as directed under Tests for Calcium.

## Barium, $Ba^{ii}$ = 137.37.

Occurs in nature chiefly as sulphate in *barite* or *heavy spar*, $BaSO_4$, but also as carbonate in *witherite*, $BaCO_3$. Barium and its compounds resemble closely those of calcium and strontium.

*Barium chloride*, $BaCl_2 + 2H_2O$, is prepared by dissolving the carbonate in hydrochloric acid. It crystallizes in prismatic plates, and is used as a valuable reagent.

*Barium dioxide or peroxide*, $BaO_2$, is made by heating the oxide to a dark red heat in the air or in oxygen. When heated above the temperature at which it is formed, decomposition into oxide and oxygen takes place. This power to absorb oxygen from air and to give it up again at a higher temperature has been used as a method of preparing oxygen on the large scale. Unfortunately, the barium oxide cannot be used for an unlimited number of operations, as it loses the power to absorb oxygen after it has been heated several times. The use made of barium dioxide in preparing hydrogen dioxide has been mentioned before.

Barium dioxide is a heavy, grayish-white, amorphous powder, almost insoluble in water, with which, however, it forms a hydroxide, and to which it imparts an alkaline reaction.

*Barium oxide*, BaO, is made by heating *barium nitrate*, $Ba(NO_3)_2$, which itself is made by dissolving *barium carbonate* in nitric acid.

Barium salts, soluble in water or dilute acid, are poisonous; antidotes are sodium or magnesium sulphates.

### Tests for Barium.

(Use the reagent solution of barium chloride.)

1. The reactions of barium salts with soluble carbonates, oxalates, and phosphates are analogous to those of solutions of calcium salts.

2. Add dilute sulphuric acid or solution of a sulphate: a white precipitate of barium sulphate, $BaSO_4$, is produced immediately, even in dilute solutions. The precipitate is insoluble in all diluted acids.

3. Add calcium sulphate solution: a white precipitate, insoluble in all diluted acids, is formed *immediately* (compare with test 2 under Strontium).

4. Add potassium chromate or dichromate solution: a pale-yellow precipitate of barium chromate, $BaCrO_4$, is formed, insoluble in acetic acid, but soluble in hydrochloric or nitric acid.

5. Volatile barium compounds color a Bunsen flame yellowish-green (see remarks under test 6 for calcium).

Tests 3, 4, and 5 give conclusive proof of barium. Insoluble compounds are treated as directed under Tests for Calcium.

## Summary of Analytical Characters of the Alkaline-earth Metals and Magnesium.

| | *Magnesium.* | *Calcium.* | *Strontium.* | *Barium.* |
|---|---|---|---|---|
| Potassium dichromate . . | ..... | ..... | ..... | Yellow precipitate. |
| Potassium chromate. . . | ..... | ..... | Yellow precipitate. | Yellow precipitate |
| Calcium sulphate. . . . | ..... | ..... | White precipitate forming slowly | White precipitate forming at once. |
| Ammonium carbonate . . | White precipitate soluble in $NH_4Cl$. | White precipitate. | White precipitate. | White precipitate. |
| Ammonium hydroxide. . | White precipitate. | ..... | ..... | ..... |
| Ammonium oxalate. . . | No precipitate unless very concentrated | White precipitate in dilute solution | White precipitate in strong solution. | White precipitate in strong solution. |
| Sodium phosphate . . . | White precipitate. | White precipitate. | White precipitate. | White precipitate |
| Flame color . . . . . | ..... | Yellowish-red. | Red. | Yellowish-green. |
| One part of hydroxide is soluble in . . . . . | 50,000 parts of water. | 666 parts of water. | 50 parts of water. | 28.6 parts of water. |
| One part of sulphate is soluble in . . . . . | 1.5 parts of water. | 400 parts of water. | 8000 parts of water. | 400,000 parts of water. |

### Radium, $Ra^{11} = 226.4$.

This element was discovered in 1899. While radium is closely related to barium it has not been found in the native barium compounds, except when they occur associated with uranium, as in pitch-blende, an ore from which uranium compounds are extracted. This ore contains, however, but 0.1 gram of radium in 1000 kilograms, which is equal to 0.00001 per cent. The residue left, after the uranium has been eliminated, contains from 2 to 3 times as much radium as the original ore. From 1000 kilograms of this residue 10 to 15 kilograms of

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Questions.—Which metals form the group of the alkaline earths, and in what respect do their compounds differ from those of the alkali-metals? How is calcium found in nature? What is burned lime; from what, and by what process is it made, and how does water act on it? What is lime-water; how is it made, and what are its properties? Mention some varieties of calcium carbonate as found in nature, and how is it obtained by an artificial process from the chloride? What is Plaster-of-Paris, and what is gypsum; what are they used for? State composition and mode of manufacturing bleaching-powder; what are its properties, and how do acids act upon it? What is bone-black, bone-ash, acid phosphate, and precipitated tricalcium phosphate? How are they made? Give tests for barium, calcium, and strontium; how can they be distinguished from each other? Which compounds of barium and strontium are of interest, and what are they used for?

radiferous barium salt (chloride or bromide) are extracted, and from this the radium salt is prepared by repeated fractional crystallization. The small yield of radium obtained after long and tedious operations make it the most costly material of the day.

Both the chloride and bromide of radium are white, crystalline substances turning grayish in the course of time. Lack of a liberal supply of radium has so far prevented a closer study of its chemical behavior.

Radium metal has been isolated, but when reference is made to the use of radium in any investigation, the salts of radium are always meant, usually the chloride or bromide. These are now being successfully obtained in Denver from the Colorado carnotite ores by the Bureau of Mines, in connection with the National Radium Institute. The cost of producing one gram of radium as radium bromide in Denver in 1915 was $36,050, while that from Europe was selling at about $140,000 a gram. The demand for radium will increase, for the two or three surgeons who have a sufficient amount of this element to entitle them to speak from experience, are obtaining results in the cure of cancer that are increasingly encouraging as their knowledge of its application improves.

The discussion of the peculiar properties of radium salts should be preceded by that of several closely related physical phenomena.

**Discharge through Gases.**—When an electric current of sufficiently high E. M. F. is discharged through a gas, for instance, through air, the gas is rendered luminous by its passage—*i. e.*, we have what is called an *electric spark*, in appearance like that of a flash of lighting. This spark in many cases exerts chemical action, as, for instance, when oxygen is converted into ozone.

If the discharge takes place in a gas inclosed in a glass globe from which the gas may be removed by means of an air-pump, it is found that at a sufficiently reduced pressure the spark ceases and the interior of the globe assumes a beautiful luminosity, the nature of which depends on the kind of gas operated on.

By exhausting the air from suitably constructed bulbs or tubes still further until an almost perfect vacuum is obtained, the electric discharges passing through this vacuum again show decided changes. If the cathode of such a vacuum tube be formed of a metallic disk, while the anode be a straight wire, then on passing the current through the vacuum tube a pale purplish beam of light radiates from the face of the disk. This beam is known as the *cathode ray;* it has been shown to consist of streams of portions of matter negatively charged, and moving with great velocity.

**Röntgen Rays.**—During the generation of the cathode rays in the vacuum tube another kind of rays of a very peculiar character are formed. They have been called *Röntgen rays*, after their discoverer, who himself named them *x*-rays. These rays differ from other rays in many respects; thus they can pass readily through many kinds of matter which are opaque to ordinary light; they cause many substances to emit light when they fall upon them; they affect photographic plates, and have a decided physiological action on various parts of the human body. They are not particles, but electric waves, and were discovered in 1895.

**Radio-activity.**—In 1896 the French scientist Becquerel discovered that the metal uranium and its compounds exert spontaneously and continuously a certain influence upon their surroundings. This influence was found to be due to rays (now called *Becquerel rays*) of a peculiar kind. They act upon the photographic plate; they pass through black paper and metals; they render the gases through which they pass conductors of electricity. Any substance exhibiting the power of sending out such rays is said to be radio-active. Besides uranium and its compounds those of thorium were found to possess the same properties.

The subject of radio-activity was next studied by Madame Curie, who showed that certain minerals (such as pitch-blende) containing uranium are more radio-active than uranium itself, and in the course of her investigation demonstrated that in uranium ores are several substances which show radio-activity to a remarkable extent.

The work, carried yet further by a number of scientists, has brought out the following results: Three substances, named *polonium*, *actinium*, and *radium*, have been obtained from pitch-blende and show a radio-activity a million times greater than that of uranium or thorium.

Of these three substances at least one—the radium—has been positively proven to be an elementary substance of metallic nature forming well-defined salts, such as radium chloride and bromide. Radium salts show all the previously mentioned properties of Becquerel rays, but in addition they exhibit some other features.

Thus, radium salts are permanently luminous and render luminous (or phosphorescent) for a shorter or longer period a great number of other substances. The most sensitive are barium platinocyanide, zinc sulphide, diamond, etc. Not only do radium salts impart luminosity to other substances, but these salts communicate little by little their radio-active properties to substances in their neighborhood, and these in turn emit Becquerel rays for some time.

Another startling discovery was made when it was shown that radium salts develop heat continuously, and consequently are in themselves warmer than their surroundings. A small flask containing 0.7 gram of radium bromide shows a temperature of 3° C. higher than the surrounding air. Calorimetric measurements have shown that radium bromide evolves enough heat to convert per hour its own weight of ice into water, or that 1 gram of radium bromide will raise the temperature of 80 grams of water 1° C. per hour.

Of great interest is the physiological action of radium compounds on the animal system. Radium bromide, even when enclosed in a wooden or metallic box, brought near the closed eye causes the sensation of light. While nothing is felt when radium salts are brought close to our body, yet a strong influence, similar to that of Rontgen rays, is exerted upon the tissues. This is shown by the fact that days or weeks after the body had been exposed to radium rays the skin reddens and, if the exposure was of sufficient duration, sores and ulcerations will form which require a long time for healing. A sealed glass tube, containing a little radium bromide, when placed in a bowl of water with small fishes cause their death in a few hours. Attempts are now being made to use radium rays, like Röntgen rays, in the treatment of skin diseases, lupus, etc.

Just as sun rays are made up of heat rays, light rays, and rays of actinic power, so it has been found that there is a difference in the rays of a radio-active body. There are at least three kinds, of which the first group, called *alpha* rays, causes ionization in gases, and is almost completely blocked by a piece of paper. The rays consist of particles of about twice the weight of a hydrogen atom, each possessing a positive charge of electricity equal to that on a univalent positive ion, and moving with tremendous velocity. The *beta* rays produce photographic effects, readily pass through paper and thin sheets of metal, are identical with cathode rays, and possess a negative charge of electricity. They consist of minute particles, called *electrons* or *corpuscles* which weigh about $\frac{1}{1700}$ part of the weight of an atom of hydrogen, and move with a velocity nearly equal to that of light. The *gamma* rays resemble *x*-rays and probably result from the impact of beta rays, just as *x*-rays are produced by the impact of cathode rays on the walls of a Crookes' tube.

The elevated temperature and luminosity of radium salts are believed to be due to the bombardment of the mass in its interior by the alpha and beta corpuscles.

Radium is constantly throwing off a new radio-active body of the nature of a gas, which can be collected, and is called radium *emanation*. This emanation likewise spontaneously transforms itself into other active substances. Ultimately the radio-activity ceases and the substances come to rest as new kinds of matter.

It is believed that radium is originally produced by uranium, for every known uranium ore contains radium and radium emanation in quantities proportional to the amounts of uranium present.

**Radio-activity and the Atomic Theory.**—Some of the elements are undeniably capable of spontaneous decomposition and transmutation into other elements. These facts necessarily require a modification of the Dalton atoms. It is now believed that the atom, as revealed in chemistry, is a mass of a great number of small corpuscles which have come to a state of stability or equilibrium, in which state they cannot be separated by our ordinary chemical operations, and thus appear as single units or atoms. In radium and in other radio-active bodies these complexes of corpuscles are in unstable equilibrium and possess potential energy which has a tendency to diminish in quantity, thus causing the state of unrest exhibited by radio-active bodies. The potential energy becomes kinetic in the form of heat, light, etc., and meantime the complexes are transformed to stable forms which do not possess radio-activity and which act like the chemical atoms.

This would involve the transformation of one element into a new element, and that is exactly what has been found to take place in the case of radium, namely, that the emanation from radium contains helium.

**Measurement of Radio-activity.**—Atmospheric air is practically a non-conductor of electricity, but when subjected to the rays of radio-active substances, it is ionized and becomes a conductor. If a uranium or radium salt be placed about 1 or 2 inches from the knob of a delicate, well-insulated charged electroscope, the latter will be quickly discharged. By comparing the times required for the discharge of an electroscope by different samples of radio-active substances, a quantitative measure of their radio-activity is obtained. The radio-activity of uranium is taken as the unit of intensity. If a radium salt is said to have an activity of 1,000,000, that means that it causes a conductivity in air one million times greater than that caused by an equal weight of uranium salt.

## 26. ALUMINUM.

$Al^{iii} = 27.1$.

Aluminum occurs in group III of the periodic table of elements, together with a number of other metals which are very rare and almost exclusively of scientific interest. Aluminum and the metals very similar to it constitute the group known as the *metals of the earths*, of which aluminum is the most abundant, best known, most useful, and the only one that is studied in an elementary course. Another element of group III that we have studied is boron, which, like aluminum, is constantly trivalent, but it is an acidic (or non-metallic) element. Aluminum hydroxide is basic, but it shows feebly acidic character toward strong bases, like sodium hydroxide.

In the analytical classification of metals, aluminum falls in the ammonium sulphide group, because it happens to be precipitated by that reagent, although not as sulphide, but as hydroxide, as the result of hydrolysis of the sulphide.

**Occurrence in Nature.**—Aluminum is found almost exclusively in the solid mineral portion of the earth; rarely more than traces of aluminum compounds are found dissolved in water, and the occurrence of aluminum in the animal organism seems to be purely accidental.

By far the largest quantity of aluminum is found in combination with silicic acid in the various silicated rocks, forming the greater mass of our earth, such as feldspar, slate, basalt, granite, mica, hornblende, etc., or in the various modifications of clay formed by their decomposition.

The minerals known as *corundum*, *ruby*, *sapphire*, and *emery*, are aluminum oxide in a crystallized state, and more or less colored by traces of other substances.

**Preparation.**—Aluminum was isolated by Wöhler in 1827. For a number of years it was very expensive because its production depended upon the reduction of aluminum chloride by heating with metallic sodium, thus:

$$AlCl_3 + 3Na = Al + 3NaCl.$$

The process by which the metal is obtained now on a large scale was devised in this country in 1886 by Charles Martin Hall at twenty-two years of age, and simultaneously in France by Paul Héroult, at the same age. It consists in electrolyzing a solution of aluminum oxide in molten cryolite (aluminum sodium fluoride, $AlF_3.3NaF$) in a carbon-lined cell. The carbon lining is the cathode, and bars of carbon are used as anode. The aluminum oxide, which dissolves in molten cryolite to the extent of about 25 per cent., is decomposed by the current into metal and oxygen, the metal sinking to the bottom of the cell, whence it is drawn off at intervals, the oxygen uniting with the carbon of the anode. The process is continuous, aluminum oxide being fed into the bath as fast as it is decomposed The cryolite is not affected by the current of the amperage and voltage used.

The commercial manufacture of aluminum was begun in this country in 1888 with an output of 50 pounds a day, selling at $2 per pound, while the annual output now is 40,000,000 pounds, selling at about twenty-two cents per pound under normal conditions.

The raw material from which all metallic aluminum is now produced is bauxite, $Al_2O_3.2H_2O$, which contains ferric oxide as an impurity. It is named from Baux, in France, where vast deposits are located. It is also found extensively in Arkansas, Alabama, Georgia and Tennessee. Bauxite resembles clay in color and texture.

**Properties.**—Aluminum is an almost silver-white metal of a very

low specific gravity (2.67); it is capable of assuming a high polish, and for this reason is used for ornamental articles; it is very ductile and malleable and ranks with silver in hardness, as also in its power of conducting heat and electricity. It melts between 600° and 700° C.

The chief uses of aluminum are the making of cooking utensils, parts of automobiles, instruments and apparatus, the replacement of copper in long distance electric lines, aluminum paint, for solidifying steel castings by removing the gases which make the castings unsound (an ounce of aluminum is added to a ton of steel as the metal is poured), etc.

Aluminum forms alloys with nearly all metals, lead being an exception. The hardness and elasticity of tin is increased by addition of aluminum; readily obtainable alloys with zinc are used as solders for aluminum. A small quantity of aluminum added to wrought-iron so increases its fusibility that it may be poured as easily as cast-iron. Largely used is *aluminum-bronze*, an alloy resembling gold and composed of 10 parts of aluminum with 90 of copper; it fuses easily and is more resistant chemically and mechanically than any other bronze. *Magnalium* is an alloy containing from 6 to 30 per cent. of magnesium, which is more easily worked on the lathe or polished than is aluminum.

Aluminum would be an ideal base for artificial dentures, were it not that the corrosive action of alkaline fluids upon it limits its use.

Aluminum is not oxidized to any great extent in dry or moist air nor is it affected by hydrogen sulphide. It is not readily acted on by nitric or sulphuric acid, but easily dissolves in hydrochloric acid and in solutions of the alkali hydroxides (see under Hydrogen).

At elevated temperature, aluminum has such a great affinity for oxygen that it reduces all metallic oxides except magnesium oxide. Goldschmidt used this property to develop a method of preparing pure chromium, manganese, uranium, etc., the oxides of which are very hard to reduce by other means. The Goldschmidt method is known as *aluminothermy*. The heat produced by the chemical action is so great that the liberated metal is obtained in the molten state, and also the aluminum oxide formed. When a mixture of iron oxide and powdered aluminum is ignited by a piece of burning magnesium ribbon, molten iron having a temperature of about 3000° C. is produced. This intense heat and molten iron are now used for welding broken objects which cannot be conveniently taken to shops, for example, propeller shafts, fly-wheels, rails, etc. The mixture of aluminum powder and oxide of a metal is known as *thermit*. Aluminum reduces sulphides with the same vigor as oxides.

**Aluminum Hydroxide** (*Alumini Hydroxidum*) $\mathbf{Al(OH)_3 = 78.12.}$—Obtained by adding ammonia water or solution of sodium carbonate to solution of alum, when aluminum hydroxide is precipitated in the form of a highly gelatinous substance, which, after being well washed, is dried at a temperature not exceeding 40° C. (104° F.).

$$2KAl(SO_4)_2 + 6NH_4OH = K_2SO_4 + 3(NH_4)_2SO_4 + 2Al(OH)_3;$$
$$2KAl(SO_4)_2 + 3Na_2CO_3 + 3H_2O = K_2SO_4 + 3Na_2SO_4 + 3CO_2 + 2Al(OH)_3.$$

When aluminum hydroxide is heated, water is expelled and the oxide is left, which is often termed *alumina.*

The usual decomposition between a soluble carbonate and any soluble salt (provided decomposition takes place at all) is the formation of an insoluble carbonate; according to this rule, the addition of a soluble carbonate to alum should produce aluminum carbonate. The basic properties of aluminum oxide, however, are so weak that it is not capable of uniting with so weak an acid as carbonic acid, and it is for this reason that the decomposition takes place as shown by the above formula, with liberation of carbon dioxide, while the hydroxide is formed. (Other metals, the oxides of which have weak basic properties, show similar reactions, as, for instance, chromium, and iron in the ferric salts.)

The weak basic properties of aluminum are shown also by the fact that aluminum sulphate, chloride, and nitrate, and even alum itself, have an acid reaction, while the corresponding salts of the alkalies or alkaline earths are neutral.

Aluminum salts in solution give the ion $Al^{\cdots}$, which forms insoluble compounds with hydroxyl ion $(OH)'$, carbonate ion $CO_3''$, phosphate ion $PO_4'''$, sulphide ion $S''$, etc. The carbonate and sulphide are hydrolyzed with elimination of $CO_2$ and $H_2S$ respectively. Aluminum hydroxide has such weak basic properties that it actually shows an acid character toward the active bases, and is dissolved by them to form compounds called aluminates. This means that $Al(OH)_3$ has two modes of ionization, namely,

$$Al(OH)_3 \rightleftarrows Al^{\cdots} + 3(OH)';$$
$$Al(OH)_3 \rightleftarrows AlO_3''' + 3H^{\cdot}.$$

The first mode takes place mainly, and in the presence of acids, salts are formed thus:

$$Al^{\cdots} + 3(OH)' + 3H^{\cdot} + 3Cl' = Al^{\cdots} + 3Cl' + 3H_2O.$$

The second mode of ionization takes place to a less extent, but in the presence of excess of alkalies action results thus:

$$AlO_3''' + 3H^{\cdot} + 3Na^{\cdot} + 3(OH)' = AlO_3''' + 3Na^{\cdot} + 3H_2O.$$

These reactions are generally written thus:

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O;$$
$$Al(OH)_3 + 3NaOH = Na_3AlO_3 + 3H_2O.$$

The compounds of the form $Na_3AlO_3$, called aluminates, are largely hydrolyzed by water into NaOH and $Al(OH)_3$. Hence, an excess of alkali is required to dissolve the aluminum hydroxide. Ammonium hydroxide is too weak a base to unite with it.

On the large scale, aluminum hydroxide is made by heating a mixture of bauxite ($Al_2O_3.2H_2O$) and sodium carbonate, whereby sodium aluminate is formed thus:

$$Al_2O_3.2H_2O + 3Na_2CO_3 = 2Na_3AlO_3 + 3CO_2 + 2H_2O.$$

The sodium aluminate is extracted with water, the impurity of iron oxide in the bauxite remaining undissolved. The solution is treated with carbon dioxide, whereby bluish-white, gelatinous aluminum hydroxide is precipitated,

$$2Na_3AlO_3 + 3CO_2 + 3H_2O = 2Al(OH)_3 + 3Na_2CO_3.$$

The hydroxide, when separated and washed, may be dissolved in acids to form the salts of aluminum. Solution of sodium aluminate is used as a mordant (see below).

Some aluminum hydroxide is also made by boiling cryolite with milk of lime, a solution of sodium aluminate being obtained,

$$AlF_3.3NaF + 3Ca(OH)_2 = Na_3AlO_3 + 3CaF_2 + 3H_2O.$$

By treating the solution with carbon dioxide, aluminum hydroxide is precipitated. The sodium carbonate formed is also recovered.

Aluminum hydroxide, in common with many other substances, as hydroxide of iron, chromium, tin, tannic acid, etc., has the power of uniting with dyes and forming colored compounds which adhere firmly to cotton and linen fabrics. Such substances are called mordants (meaning biting), and without their use it is impossible to dye cotton and linen permanently with most dyes. The insoluble compounds of dyes with mordants are called lakes. When aluminum hydroxide is to be the mordant, the fabric is immersed in a hot solution of alum, aluminum sulphate or acetate, or sodium aluminate, by which some aluminum hydroxide, formed by hydrolysis of the compounds, is taken up by the fibres of the fabric. The latter is then boiled in water containing the dye, which unites with the mordant in the fibres, to form an insoluble permanent color.

*Experiment* 29.—Dissolve 10 grams of sodium carbonate in 100 c.c. of water, heat it to boiling, and add to it, with constant stirring, a hot solution, made by dissolving 10 grams of alum in 100 c.c. of water. Wash the precipitate first by decantation, and then upon a filter, until the washings are not rendered turbid by barium chloride. Dry a portion of the precipitate at a low temperature, and use as aluminum hydroxide. Mix a small quantity of the wet precipitate with a decoction of logwood (made by boiling about 0.2 gram of logwood with 50 c.c. of water), agitate for a few minutes, and filter. Notice that the red color of the solution has entirely disappeared, or nearly so, in consequence of the combination of the aluminum hydroxide and coloring matter.

**Aluminum Sulphate, $Al_2(SO_4)_3.18H_2O = 666.69$.**—A white crystalline powder, soluble in about its weight of water, obtained by dissolving the oxide or hydroxide in sulphuric acid and evaporating the solution to dryness over a water-bath.

$$2Al(OH)_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 6H_2O.$$

It crystallizes from water in leaflets.

On the large scale the aluminum hydroxide is obtained from bauxite or cryolite, as described above. An impure sulphate is made by heating bauxite with sulphuric acid, and a nearly pure salt is obtained by heating pure clay (kaolin), with sulphuric acid, and filtering out the precipitated silicic acid.

$$H_2Al_2(SiO_4)_2 + 3H_2SO_4 = Al_2(SO_4)_3 + 2H_2SiO_3 + 2H_2O.$$

Aluminum sulphate is used as a mordant, as an ingredient in sizes for paper, for purifying sewage, and for making alums.

**Alum.**—Alum is the general name for a group of isomorphous double sulphates containing an atom each of a univalent and a trivalent metal, combined in crystallizing with 12 molecules of water. The general formula of an alum is consequently $M^{i}M^{iii}(SO_4)_2.12H_2O$. $M^{i}$ represents in this case a univalent, $M^{iii}$ a trivalent metal.

Alums known are, for instance:

Ammonium-aluminum sulphate, $NH_4Al(SO_4)_2.12H_2O$.
Potassium-chromium sulphate, $KCr(SO_4)_2.12H_2O$.
Ammonium-ferric sulphate, $NH_4Fe(SO_4)_2.12H_2O$.

The official *alum, alumen,* is the *potassium alum,* $KAl(SO_4)_2.12H_2O = 474.53$, or the *ammonium alum* $(NH_4)Al(SO_4)_2.12H_2O = 453.47$. Both are white salts crystallizing in large octahedrons, and have an acid reaction to litmus and a sweetish astringent taste. Potassium alum is soluble in 10 parts of cold and 0.3 part of boiling water. Between 20° and 90° C. ammonium alum is more soluble in water than potassium alum, but below 20° C. or above 90° C. it is less soluble than potassium alum.

Alum is manufactured on a large scale by decomposing certain kinds of clay (aluminum silicates) by sulphuric acid, when aluminum sulphate is formed, to the solution of which potassium or ammonium sulphate is added, when, on evaporation, potassium or ammonium alum crystallizes.

Deposits of a basic alum, called *alunite,* $KAl_3(OH)_6(SO_4)_2$, occur in nature. An enormous deposit of this material in very pure condition is located in the southwest corner of New Mexico. When alunite is heated and then extracted with hot water, alum is dissolved, while an insoluble residue of aluminum hydroxide and some impurity of iron hydroxide remains.

Alum crystals melt at 90° C. A solution of alum, as well as sodium phosphate, is used for fire-proofing. The crystals of alum distributed through the fabric melt when heated and prevent access of oxygen to the fabric. A solution of alum will dissolve a good proportion of aluminum hydroxide forming so-called neutral alum, a basic salt which is used as a mordant. It is most easily prepared by adding sodium carbonate to a solution of alum slowly while stirring until a permanent precipitate begins to form.

**Dried Alum** (*Alumen Exsiccatum*) **$KAl(SO_4)_2$ = 258.34** or **$(NH_4)Al(SO_4)_2$ = 237.28** (*Burnt Alum*).—This is alum, from which the water of crystallization has been expelled by heat. It is a white powder, dissolving very slowly in cold, but quickly in boiling, water.

**Aluminum Chloride, $AlCl_3$.**—This compound is of interest on account of being the salt from which the metal was formerly obtained. Most chlorides may be formed by dissolving the metal, its oxide, hydroxide, or carbonate in hydrochloric acid. Accordingly aluminum chloride may be obtained in solution:

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O.$$

On evaporating the solution to dryness, however, and heating the dry mass further with the view of expelling all water, decomposition takes place, hydrochloric acid escapes, and aluminum oxide is left:

$$2AlCl_3 + 3H_2O = Al_2O_3 + 6HCl.$$

Aluminum chloride, consequently, cannot be obtained in a pure state (free from water) by this process, but it may be made by exposing to the action of chlorine a heated mixture of aluminum oxide and carbon. Neither carbon nor chlorine alone causes decomposition of the aluminum oxide, but by the united efforts of these two substances decomposition is accomplished:

$$Al_2O_3 + 3C + 6Cl = 3CO + 2AlCl_3.$$

**Clay.**—Clay is the name applied to a large class of mineral substances, differing considerably in composition, but possessing in common the two characteristic features of plasticity and the predominance of aluminum silicate in combination with water. A white clay, known as *kaolin,* consists chiefly of a silicate of the composition $H_2Al_2(SiO_4)_2$.

The various kinds of clay have been formed in the course of time from such double silicates as feldspar and others, by a process which is partly of a mechanical, partly of a chemical nature, and consists chiefly in the disintegration of rocks and a removal of potassium and sodium by the chemical action of carbonic acid, water, and other agents

The various kinds of clay are used in the manufacture of *bricks, earthenware, stoneware, porcelain,* etc. The process of burning these substances accomplishes the hardening by expelling water which is present in the clay. Pure clay is white; the red color of the common varieties is due to the presence of ferric oxide. For china or porcelain, clay is used containing silicates of the alkalies which, in burning, melt, causing the production of a more homogeneous mass, while in common earthenware the pores, produced by expelling the moisture, remain unfilled.

**Glass.**—Glass is similar in composition to the better varieties of porcelain. All varieties of glass are mixtures of fusible, insoluble silicates, made by fusing silicic acid (white sand) with different metallic oxides or carbonates, the silicic acid combining chemically with the metals. Sodium and calcium are the chief metals in common glass, though potassium, lead, and others also are frequently used. Color is imparted to the glass by the addition of certain metallic oxides, which have a coloring effect, as, for instance, manganese violet, cobalt blue, chromium green, etc.

**Cement** or **Hydraulic Mortar** is the name given to a finely powdered mineral, consisting chiefly of basic silicates of lime and alumina, and having the power of forming an insoluble solid mass when mixed with water. Some native limestones, containing also magnesium carbonate and aluminum silicate, furnish cement after being heated to expel water and carbon dioxide. Other cements are made by burning mixtures of limestone and clay of a suitable composition. The slag of iron furnaces also furnishes the material for cement.

**Ultramarine** is a beautiful blue substance, found in nature as the mineral "*lapis lazuli*," which was highly valued by artists as a color before the discovery of the artificial process for manufacturing it.

Ultramarine is now manufactured on a very large scale by heating a mixture of clay, sodium sulphate and carbonate, sulphur, and charcoal in large crucibles, when decomposition takes place and the beautiful blue compound is obtained. As neither of the substances used in the manufacture has a tendency to form colored compounds, the formation of this blue ultramarine is rather surprising, and the true chemical constitution of it is yet unknown.

Ultramarine is insoluble in water and is decomposed by acids with liberation of hydrogen sulphide, which shows the presence of sodium sulphide. A green ultramarine is now also manufactured. The approximate formula of the blue compound is $Na_2S_2.4NaAlSiO_4$.

### Tests for Aluminum.

(Use about a 5 per cent. solution of alum or aluminum sulphate.)

1. To the solution add solution of potassium or sodium hydroxide: a faintly bluish-white gelatinous precipitate of aluminum hydroxide, $Al(OH)_3$, is produced. The physical appearance of the precipitate is characteristic. It is soluble in excess of the alkali, forming an aluminate, thus:

$$Al(OH)_3 + 3NaOH = Al(ONa)_3 + 3H_2O.$$

This shows that $Al(OH)_3$ has weak acid character toward strong alkalies. It is reprecipitated on adding ammonium chloride and heating.

Aluminum hydroxide is soluble in acids, even acetic acid.

2. To the solution add ammonia water: the same precipitate as above is obtained, but it is insoluble in an excess of the reagent (difference from zinc) and also in ammonium chloride solution (difference from magnesium).

3. A solution of a carbonate produces the same precipitate as above, with liberation of carbon dioxide, not very noticeable in dilute solutions (see explanation in text).

4. Solution of ammonium sulphide produces the same precipitate, with generation of hydrogen sulphide:

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = 2Al(OH)_3 + 3(NH_4)_2SO_4 + 3H_2S.$$

5. Solution of sodium phosphate produces a white precipitate of aluminum phosphate, $AlPO_4.4H_2O$, soluble in mineral acids, but not acetic, and in fixed alkalies (difference from iron).

6. Heat a dry aluminum salt on charcoal strongly with the blowpipe flame. The residue is aluminum oxide, which, when moistened with solution of cobalt nitrate and again heated, gives a blue compound, cobalt aluminate.

Test 1 combined with tests 5 and 6 are conclusive evidence of the presence of aluminum. The salts are white, have a sweetish, astringent taste, are acid to litmus, and are decomposed by heat, leaving a residue of oxide.

**Cerium, Ce = 140.25.** This element occurs in nature sparingly in a few rare minerals, chiefly as silicate in *cerite*. In its general deportment cerium resembles aluminum. Cerous solutions give with ether ammonium sulphide or ammonium and sodium hydroxide, a white precipitate of cerous hydroxide, $Ce_2(OH)_6$. Ammonium oxalate forms a white precipitate of *cerium oxalate, cerii oxalas*, $Ce_2(C_2O_4)_3 10H_2O$, which is the only official cerium preparation. Cerium oxalate is a white, granular powder, insoluble in water and alcohol, but soluble in hydrochloric acid. Exposed to a red heat it is decomposed and converted into reddish-yellow ceric oxide. If this oxide, or the residue obtained by heating any cerium salt to red heat, is dissolved in concentrated sulphuric acid, and a crystal of strychnine added, a deep blue color appears, which changes first to purple and then to red. The official cerium oxalate contains also a small quantity of the oxalates of didymium, lanthanum, and other associated elements.

**Monazite sand,** found in North Carolina and elsewhere contains, besides cerite, the silicates or oxides or phosphates of other earth metals, especially of *zirconium, erbium,* and *thorium.* It is chiefly the oxide of thorium which is used in the mantle of the Welsbach incandescent burner, on account of the bright white light which this oxide emits at a comparatively low temperature.

## Summary of Analytical Characters of the Earth Metals and Chromium.

| | *Aluminum,* | *Cerium.* | *Chromium.* |
|---|---|---|---|
| Ammonium sulphide . | White precipitate. | White precipitate. | Green precipitate. |
| Potassium hydroxide . | White precipitate. Soluble in KOH Not re-precipitated by boiling. | White precipitate. Insoluble in KOH | Green precipitate. Soluble in KOH. Re-precipitated by boiling. |
| Ammonia water. . . | White precipitate. | White precipitate. | Green precipitate. |
| Ammonium carbonate | White precipitate. | White precipitate. | Green precipitate. |

Questions.—Mention some varieties of crystallized aluminum oxide found in nature and some silicates containing it. Give the general formula of an alum, and mention some alums. Which alums are official, how are they made, what are their properties, and what are they used for? What is dried alum, and how does it differ from common alum? How is aluminum chloride made? How is aluminum obtained? State the properties of aluminum. What change takes place when ammonium hydroxide, and what change when sodium carbonate is added to a solution of alum? What is the composition of earthenware, porcelain, and glass; how and from what materials are they manufactured? What is ultramarine? Give tests for aluminum compounds.

## 27. IRON, COBALT, AND NICKEL.

**General Remarks Regarding the Metals of the Iron Group.**—The six metals (Fe, Co, Ni, Mn, Cr, Zn) belonging to this group are distinguished by forming sulphides (chromium excepted) which are insoluble in water, but soluble in dilute mineral acids; they are, consequently, not precipitated from their neutral or acid solutions by hydrogen sulphide, but by ammonium sulphide as sulphides (chromium as hydroxide); their oxides, hydroxides, carbonates, phosphates, and sulphides are insoluble; their chlorides, iodides, bromides, sulphates, and nitrates are soluble in water.

With the exception of zinc, these metals are magnetic; they decompose water at a red heat, the oxide being formed and hydrogen liberated; in dilute hydrochloric or sulphuric acid they dissolve with formation of chlorides or sulphates respectively, and liberation of hydrogen.

Zinc is constantly bivalent, nickel is usually bivalent, but trivalent in a few compounds, cobalt is bi- and trivalent, iron and chromium are bi-, tri-, and sexivalent, manganese is bi-, tri-, sexi-, and septivalent. All the metals, except zinc, form several oxides, the higher ones of which have acid character, as iron trioxide, chromium trioxide, manganese trioxide and heptoxide.

Iron, cobalt and nickel are very similar in properties and fall in group VIII of the periodic table of elements.

### Iron (Ferrum).

$Fe^{ii}$ or $^{iii}$ = 55.84.

**Occurrence in Nature.**—Among all the heavy metals, iron is both the most useful and the most widely and abundantly diffused in nature. It is found, though usually in but small quantities, in nearly all forms of rock, clay, sand, and earth; its presence in these being indicated generally by their color (red, reddish-brown, or yellowish-red), as iron is the most common of all natural, inorganic coloring agents. It is found also, though in small quantities, in plants, and in somewhat larger proportions in the animal system, chiefly in the blood. In the metallic state iron is scarcely ever found, except in the meteorites or metallic masses which fall occasionally upon our earth out of space.

The chief compounds of iron found in nature are:

| | |
|---|---|
| Hematite, ferric oxide, | $Fe_2O_3$. |
| Magnetic iron ore, ferrous-ferric oxide, | $FeO.Fe_2O_3$. |
| Spathic iron ore, ferrous carbonate, | $FeCO_3$. |
| Iron pyrite, disulphide of iron, | $FeS_2$. |

The carbonate and sulphate are found sometimes in spring-waters which, when containing considerable quantities of iron, are called

chalybeate waters. Finally, iron is a constituent of some organic substances which are of importance in the animal system.

**Manufacture of Iron.**—There is no other metal manufactured in such immense quantities as iron, the use of which in thousands of different tools, machines, and appliances is highly characteristic of our present age. Iron is manufactured from the above-named oxides or the carbonate by heating them with coke and limestone in large blast furnaces, which have a somewhat cylindrical shape, and are constantly fed from above with a mixture of the substances named, while hot air is forced into the furnace through suitable apertures near its hearth. The main chemical change which takes place in the upper and less heated part of the furnace is a deoxidation of the iron oxide by the carbon monoxide resulting from the excess of carbon.

$$Fe_2O_3 + 3CO = 3CO_2 + 2Fe.$$

The heat necessary for this decomposition and fusion of the reduced iron is produced by the combustion of the fuel, maintained by the oxygen of the air blown into the furnace. At the same time the lime and other bases combine with the silica contained in the ore, forming a fusible glass, called *cinder* or *slag*. The iron and slag collect at the bottom of the furnace, where they separate by gravity, and are run off every few hours.

Iron thus obtained is known as *cast-iron*, or *pig-iron*, and is not pure, but always contains, besides silicon (also sulphur, phosphorus, and various metals), a quantity of carbon varying from 2 to 5 per cent. It is the quantity of this carbon and its condition which imparts to the different kinds of iron different properties. *Steel* contains from 0.16 to 2 per cent., *wrought-* or *bar-iron* but very small quantities of carbon. Wrought-iron is made from cast-iron by the process known as puddling, which is a burning-out of the carbon by oxidation, accomplished by agitating the molten mass in the presence of an oxidizing flame. Steel is made either from cast-iron by partially removing the carbon, or from wrought-iron by recombining it with carbon—*i. e.*, by agitating together molten wrought- and cast-iron in proper proportions.

**Properties.** The high position which iron occupies among the useful metals is due to a combination of valuable properties not found in any other metal. Although possessing nearly twice as great a tenacity or strength as any of the other metals commonly used in the metallic state, it is yet one of the lightest, its specific gravity being about 7.7. Though being when cold the least yielding or malleable of the metals in common use, its ductility when heated is such that it admits of being rolled into the thinnest sheets and drawn into the finest wire, the strength of which is so great that a wire of one-tenth of an inch in diameter is capable of sustaining 700 pounds. Finally, iron is, with the exception of platinum, the least fusible of all the useful metals.

For certain articles, such as armor plate, rock breakers, lathe tools, etc., steel is hardened by alloying it with small quantities of certain other metals, chiefly with chromium, nickel, or manganese.

Iron is little affected by dry air, but is readily acted upon by moist air, when ferric oxide and ferric hydroxide (rust) are formed.

**Hardening and Tempering Steel.**—Steel contains carbon both in the elementary state as graphite, and chemically combined as iron carbide. Within certain limits the tenacity of the metal, and its hardness after having been heated and suddenly cooled, bear a direct ratio to the amount of combined carbon. The more of the latter is present the harder is the steel and *vice versâ*.

If steel be heated to redness and suddenly chilled it has attained its maximum hardness; if, however, it be permitted to cool slowly after heating, it becomes soft. Any degree of hardness between these extremes can be obtained by the process known as tempering or "letting down." It consists in carefully reheating the previously hardened metal to a certain temperature and then plunging it into cold water. To the experienced worker the required temperature is indicated by a series of colors appearing successively on the surface of the steel. These colors are due to a gradually thickening film of iron oxides while the iron softens. The colors pass successively from pale yellow through several shades of darker yellow to brown, purple, blue, and bluish black. The highest temperature gives the least hardness and *vice versâ*.

In hardening steel, prior to tempering, care should be taken not to injure the metal by overheating, which causes oxidation of the carbon and blisters the metallic surface, rendering a fine temper impossible. In tempering small instruments a coating of some material, such as soap, is necessary to prevent oxidation as far as possible.

Elasticity and tenacity desired for specific purposes, as in the case of springs, is imparted to steel by hammering. This causes a condensation of the particles and the conversion of the crystalline structure to a fibrous condition, in which state steel is more elastic, tougher, and of greater tensile strength.

Iron forms two series of compounds, distinguished as ferrous and ferric compounds; in the former, iron is bivalent, in the latter, apparently trivalent. Almost all ferrous compounds show a tendency to pass into ferric compounds when exposed to the air, or more readily when treated with oxidizing agents, such as nitric acid, chlorine, etc. As the reaction of iron in ferrous and ferric compounds differs considerably, they must be studied separately. Ferrous oxide and hydroxide are more strongly basic than ferric oxide and hydroxide.

**Reduced Iron** (*Ferrum Reductum*).—This is metallic iron, obtained as a very fine, grayish-black, lustreless powder by passing hydrogen gas (purified and dried by passing it through sulphuric acid) over ferric oxide, heated in a glass tube:

$$Fe_2O_3 + 6H = 3H_2O + 2Fe.$$

The official article should have at least 90 per cent. of metallic iron.

**Ferrous Oxide, FeO** (*Monoxide or Suboxide of Iron*).—This compound is little known in the separate state, as it has (like most ferrous compounds) a great tendency to absorb oxygen from the air. The *ferrous hydroxide*, $Fe(OH)_2$, may be obtained by the addition of any alkaline hydroxide to the solution of any ferrous salt, when a white

precipitate is produced which rapidly turns bluish-green, dark gray, black, and finally brown, in consequence of absorption of oxygen (see Plate I, 2):

$$FeSO_4 + 2NH_4OH = (NH_4)_2SO_4 + Fe(OH)_2;$$
$$2Fe(OH)_2 + O + H_2O = 2Fe(OH)_3.$$

The precipitation of ferrous hydroxide is not complete, some iron always remaining in solution.

Ferrous oxide is a strong base, uniting with acids to form salts, which have usually a pale green color.

**Ferric Oxide, $Fe_2O_3$.**—A reddish-brown powder, which may be obtained by heating ferric hydroxide to expel water:

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O.$$

It is a feeble base; its salts show usually a brown color.

In the preparation of fuming sulphuric acid (which see) by heating ferrous sulphate there is left a residue of ferric oxide, known as *rouge*, which is used as a red pigment and as a polishing powder.

$$4FeSO_4 + H_2O = 2Fe_2O_3 + H_2SO_4.SO_3 + 2SO_2.$$

A specially fine variety of rouge for polishing is manufactured by heating ferrous oxalate, $FeC_2O_4$, in contact with the air.

**Ferric Hydroxide, $Fe(OH)_3$ = 106.86.**—Ferric hydroxide is obtained by precipitation of ferric sulphate or ferric chloride by ammonium or sodium hydroxide (see Plate I, 3):

$$Fe_2(SO_4)_3 + 6NH_4OH = 3(NH_4)_2SO_4 + 2Fe(OH)_3.$$

Precipitation is complete, no iron remaining in solution as in the case of ferrous salts.

Ferric hydroxide is a reddish-brown powder, sometimes used as an antidote in arsenic poisoning; for this purpose it is not used in the dry state, but after having been freshly precipitated and washed, it is mixed with water, and this mixture used.

*Ferric hydroxide with magnesium oxide*, U. S. P., is a mixture freshly made, when called for, by adding magnesia to a solution of ferric sulphate, when magnesium sulphate and ferric hydroxide are formed; the two substances are not separated from each other, the mixture being intended for immediate administration as an antidote in cases of arsenic poisoning.

**Ferrous-ferric Oxide, $FeO.Fe_2O_3$** (*Magnetic Oxide*).—This compound, which shows strong magnetic properties, has been mentioned above as one of the iron ores, and is known as *lodestone*. It has a metallic lustre and iron-black color, and is produced artificially by the combustion of iron in oxygen, or in the hydrated state by the addition of ammonium hydroxide to a mixture of solutions of ferrous and ferric salts.

precipitate is produced which rapidly turns bluish-green, dark gray, black, and finally brown, in consequence of absorption of oxygen (see Plate I, 2):

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$$2Fe(OH)_2 + O + H_2O = 2Fe(OH)_3.$$

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Ferrous oxide is a strong base, uniting with acids to form salts, which have usually a pale green color.

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It is a feeble base; its salts show usually a brown color.

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Precipitation is complete, no iron remaining in solution as in the case of ferrous salts.

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**Iron Trioxide, $FeO_3$.**—Not known in a separate state, but in combination with alkalies. In these compounds, called *ferrates*, $FeO_3$ acts as an acid oxide, analogous to chromium trioxide, $CrO_3$, in chromates. The composition of potassium ferrate is $K_2FeO_4$.

**Ferrous Chloride, $FeCl_2.4H_2O$** (*Protochloride of Iron*).—Ferrous chloride is obtained as pale green crystals, by dissolving iron in hydrochloric acid:

$$Fe + 2HCl = FeCl_2 + 2H.$$

The anhydrous salt cannot be obtained by driving out the water from the crystals by heating, as decomposition takes place with loss of hydrochloric acid; but it may be made by heating iron in a current of dry hydrochloric acid gas, whereby colorless crystals sublime into the cooler parts of the apparatus. The solution and salt absorb oxygen very readily:

$$3FeCl_2 + O = FeO + 2FeCl_3.$$

**Ferric Chloride** (*Ferri Chloridum*) **$FeCl_3.6H_2O$ = 270.31** (*Chloride, Sesquichloride, or Perchloride of Iron*).—Ferric chloride is obtained by adding to the solution of ferrous chloride (obtained as mentioned above) hydrochloric and nitric acids in sufficient quantities, and applying heat until complete oxidation has taken place. The nitric acid oxidizes the hydrogen of the hydrochloric acid to water, while the chlorine combines with the ferrous chloride, nitrogen dioxide being formed also:

$$3FeCl_2 + HNO_3 + 3HCl = 3FeCl_3 + 2H_2O + NO.$$

By sufficient evaporation of the solution, ferric chloride is obtained as a crystalline mass of an orange-yellow color; it is very deliquescent, has an acid reaction, and a strongly styptic taste. The water of crystallization cannot be expelled by heat, because heat decomposes the salt, free hydrochloric acid and ferric oxide being formed. The anhydrous salt sublimes as dark scales when chlorine is passed over heated iron. In solution ferric chloride, like ferric salts in general, can be reduced to ferrous salt by heating with metallic iron, or by long contact with the same in the cold, thus:

$$2FeCl_3 + Fe = 3FeCl_2.$$

The same result is produced by hydrogen sulphide and by stannous chloride,

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$
$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

*Experiment* 30.—Dissolve by the aid of heat 1 gram of fine iron wire in about 4 c.c. of hydrochloric acid, previously diluted with 2 c.c. of water. Filter the warm solution of ferrous chloride, mix it with 2 c.c. of hydrochloric acid, and add to it slowly and gradually about 0.6 c.c. of nitric acid. Evaporate in a fume chamber as long as red vapors escape; then test a few drops with potassium ferricyanide, which should not give a blue precipitate; if it does, the solution

has to be heated with a little more nitric acid until the conversion into ferric chloride is complete and the potassium ferricyanide produces no precipitate. Ferric chloride thus obtained may be mixed with 4 c.c. of hot water and set aside, when it forms a solid mass of $FeCl_3.6H_2O$. How much $FeCl_3$, how much $FeCl_3$, and how much $FeCl_3.6H_2O$ can be obtained from 1 gram of iron?

**Solution of Ferric Chloride** (*Liquor Ferri Chloridi*).—This is a solution in water, containing 29 per cent. of the anhydrous ferric chloride. It is a reddish-brown liquid of specific gravity 1.315, having the taste and reaction of the dry salt. This solution, mixed with alcohol in the proportion of 35 to 65 parts by volume, and left standing in a closed vessel for at least three months, forms the *tincture of ferric chloride, Tinctura ferri chloridi.* By the action of the alcohol some ferric chloride is reduced to the ferrous state, while at the same time a number of other compounds are formed, imparting to the liquid an ethereal odor.

Solutions of ferric salts usually have a brown color and show an acid reaction. This is due to the partial hydrolysis of the salts, forming ferric hydroxide and free acid. Addition of acid, by preventing hydrolysis, renders the solutions colorless or nearly so. Hydrolysis is increased by heating the solutions, hence hot ferric solutions have a deeper color than cold ones.

Ferrous salts are much less hydrolyzed than ferric salts, as ferrous iron is a stronger base than ferric iron. They also are not as acid to litmus as the ferric salts.

**Dialyzed iron** is an aqueous solution of about 5 per cent. of ferric hydroxide with some ferric chloride. It is made by slowly adding ammonium hydroxide to a solution of ferric chloride as long as the precipitate of ferric hydroxide formed is redissolved in the ferric chloride solution, on shaking violently. The clear solution thus obtained is placed in a dialyzer floating in water which latter is renewed every day until it shows no reaction with silver nitrate. The ammonium chloride passes through the membrane of the dialyzer into the water, while all iron, as hydroxide with some chloride, is left in solution.

The combination of an oxide or hydroxide with a normal salt is called usually a basic salt or oxy-salt; dialyzed iron is a highly basic oxychloride of iron.

**Ferrous iodide, $FeI_2$, and Ferrous bromide, $FeBr_2$,** may both be obtained by the action of iodine and bromine, respectively, on iron filings, when combination takes place. Both salts are unstable, absorbing oxygen from the air very readily.

*Experiment* 31.—Cover some fine iron wire with water, heat gently, and add iodine in fragments as long as the red color of iodine disappears. Notice that the iron is dissolved gradually, the result of the reaction being the formation of a pale green solution of ferrous iodide.

Ferrous iodide does not unite with iodine to form ferric iodide, because the latter undergoes hydrolysis in solution with formation of hydriodic acid, which, being a good reducing agent, reduces the ferric iodide to ferrous iodide.

**Ferrous Sulphide, FeS.**—Easily obtained as a black, brittle mass by heating iron filings with sulphur, when the elements combine. It is used chiefly for liberating hydrogen sulphide, by the addition of sulphuric acid. Iron combines with sulphur in several proportions; some of these iron sulphides are found in nature.

**Ferrous Sulphate** (*Ferri Sulphas*), $FeSO_4.7H_2O$ = **278.02** (*Sulphate of Iron, Green Vitriol, Copperas*).—Obtained by dissolving iron in dilute sulphuric acid, evaporating, and crystallizing:

$$Fe + H_2SO_4 = 2H + FeSO_4.$$

Also obtained as a by-product in some branches of chemical industry, and by heap-roasting of the native iron sulphide:

$$FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4.$$

Ferrous sulphate crystallizes in large, bluish-green prisms; it is soluble in water, insoluble in alcohol. Exposed to the air, it loses water of crystallization and absorbs oxygen.

The *exsiccated ferrous sulphate*, U. S. P., is made by expelling nearly all the water of crystallization by heating to 100° C. (212° F.); the *granulated* (*precipitated*) *ferrous sulphate* is made by quickly cooling a hot saturated solution of ferrous sulphate, slightly acidulated with sulphuric acid, while stirring, when ferrous sulphate separates as a crystalline powder, which is filtered, washed with alcohol, and dried.

*Experiment* 32. In a flask put 10 c c. of concentrated sulphuric acid diluted with 40 c.c. of water, add iron wire, card teeth, or nails, in portions, until the acid is exhausted, as seen by the cessation of effervescence. Gently heating facilitates the action at the end. Note the bad odor of the hydrogen, due to impurities, and the dark flakes of carbon in the solution. Finally, filter the hot solution and set it aside to crystallize. If crystals do not form, evaporate further.

Ferrous sulphate readily forms double salts with alkali sulphates, which are not efflorescent, and in the dry state are less readily oxidized than ferrous sulphate. When a hot, strong solution of 1 part of ammonium sulphate is added to a similar solution of 2 parts of crystals of ferrous sulphate, on cooling, a salt with the composition, $(NH_4)_2SO_4.FeSO_4.6H_2O$, separates (Mohr's salt). This is often used when a stable ferrous salt is wanted.

**Ferric Sulphate,** $Fe_2(SO_4)_3$.—The solution of this salt, *Liquor ferri tersulphatis*, is made by adding sulphuric and nitric acids to a solution of ferrous sulphate and heating:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

The action of nitric acid is similar to that described above under Ferric Chloride. The hydrogen of the sulphuric acid is oxidized, and the radical $SO_4$ unites with the ferrous sulphate, nitric oxide being liberated.

*Experiment* 33.—Dissolve several crystals of ferrous sulphate in about 20 c.c. of water, add about 5 c.c. of dilute sulphuric acid. Warm the solution and add concentrated nitric acid, in drops, until the dark color first produced suddenly turns to reddish-brown. Note the red fumes of oxide of nitrogen escaping. The dark color is due to the union of nitric oxide, NO (see reaction above), with unoxidized ferrous sulphate (see test 2 for nitric acid). Heat the solution

to expel oxide of nitrogen and excess of nitric acid. Dilute a few drops and test with ferricyanide, as in Experiment 30.

Solution of ferric sulphate is used in the preparation of *Ferric ammonium sulphate*, $FeNH_4(SO_4)_2.12H_2O$ (*iron alum* or *ammonio-ferric alum*), which is made by mixing a solution of ferric sulphate with ammonium sulphate and crystallizing. The salt has a pale violet color and is readily soluble in water.

**Solution of Ferric Subsulphate** (*Liquor Ferri Subsulphatis*) (*Monsel's Solution*).—This is a solution similar to the preceding, but contains less sulphuric acid, and is therefore looked upon as a basic ferric sulphate, of the doubtful composition $5Fe_2(SO_4)_3.2Fe(OH)_3$.

**Ferrous Carbonate, $FeCO_3$.**—Occurs in nature; may be obtained by mixing solutions of ferrous sulphate and sodium carbonate or bicarbonate:

$$FeSO_4 + 2NaHCO_3 = Na_2SO_4 + FeCO_3 + CO_2 + H_2O.$$

The precipitate is first nearly white, but soon assumes a gray color from oxidation. The *saccharated ferrous carbonate*, U. S. P., is made by mixing the washed precipitate with sugar, and drying. The sugar prevents, to some extent, rapid oxidation. The preparation contains 15 per cent. of ferrous carbonate.

*Ferric carbonate* does not exist, the affinity between the feeble ferric oxide and the weak carbonic acid not being sufficient to unite them chemically.

**Ferrous Phosphate, $Fe_3(PO_4)_2$.**—When sodium phosphate is added to solution of ferrous sulphate, a precipitate of the composition $FeHPO_4$ is formed:

$$Na_2HPO_4 + FeSO_4 = FeHPO_4 + Na_2SO_4.$$

If, however, sodium acetate is added, a precipitate of the composition $Fe_3(PO_4)_2$ is formed:

$$3FeSO_4 + 2Na_2HPO_4 = Fe_3(PO_4)_2 + 2Na_2SO_4 + H_2SO_4.$$

The sulphuric acid liberated, as shown in this formula decomposes the sodium acetate, forming sodium sulphate and free acetic acid. Ferrous phosphate is a slate-colored powder, absorbing oxygen readily, becoming darker in color.

**Ferric Phosphate, $FePO_4$.**—Ferric phosphate may be obtained from ferric chloride solution by precipitation with an alkali phosphate. The *ferric phosphate* of the U. S. P. is a scale compound. (See Index.)

**Ferric Hypophosphite, $Fe(H_2PO_2)_3$ = 251.01** (*Hypophosphite of Iron*).—It is obtained by adding a solution of sodium hypophosphite to a solution of ferric chloride or sulphate, free from excess of acid. The precipitate is filtered, washed, and dried. It is a grayish-white powder, slightly soluble in water, soluble in hydrochloric acid, in hypophosphorous acid, and in a warm, concentrated solution of an alkali citrate.

## Tests for iron.

| | *Ferrous salts.* (Use $FeSO_4$) | *Ferric salts.* (Use $FeCl_3$.) |
|---|---|---|
| 1. Ammonium sulphide. | Black precipitate of ferrous sulphide (Plate I., 1). $FeSO_4 + (NH_4)_2S = (NH_4)_2SO_4 + FeS.$ | Black precipitate of ferrous sulphide mixed with sulphur. $2FeCl_3 + 3[(NH_4)_2S] = 6NH_4Cl + 2FeS + S.$ |
| 2. Hydrogen sulphide. | No change, except sometimes a slight black discoloration, due to the formation of a trace of FeS. | Ferric salts are converted into ferrous salts with precipitation of sulphur. $2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$ |
| 3. Ammonium, sodium, or potassium hydroxide. | White precipitate of ferrous hydroxide soon turning green, black, and brown. Precipitation not complete (Plate I., 2). $FeCl_2 + 2NaOH = 2NaCl + Fe(OH)_2.$ | Reddish-brown precipitate of ferric hydroxide. Precipitation is complete (Plate I., 3). $FeCl_3 + 3(NH_4OH) = 3NH_4Cl + Fe(OH)_3.$ |
| 4. Ammonium, sodium, or potassium carbonate | White precipitate of ferrous carbonate, soon turning darker. $FeCl_2 + Na_2CO_3 = 2NaCl + FeCO_3.$ | Reddish-brown precipitate of ferric hydroxide, with liberation of carbon dioxide (Plate I., 3). $2FeCl_3 + 3Na_2CO_3 + 3H_2O = 6NaCl + 2Fe(OH)_3 + 3CO_2.$ |
| 5. Alkali phosphates or arsenates | Almost white precipitate, soon turning darker. | A yellowish-white precipitate is produced. |
| 6. Potassium ferrocyanide. $K_4Fe(CN)_6$. | Almost white precipitate, $K_2Fe[Fe(CN)_6]$, soon turning blue by absorption of oxygen (Plate I., 4). | Dark-blue precipitate of ferric ferrocyanide, or Prussian blue. Decomposed by alkalies; insoluble in acids (Plate I., 5). $4FeCl_3 + 3[K_4Fe(CN)_6] = 12KCl + Fe_43[Fe(CN)_6].$ |
| 7. Potassium ferricyanide. $K_6Fe_2(CN)_{12}$. | Blue precipitate of ferrous ferricyanide, or Turnbull's blue. $3FeCl_2 + K_6Fe_2(CN)_{12} = 6KCl + Fe_3Fe_2(CN)_{12}$ | No precipitate is produced, but the liquid is darkened to a greenish-brown hue. |
| 8. Tannic acid. | No change, provided oxidation of the ferrous salt has not taken place. | A dark greenish-black precipitate of ferric tannate is produced. |
| 9 Potassium sulphocyanate. KCNS. | As above. | Deep blood-red solution of ferric sulphocyanate, $Fe(CNS)_3$ (Plate I., 6). |

**Remarks to Tests.**—In test 1 iron in the ferric state is too weakly basic to form ferric sulphide, but in the ferrous state it is a stronger base, so that the ferric sulphide breaks down at the moment of formation to ferrous sulphide and sulphur. If ferrous iron were as weakly basic as aluminum and chromium, no precipitate of sulphide would be obtained.

In test 2 no precipitate is formed, because of the acid that would be set free by the reaction. Ferric salts are easily reduced to ferrous salts, and *vice versa*. $H_2S$ is a good reducing agent, and, when acting as such, always gives a precipitate of milk of sulphur, which easily passes through filter-paper and causes annoyance in the course of qualitative analysis.

In test 4 the weak basic character of ferric iron and the resemblance to aluminum and chromium is again shown.

Tests 6, 7, 8, and 9 are not only delicate and decisive, but permit iron in either state to be detected in the presence of the other. Test 9 is the most delicate of all tests for iron. It gives positive results in dilutions in which the other tests fail.

Ferrous compounds form the divalent ion $Fe^{\cdot\cdot}$, which is pale-green, and ferric compounds form the trivalent ion $Fe^{\cdot\cdot\cdot}$, which is nearly colorless. The ionic reactions for the tests for iron are of the same form as those given under the tests for calcium. In test 2, the reduction of ferric to ferrous salt by $H_2S$ is expressed by the ionic equation:

$$2Fe^{\cdot\cdot\cdot} + 6Cl' + 2H^{\cdot} + S'' = 2Fe^{\cdot\cdot} + 2H^{\cdot} + 6Cl' + S.$$

Each of the iron ions loses a charge of electricity and the sulphur ion loses its two charges, which mutually neutralize each other, and elementary sulphur is precipitated. The reduction with ammonium sulphide is represented by a similar equation.

The formation of ferric from ferrous chloride is expressed thus:

$$Fe^{\cdot\cdot} + 2Cl' + Cl = Fe^{\cdot\cdot\cdot} + 3Cl'.$$

The iron ion assumes another positive charge, becoming trivalent ion, and the chlorine atom assumes a negative charge, becoming chlorine ion. A similar equation holds in the case of the sulphate.

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QUESTIONS—Which metals belong to the "iron group," and what are their general properties? How is iron found in nature, and what compounds are used in its manufacture? Describe the process for manufacturing iron on a large scale, and state the difference between cast-iron, wrought-iron, steel, and reduced iron. State the composition and mode of preparation of ferrous and ferric hydroxides. What are their properties? Describe in words and chemical symbols the process for making ferric chloride. What is tincture of chloride of iron? How are ferrous iodide and bromide made? State the properties of ferrous sulphate. Under what other names is it known, and how is it made? What change takes place when soluble carbonates are added to soluble ferrous and ferric salts? Mention agents by which ferrous compounds may be converted into ferric compounds, and these into ferrous compounds. Explain the chemical changes taking place. Mention tests for ferrous and ferric compounds.

### Cobalt and Nickel, Co = 58.97, Ni = 58.68.

These two metals show much resemblance to each other in their chemical and physical properties, and occur in nature often associated with each other as sulphides or arsenides.

Both metals are nearly silver-white; the salts of cobalt show generally a red, those of nickel a green color. The solutions of both metals give a black precipitate of the respective sulphides on the addition of ammonium sulphide. Ammonium hydroxide produces in solutions of cobalt a blue, in solutions of nickel a green precipitate of the hydroxides, both of which are soluble in an excess of the reagent; potassium or sodium hydroxide produces similar precipitates, which are insoluble in an excess. Sodium carbonate produces in solutions of cobalt a violet, and in solutions of nickel a green precipitate of the respective carbonates. (Plate I., 7 and 8.)

Cobalt is used chiefly when in a state of combination (for coloring glass blue); nickel when in the metallic state. (German silver is an alloy of nickel, copper, and zinc.)

## 28. MANGANESE. CHROMIUM. URANIUM.

### Manganese, Mn = 54.93.

The principal ore is the dioxide (black oxide of manganese, pyrolusite), $MnO_2$, which is always accompanied by iron compounds. Other forms occurring in nature are braunite, $Mn_2O_3$, hausmannite, $Mn_3O_4$, and manganese spar, $MnCO_3$. In small quantities it is a constituent of many minerals.

*Metallic manganese* resembles iron in its physical and chemical properties, and may be obtained by reducing the carbonate with charcoal. Manganese is darker in color than iron, considerably harder, and somewhat more easily oxidized. Alloys of iron and manganese (20 to 80 per cent.), known as ferro-manganese, are used in the arts.

**Oxides of Manganese.**—Six oxides are known. $MnO_3$ and $Mn_2O_7$ have been obtained in the free state, but they are very unstable, and are known best through their compounds:

| | |
|---|---|
| Manganous oxide (monoxide or protoxide), | $MnO$. |
| Manganous manganic oxide, | $MnOMn_2O_3 = Mn_3O_4$. |
| Manganic oxide (sesquioxide), | $Mn_2O_3$. |
| Manganese dioxide (binoxide, peroxide, black oxide), | $MnO_2$. |
| Manganese trioxide, | $MnO_3$. |
| Manganese heptoxide, | $Mn_2O_7$. |

The chemical behavior of these oxides varies with the degree of oxidation, or, in other words, with the valence of the manganese. $MnO$ is strongly basic; $Mn_2O_3$ is weakly basic; $MnO_2$ has feebly acidic character; $MnO_3$ is more strongly acidic, being the anhydride of manganic acid, $H_2MnO_4$, which is known only in its salts; $Mn_2O_7$ is the anhydride of permanganic acid, which is known in aqueous solution, and has strong acid character.

The only stable salts of manganese are the manganous salts, derived from manganous oxide, MnO, in which the valence of manganese is 2. When any

oxide of manganese (or compounds of those oxides which are unstable in the free state) is heated with an acid, a manganous salt is obtained. In this action the oxides higher than MnO give off oxygen, or oxidize the excess of acid (see action of hydrochloric acid on $MnO_2$). The decomposition of potassium permanganate, which has been used hitherto as an oxidizer, may now be explained. In dilute sulphuric acid solution permanganic acid is liberated thus:

$$2KMnO_4 + H_2SO_4 = K_2SO_4 + 2HMnO_4.$$

The acid is stable enough when nothing else is present that can be oxidized, but if such a substance is added the permanganic acid breaks down to manganous oxide and oxygen:

$$2HMnO_4 = H_2O + Mn_2O_7,$$
$$Mn_2O_7 = 5O + 2MnO,$$
$$2MnO + 2H_2SO_4 = 2MnSO_4 + 2H_2O.$$

The manganous oxide is dissolved by the acid to form the colorless manganous sulphate, $MnSO_4$. The oxygen does not escape, but goes to the reducing compound. Conversely, when oxygen is forcibly added to any of the lower oxides in the presence of alkalies, the $MnO_3$ state of oxidation is attained, that is, salts of manganic acid, or manganates, are produced, as $K_2MnO_4$, from which the more stable permanganates are readily obtained (see below).

While manganous salts are stable and do not absorb oxygen like ferrous salts, manganous hydroxide and carbonate readily absorb oxygen and turn dark, resembling in this respect iron.

*Manganous oxide* is a greenish-gray powder obtainable by heating the carbonate; or as a nearly white hydroxide by precipitating a manganous salt by sodium hydroxide. It is a strong base, saturating acids completely, and forming salts which have generally a rose color or a pale reddish tint.

**Manganese Dioxide, $MnO_2$.**—Manganese dioxide is by far the most important compound of manganese found in nature, as it is largely used for generating chlorine and oxygen, as described in former chapters.

**Precipitated Manganese Dioxide** (*Mangani Dioxidum Præcipitatum*) **$MnO_2$ = 86.93,** is obtained by pouring a mixture of ammonia water and hydrogen peroxide into a solution of manganese sulphate, when manganese dioxide mixed with some oxide is precipitated as a heavy, black powder:

$$MnSO_4 + 2NH_4OH + H_2O_2 = (NH_4)_2SO_4 + 2H_2O + MnO_2.$$

*Experiment* 34.—Mix 10 c.c. of 5 per cent. ammonia water with 10 c.c. of 1.5 per cent. hydrogen dioxide solution, and pour slowly while stirring *into* 20 c.c of a 5 per cent. solution of manganous sulphate. Let the mixture stand for one hour, stirring frequently. Then filter and wash thoroughly with hot water, let drain, and dry. Heat some of the precipitate with hydrochloric acid in a test-tube and explain the result.

**Manganese Sulphate, $MnSO_4.4H_2O$ = 223.06.**—Manganese sulphate may be obtained by dissolving the oxide or dioxide in sulphuric acid; in the latter case oxygen is evolved:

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

As manganese dioxide generally contains iron oxide, the solution contains sulphates of both metals. By evaporating to dryness and strongly igniting, the iron salt is decomposed. The ignited mass is now lixiviated with water, and the filtered solution evaporated for crystallization.

It is an almost colorless, or pale rose-colored substance, easily soluble in water.

Various hydrates of manganous sulphate are obtainable. Above 25° C. a solution gives crystals having the composition, $MnSO_4.4H_2O$. Between 7° and 20° C. crystals of the composition $MnSO_4.5H_2O$, isomorphous with $CuSO_4.5H_2O$ are obtained. Below 6° C. the product is $MnSO_4.7H_2O$, which is isomorphous with $ZnSO_4.7H_2O$, $MgSO_4.7H_2O$, $FeSO_4.7H_2O$, etc.

**Manganese Hypophosphite, $Mn(PH_2O_2)_2.H_2O$ = 203.05.**—Manganese hypophosphite may be made by mixing a solution of 1 part of calcium hypophosphite with a solution of 1.31 parts of manganous sulphate, allowing the precipitate of calcium sulphate to settle, and evaporating the filtrate to dryness. It is a pink crystalline powder, permanent in the air, and soluble in 6.6 parts of water. Its chief use is as a constituent of compound syrup of hypophosphites.

**Potassium Permanganate** (*Potassii Permanganas*) **$KMnO_4$ = 158.03.**—Whenever a compound (any oxide or salt) of manganese is fused with alkali carbonates (or hydroxides) and alkali nitrates (or chlorates) the manganese is converted into manganic acid, which combines with the alkali, forming potassium (or sodium) manganate:

$$3MnO_2 + 3K_2CO_3 + KClO_3 = 3K_2MnO_4 + 3CO_2 + KCl.$$

The fused mass has a dark green color, and when dissolved in water gives a dark emerald-green solution, from which, by evaporation, green crystals of *potassium manganate* may be obtained.

The green solution is decomposed easily by any acid (or even by water in large quantity) into a red solution of potassium permanganate and a precipitate of manganese dioxide.

$$3K_2MnO_4 + 2H_2SO_4 = MnO_2 + 2K_2SO_4 + 2KMnO_4 + 2H_2O.$$

By evaporation and crystallization potassium permanganate is obtained in slender, prismatic crystals, of a dark purple color, and a somewhat metallic lustre. The solution in water has a deep purple, or, when highly diluted, a pink color (Plate II, 1). It is a powerful oxidizing agent, and an excellent disinfectant, both properties being due to the facility with which a portion of the oxygen is given off to any substance which has affinity for it. If the oxidation takes place in the absence of an acid, a lower oxide of manganese is formed, which separates as an insoluble substance. If an acid is present, both the potassium and manganese combine with it, forming salts, thus:

$$2(KMnO_4) + 6HCl + x = 2KCl + 2MnCl_2 + 3H_2O + xO_5.$$

$x$ represents here any substance capable of combining with oxygen while in solution.

*Experiment* 35.—Heat in an iron crucible a mixture of 2 grams manganese dioxide, 2 grams potassium hydroxide, and 1 gram potassium chlorate, until the fused mass has turned dark green. Dissolve the cooled mass with water, filter the green solution of potassium manganate, and pass carbon dioxide through it until it has assumed a purple color, showing that the conversion into permanganate is complete. Notice that the acidified solution is readily decolorized by ferrous salts and other deoxidizing agents.

**Permanganic Acid, $HMnO_4$.**—Permanganic acid can now be obtained in solution by electrolysis of potassium permanganate. It has the color of the potassium salt, is stable, and from it the permanganates of other metals may be made.

## Tests for Manganese.

(A 5 per cent. solution of manganous sulphate may be used.)

1. Ammonium sulphide produces a yellowish-pink or flesh-colored precipitate of hydrated manganous sulphide, $MnS.H_2O$, soluble in acetic and in mineral acids (Plate II, 2).

2. Ammonium (or sodium) hydroxide produces a white precipitate of manganous hydroxide, which soon darkens by absorption of oxygen (Plate II, 3) and dissolves in oxalic acid with a rose-red color. The presence of ammonium salts prevents the precipitation of manganous hydroxide by ammonia water (see test 2 for magnesium).

3. Sodium (or potassium) carbonate produces a nearly white precipitate of manganous carbonate, which oxidizes to brown manganic hydroxide.

4. Any compound of manganese heated on platinum foil with a mixture of sodium carbonate and nitrate forms a bluish-green mass, giving a green solution in water, which turns red on addition of an acid. (See explanation above.)

5. Manganese compounds fused with borax on a platinum wire give a violet color to the borax bead. Only a very small quantity of the manganese compound should be used.

6. Heat a trace of manganese compound (not the dioxide) with about 5 c.c. of dilute nitric acid and a small knife-pointful of red oxide of lead (minium) to boiling, dilute with water, and let stand to settle. A reddish-purple color of permanganic acid will be seen. This is a very delicate test.

Tests 4, 5, and 6 are the most decisive for manganese compounds. Test 2 is also characteristic. Permanganate is usually recognized by its color and action on reducing agents. Manganese salts are neutral and colorless, or light red to pink.

The most common ions of manganese are the divalent $Mn^{\cdot\cdot}$ ions of the manganous salts, and the univalent permanganate ions $MnO_4'$, which are purple (see page 154). The divalent manganate ions $MnO_4''$, which are green, exist only in neutral or alkaline solutions. In acid solutions they pass into $MnO_4'$ ions. The ionic equations in the tests above for manganous ions, $Mn^{\cdot\cdot}$, are similar to those given under the tests for calcium.

## Chromium, Cr = 52.

This element is a member of the chromium family, which includes also molybdenum, tungsten, and uranium. They fall in the seventh column of the periodic table, which also contains the sulphur, selenium, tellurium family. A feature common to the elements of the chromium family is that they form oxides of the type $MO_3$ (M = element), which, like $SO_3$, are acidic oxides, and form acids like $H_2SO_4$ in composition. Sodium chromate, $Na_2CrO_4.10H_2O$, and potassium chromate, $K_2CrO_4$, are isomorphous with sodium sulphate and potassium sulphate respectively.

Chromium is found in nature almost exclusively as ferrous chromite, $FeO.Cr_2O_3$ or $Fe(CrO_2)_2$, known as the mineral chromite or chrome-iron ore; to some extent also as lead chromate (crocoisite), $PbCrO_4$. It may be obtained by heating the oxide, $Cr_2O_3$, with carbon in an electric furnace, or more conveniently by reducing the oxide with aluminum powder (Goldschmidt's method). It is steel-gray, very hard and almost infusible, dissolves in hydrochloric acid with evolution of hydrogen, forming chromous chloride, in which respect its behavior is like that of iron. Metallic chromium is used in small proportion as an admixture to steel to which it imparts great hardness.

Chromium gives four kinds of compounds, nearly all of which are colored, which fact gave rise to the name chromium, from the Greek χρῶμα (chroma), color. Chromium trioxide, $CrO_3$, gives chromic acid, chromates and dichromates. Chromic oxide, $Cr_2O_3$, and hydroxide, $Cr(OH)_3$, are weakly basic, and also sometimes show a very weakly acid character. They give rise to the chromic salts, as chloride, sulphate, acetate, etc., but not to carbonate or sulphide in aqueous solution, in which respect the behavior is like that of aluminum. The hydroxide in some instances combines with bases to form chromites, such as sodium chromite, $NaCrO_2$. From chromous hydroxide, $Cr(OH)_2$, the chromous salts, as $CrCl_2$ and $CrSO_4$, are derived. These salts, like ferrous salts, are very easily oxidized by the air, and give precipitates of chromous carbonate and sulphide, indicating that chromium in them is more basic than in the chromic salts.

**Potassium Dichromate, $K_2Cr_2O_7$ = 294.2** (*Bichromate or Red Chromate of Potash*).—This salt and the corresponding sodium salt are by far the most important of all chromium compounds, and are the source from which they are obtained.

Potassium dichromate is manufactured on a large scale by exposing a mixture of the finely ground chrome-iron ore with potassium carbonate and calcium hydroxide to the heat of an oxidizing flame in a reverberatory furnace, when both constituents of the ore become oxidized, ferric oxide and chromic acid being formed, the latter

combining with the potassium, forming normal potassium chromate, $K_2CrO_4$.

$$2(FeOCr_2O_3) + 4K_2CO_3 + 7O = Fe_2O_3 + 4CO_2 + 4(K_2CrO_4).$$

By treating the furnaced mass with water a yellow solution of potassium chromate is obtained, which, upon the addition of sulphuric acid, is decomposed into potassium dichromate and potassium sulphate:

$$2(K_2CrO_4) + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

The two salts may be separated by crystallization. Potassium dichromate forms large, orange-red, transparent crystals, which are easily soluble in water; heated by itself oxygen is evolved, heated with hydrochloric acid chlorine is liberated, heated with organic matter or reducing agents these are oxidized.

**Sodium Dichromate, $Na_2Cr_2O_7.2H_2O$** (*Bichromate of Soda*).—Sodium dichromate is manufactured by a process analogous to that used for potassium dichromate. The crystallized compound resembles the potassium salt, but dissolves in less than its own weight of water. The crystals being deliquescent, a granulated anhydrous salt which is but slightly hygroscopic, is also manufactured, and has largely replaced the use of potassium dichromate.

**Chromium Trioxide** (*Chromii Trioxidum*) **$CrO_3$ = 100** (*Chromic Acid, Chromic Anhydride*).—Chromium trioxide is prepared by adding sulphuric acid to a saturated solution of potassium dichromate, when chromium trioxide separates in crystals:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2CrO_3.$$

Thus prepared, it forms deep purplish-red, needle-shaped crystals, which are deliquescent, and very soluble in water; it is destructive to animal and vegetable matter, and one of the strongest oxidizing agents; the solution in water has strong acid properties, but neither chromic nor dichromic acid are known in a pure state, as an aqueous solution of chromium trioxide on concentration breaks up into the oxide and water.

*Experiment* 36. Dissolve a few grams of potassium dichromate in water and add to 4 volumes of the cold saturated solution 5 volumes of strong sulphuric acid; chromium trioxide separates on cooling. Collect the crystals on asbestos, wash them with a little nitric acid, and dry them by passing warm dry air through a tube in which they have been placed for this purpose.

**Chromates and dichromates.** When chromium trioxide is dissolved in water, dichromic acid is mainly formed thus:

$$2CrO_3 + H_2O = H_2Cr_2O_7,$$

which gives the ions $2H^{\cdot}$ and $Cr_2O_7''$. The $Cr_2O_7''$ ion is yellowish red in color. There is, however, a slight amount of chromic acid formed, thus:

$$CrO_3 + H_2O = H_2CrO_4,$$

which gives the ions $2H^{\cdot}$ and $CrO_4''$. The ion $CrO_4''$ is yellow. Chromic acid is known through its salts, the chromates, which give the ion, $CrO_4''$.

Potassium and sodium chromate in solution show a basic reaction which is not due to any weak acid character of chromic acid, but to the fact that chromates have a great tendency to pass to salts of dichromic acid. They are decomposed to some extent by water, thus:

$$2K_2CrO_4 + H_2O = K_2Cr_2O_7 + 2KOH.$$

If an acid, even a weak one, is added to the solution, the decomposition becomes practically complete by the removal of the KOH by union with the acid. The color changes from yellow to red, and, upon concentration, the rather moderately soluble dichromate crystallizes out in the case of the potassium salt. Potassium dichromate is almost neutral in reaction; it is, therefore, not an acid chromate. In fact acid chromates are not known in which respect chromic acid differs from sulphuric acid. The acid salt of the composition, $KHCrO_4$, which we would expect to be formed by acidifying a solution of the chromate, changes at once into the salt of dichromic acid, thus:

$$2KHCrO_4 = K_2Cr_2O_7 + H_2O.$$

Although potassium dichromate contains no acid hydrogen, it acts essentially like an acid salt toward alkalies. When potassium hydroxide is added to the dichromate the solution turns yellow, and upon evaporation a salt of the composition, $K_2CrO_4$, is obtained. The reason for this is the fact that, although the dichromate dissociates in the main into $2K^{\cdot}$ and $Cr_2O_7''$ ions, it also dissociates to a slight extent, thus:

$$K_2Cr_2O_7 + H_2O \rightleftarrows 2K^{\cdot} + 2H^{\cdot} + 2CrO_4''.$$

As alkali is added, the hydrogen ions are neutralized, thus:

$$2K^{\cdot} + 2(OH)' + 2H^{\cdot} = 2K^{\cdot} + 2H_2O.$$

To keep up the equilibrium, more $H^{\cdot}$ ions and $CrO_4''$ ions are formed from the dichromate, the $H^{\cdot}$ ions react with more alkali, etc., until by this process the dichromate is practically all converted into chromate. This change is usually represented by the simple equation:

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

Many chromates, for example, those of barium, lead, silver, mercury, etc., are insoluble in water and are obtained by precipitation. The ionic reaction in the case of barium will serve to illustrate the other cases:

$$2K^{\cdot} + CrO_4'' + Ba^{\cdot\cdot} + 2Cl' = BaCrO_4 + 2K^{\cdot} + 2Cl'.$$

The same precipitates result when a solution of a dichromate is used, because it contains some $CrO_4''$ ions, and as fast as these are removed by precipitation, others are produced to take their place in the system. But the precipitation of the metal as chromate is not complete, as some dichromate of the metal remains in solution, because of the acid that is liberated in the reaction. The essential change is represented by the simple equation:

$$K_2Cr_2O_7 + 2BaCl_2 + H_2O = 2BaCrO_4 + 2KCl + 2HCl.$$

This reaction is analogous to that between barium chloride and potassium bisulphate:

$$KHSO_4 + BaCl_2 = BaSO_4 + KCl + HCl$$

with the difference that barium sulphate is so difficultly soluble, even in acids, that precipitation is practically complete, whereas the chromates are more easily soluble in acids, and precipitation therefore is only partial.

**Chromic Oxide, $Cr_2O_3$** (*Sesquioxide of Chromium*).—Chromic oxide is obtained by heating potassium dichromate with sulphur, when potassium sulphate and chromic oxide are formed:

$$K_2Cr_2O_7 + S = K_2SO_4 + Cr_2O_3.$$

By washing the heated mass with water, the chromic oxide is left as a green powder, which is used as a green color, especially in the manufacture of painted glass and porcelain. Prepared by this method at high temperature the oxide is insoluble in acids, but when obtained in the form of its hydroxide by precipitation it is soluble in acids forming the *chromic salts*. It is therefore a basic oxide.

**Chromic Hydroxide, $Cr(OH)_3$.**—A solution of potassium dichromate may be deoxidized by the action of hydrogen sulphide, sulphurous acid, alcohol, or any other deoxidizing agent, in the presence of sulphuric or hydrochloric acid:

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S = K_2SO_4 + 7H_2O + 3S + Cr_2(SO_4)_3.$$

As shown by this formula, the sulphates of potassium and chromium are formed and remain in solution, while sulphur is precipitated, the hydrogen of the hydrogen sulphide having been oxidized and converted into water.

By adding ammonium hydroxide to the solution thus obtained, chromic hydroxide is precipitated as a bluish-green gelatinous substance:

$$Cr_2(SO_4)_3 + 6NH_4OH = 3(NH_4)_2SO_4 + 2Cr(OH)_3.$$

By dissolving this hydroxide in the different acids, the various salts, such as chloride, $CrCl_3$, sulphate, etc., are obtained. Chromic sulphate, similar to aluminum sulphate, combines with potassium or ammonium sulphate and water, forming *chrome alum*, $KCr(SO_4)_2.12H_2O$; it is a purple salt, and is isomorphous with other alums.

**Perchromic Acid, $H_2Cr_2O_8$.**—This acid is of interest because it is analogous to persulphuric acid, $H_2S_2O_8$, and is formed in the test for hydrogen dioxide. The ethereal solution is obtained when an acidified saturated aqueous solution of potassium dichromate is shaken with ether and just sufficient hydrogen dioxide solution to give an intense blue color. Excess of hydrogen dioxide must be avoided. The ethereal solution is much more permanent than an aqueous solution of the acid. When it is cooled to —20° C. (—4° F.) and treated with metallic potassium, a purplish-black precipitate of potassium perchromate, $K_2Cr_2O_8$, is formed. This is stable only at low temperature, decomposing at ordinary temperature into oxygen and potassium chromate. Several other salts have been prepared; they are all very unstable.

The chemical conduct of chromium, according to the degree of oxidation or

the valence of the metal, is like that of manganese. Chromous salts, corresponding to the oxide CrO, are known, but, like ferrous salts, they are very readily oxidized and pass to the stable chromic salts, corresponding to the oxide $Cr_2O_3$. The chromates and the acid, derived from the oxide $CrO_3$, although stable when alone in solution, readily give up oxygen in acid solutions to reducing agents, just like permanganates, and the chromium gives salts of the lower oxide, $Cr_2O_3$, which are green:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2Cr_2O_7,$$
$$H_2Cr_2O_7 = H_2O + 2CrO_3;\ 2CrO_3 = Cr_2O_3 + 3O,$$
$$Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O.$$

## Tests for Chromium.

### *a. Of chromates.*

(Use the reagent solution of potassium chromate, $K_2CrO_4$.)

1. Hydrogen sulphide added to an acidified warm solution of a chromate changes the red color into green with precipitation of sulphur. The solution now contains chromium in the basic form. (See explanation above.) (Plate II, 4.) The conversion of a chromate to a chromium salt is more readily accomplished by heating the chromic solution with alcohol and hydrochloric acid; the alcohol is partly oxidized, being converted into aldehyde, which has a peculiar but pleasant odor.

2. Soluble lead salts produce a yellow precipitate of lead chromate (chrome yellow), $PbCrO_4$, insoluble in acetic, soluble in hydrochloric acid and in sodium hydroxide (Plate II, 6):

$$K_2CrO_4 + Pb(NO_3)_2 = PbCrO_4 + 2KNO_3.$$

3. Barium chloride produces a pale yellow precipitate of barium chromate, $BaCrO_4$, insoluble in sodium hydroxide.

4. Silver nitrate produces a dark red precipitate of silver chromate, $Ag_2CrO_4$ (Plate II, 7).

5. Mercurous nitrate produces a red precipitate of mercurous chromate, $Hg_2CrO_4$ (Plate II, 8).

6. On pouring a layer of ether upon a solution of hydrogen dioxide, adding a few drops of potassium dichromate solution, a little sulphuric acid, and shaking, the ether assumes a blue color, due to the formation of unstable perchromic acid. A very delicate test.

### *b. Of salts of chromium.*

(Use a 5 per cent. solution of chrome alum, or chromic chloride, $CrCl_3$.)

7. To the solution add ammonium hydroxide or ammonium sulphide: in both cases the green hydroxide of chromium, $Cr(OH)_3$, is precipitated (Plate II, 5). Compare with aluminum.

$$2CrCl_3 + 3(NH_4)_2S + 6H_2O = 6NH_4Cl + 3H_2S + 2Cr(OH)_3.$$

8. Potassium or sodium hydroxide causes a similar green precipitate of chromic hydroxide, which is soluble in an excess of the reagent, but is reprecipitated on boiling for a few minutes.

Ammonia water causes precipitation of chromic hydroxide, but the precipitate is nearly insoluble in excess of the reagent.

*c. Of chromium in any form.*

9. Compounds of chromium, when mixed with sodium (or potassium) carbonate and nitrate, give, when heated upon platinum foil or in a crucible, a yellow mass of the alkali chromate.

10. Compounds of chromium impart a green color to the borax bead. Use only a very small quantity of the chromium compound.

Chromium salts have a green or violet to purple color. Solutions of the violet salts turn green when heated. They are acid to litmus, due to hydrolysis in solution. Chromates are all red or yellow, and mostly insoluble in water. The color of a chromate is noticeable in very dilute solution (made with the aid of an acid in the case of insoluble salts).

## Uranium, U = 238.5.

This element, which belongs to the chromium family, occurs principally in the minerals uraninite and pitchblende, the latter of which is now the chief source of uranium compounds. Pitchblende contains the oxide, $U_3O_8$, along with smaller quantities of numerous other elements. By roasting the ore mixed with sodium carbonate and sodium nitrate, and extracting with water, an impure solution of sodium uranate is obtained, from which acids precipitate an insoluble yellow *sodium diuranate*, $Na_2U_2O_7.6H_2O$. This salt, sometimes called uranium yellow, is used in making uranium glass which is greenish by transmitted light and yellowish by reflected light.

Uranium forms five oxides. $UO_2$, a basic oxide, when treated with acids, gives uranous salts, for example, uranous sulphate, $U(SO_4)_2.4H_2O$. Another oxide has the formula $U_2O_3$. The most stable oxide is $U_3O_8$, which occurs in pitchblende. The peroxide of

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QUESTIONS.—How is manganese found in nature? Mention the different oxides of manganese. What is the dioxide used for? What is the color of manganese salts, of manganates, and of permanganates? How is potassium permanganate made; what are its properties, and what is it used for? Give tests for manganese. State composition and properties of potassium dichromate. How is chromium trioxide made; what are its properties; what is it used for; and under what other name is it known? By what process may chromium sesquioxide be converted into chromates? What is the composition of the oxide and hydroxide of chromium, and how are they made? Mention tests for chromates and chromium salts.

uranium has the composition $UO_4$. $UO_3$, is the anhydride of uranic acid, $H_2UO_4$. Both of these compounds when treated with acids, give basic salts, which contain the radical $(UO_2)$, known as uranyl. Uranyl sulphate $(UO_2)SO_4.3\frac{1}{2}H_2O$, and uranyl nitrate $(UO_2)(NO_3)_2.6H_2O$, are yellow salts with a green fluorescence. From their solution ammonium sulphide precipitates brown uranyl sulphide $(UO_2)S$.

**Uranium Nitrate** (*Uranii Nitras*) $\mathbf{UO_2(NO_3)_2.6H_2O = 502.62}$ (*Uranyl Nitrate*).—Uranium nitrate is prepared as described above. The official salt should contain not less than 98 per cent. of pure nitrate. It forms light yellow, somewhat efflorescent prisms of a bitter, astringent taste, which are radio-active and readily soluble in water, alcohol or ether. The aqueous solution is yellow, acid to litmus, gives a yellow precipitate by addition of alkali or ammonia water, which is insoluble in excess of reagent but soluble in ammonium carbonate solution; with ammonium sulphide solution, dark brown uranyl sulphide is obtained and with sodium phosphate solution, yellow uranyl phosphate is precipitated.

## 29. ZINC. CADMIUM.

$Zn^{ii} = 65.37$. $Cd^{ii} = 112.4$.

This element is mentioned in chapter 24 where magnesium is discussed. Magnesium, zinc and cadmium are closely related and fall in the third column of the periodic table of the elements. Zinc differs from magnesium in that the oxide of zinc can be reduced by heating with carbon, the sulphide of zinc is not hydrolyzed by water, the hydroxide shows acidic properties as shown by its combination with caustic alkalies, and zinc enters into a complex radical with ammonia.

**Occurrence in Nature.**—Zinc is found chiefly either as sulphide (zinc-blende), ZnS, or as carbonate (calamine), $ZnCO_3$; it occurs also as silicate, $H_2Zn_2SiO_5$, and as oxide in combination with the oxides of iron or manganese.

**Metallic Zinc.**—Metallic zinc is obtained by heating in retorts the oxide or carbonate mixed with charcoal, when decomposition takes place. The liberated metal is vaporized, and distils into suitable receivers, where it solidifies.

Zinc is a bluish-white metal, which slowly tarnishes in the air, becoming coated with a film of oxide and carbonate; it has a crystalline structure and is, under ordinary circumstances, brittle; when heated to about 130°–150° C. (260°–302° F.) it is malleable, and may be rolled or hammered without fracture. Zinc thus treated retains this malleability when cold; the sheet-zinc of commerce is thus made. When zinc is further heated to about 300° C. (572° F.), it loses its malleability and becomes so brittle that it may be powdered; at 410° C. (760° F.) it fuses, and at a bright red heat it

boils, volatilizes, and, if air be not excluded, burns with a splendid greenish-white light, generating the oxide.

Zinc is used by itself in the metallic state or fused together with other metals (German silver and brass contain it); galvanized iron is iron coated with metallic zinc.

Zinc combines with mercury, forming a crystalline amalgam of the composition $Zn_2Hg$. As a constituent of dental amalgam alloys zinc hastens the setting, aids in controlling shrinkage and to some extent prevents discoloration. While zinc unites with tin in all proportions, forming excellent alloys for dental dies, it is not suitable for alloying with lead.

Zinc is a bivalent metal, forming but one oxide and one series of salts, most of which have a white color.

**Zinc Oxide** (*Zinci Oxidum*) **ZnO = 81.37** (*Flores zinci, Zinc-white*).—Zinc oxide may be obtained by burning the metal, but if made for medicinal purposes, by heating the carbonate, when carbon dioxide and water escape and the oxide is left:

$$3Zn(OH)_2.2ZnCO_3 = 5ZnO + 2CO_2 + 3H_2O.$$

It is an amorphous, white, tasteless powder, insoluble in water, soluble in acids; when strongly heated it turns yellow, but on cooling resumes the white color.

*Zinc hydroxide*, $Zn(OH)_2$, is obtained by precipitating zinc salts with the hydroxide of sodium or ammonium; the precipitate, however, is soluble in an excess of either of the alkali hydroxides.

**Zinc Chloride** (*Zinci Chloridum*) **$ZnCl_2$ = 136.29.**—Made by dissolving zinc or zinc carbonate in hydrochloric acid and evaporating the solution to dryness:

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

It is met with either as a white crystalline powder, or in white opaque pieces; it is very deliquescent and easily soluble in water and alcohol; it combines readily with albuminoid substances; it fuses at about 115° C. (239° F.), and is volatilized, with partial decomposition, at a higher temperature.

**Liquor zinci chloridi,** U. S. P., is an aqueous solution of zinc chloride, containing 50 per cent. of the salt.

**Zinc oxychloride** is used extensively for dental purposes, and is made by mixing zinc oxide with a strong solution of zinc chloride. At first a plastic mass forms, which rapidly hardens. The proportions in which the two substances are mixed differ widely, the weights corresponding all the way from 3 to 9 molecules of zinc oxide for each molecule of zinc chloride. Whether or to what extent the oxychloride of zinc is a true chemical compound is not known.

**Zinc oxyphosphate** is a preparation used similarly to the oxychloride. It is made by mixing zinc oxide with phosphoric acid. The acid used is either

ortho- or metaphosphoric acid, or a mixture of both. In all cases a zinc phosphate is formed, but as the quantity of zinc oxide used is larger than needed for saturating the acid completely, the mass as used by dentists is generally a mixture of zinc phosphate with zinc oxide.

**Zinc Bromide, $ZnBr_2$ = 225.21.**—Obtained analogously to the chloride by dissolving zinc in hydrobromic acid; it is a white powder, resembling the chloride in its properties.

**Zinc Iodide, $ZnI_2$ = 319.21.**—The two elements zinc and iodine combine readily when heated with water; the colorless solution when evaporated to dryness yields a powder whose physical properties resemble those of the chloride.

**Zinc Carbonate** (*Zinci Carbonas Præcipitatus*) $2ZnCO_3.3Zn(OH)_2$ (*Precipitated Carbonate of Zinc*).—Solutions of equal quantities of zinc sulphate and sodium carbonate are mixed and boiled, when a white precipitate is formed, which is a mixture of the carbonate and hydroxide of zinc, corresponding more or less to the formula given above.

$$5ZnSO_4 + 5Na_2CO_3 + 3H_2O = 3CO_2 + 5Na_2SO_4 + 2ZnCO_3.3Zn(OH)_2.$$

Precipitated zinc carbonate is a white, impalpable powder, odorless and tasteless, insoluble in water, soluble in acids and in ammonia water.

*Experiment* 37.—Dissolve 10 grams of the zinc sulphate obtained in Experiment 3, in about 200 c.c. of water, heat to boiling, and add slowly, while stirring, concentrated solution of sodium carbonate until precipitation is complete. After the precipitate has settled, pour off the liquid, and wash the former several times with hot water by decantation. Then filter and wash the precipitate again several times with hot water, drain, and dry.

Heat some of the dried zinc carbonate gradually to redness in a porcelain crucible with the cover on. What is formed? What color has it while hot? When the crucible is cold, place the residue in a tube and add dilute acid. Does any effervescence take place. Write reaction. Compare with experiments 25 and 26.

**Zinc Sulphate** (*Zinci Sulphas*) $ZnSO_4.7H_2O$ = 287.54 (*White vitriol*).—Zinc sulphate is obtained by dissolving zinc in dilute sulphuric acid:

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

If zinc be added to strong cold sulphuric acid, no decomposition takes place, because there are no ions present, and an acid does not exhibit acid properties unless ions are formed, as explained in chapter 13.

Dilute sulphuric acid scarcely acts on *pure* zinc, but addition of a few c.c. of solution of cupric sulphate or platinic chloride causes brisk action. This is due to the deposition of the copper or platinum on the zinc, thus forming an electric couple, whereby solution of zinc is facilitated.

## Summary of analytical characters of metals of the iron group.

| | *Ferrous salts.* | *Ferric salts.* | *Manganese.* | *Zinc.* | *Cobalt.* | *Nickel.* |
|---|---|---|---|---|---|---|
| Ammonium sulphide . . . . | Black precipitate. | Black precipitate. | Flesh-colored precipitate. | White precipitate. | Black precipitate. | Black precipitate. |
| Ammonia water. . . . . | Dirty green precipitate. | Reddish-brown precipitate. | White precipitate. | White precipitate. | Blue precipitate | Green precipitate. |
| In excess of reagent . . . | Insoluble | Insoluble | Soluble. | Soluble. | Soluble | Soluble. |
| Sodium hydroxide . . . . . | Dirty green precipitate | Reddish brown precipitate. | White precipitate. | White precipitate. | Blue precipitate | Green precipitate. |
| In excess of reagent . . . | Insoluble. | Insoluble. | Insoluble. | Soluble. | Insoluble. | Insoluble. |
| Sodium carbonate . . . . . | White precipitate, turning dark. | Reddish-brown precipitate. | White precipitate, turning darker. | White precipitate. | Blue precipitate | Green precipitate. |
| Ammonium carbonate . . . | White precipitate, darkens. | Reddish-brown precipitate. | White precipitate, darkens | White precipitate. | Blue precipitate | Green precipitate. |
| In excess of reagent . . . | Insoluble. | Insoluble. | Insoluble. | Soluble. | Soluble. | Soluble. |
| Potassium ferrocyanide . . . | Pale blue precipitate turning darker. | Dark blue precipitate | White precipitate. | White precipitate. | Grayish-green precipitate. | Greenish-white precipitate |
| Potassium ferricyanide . . . | Dark blue precipitate. | No precipitate, greenish brown color. | Pale brown precipitate. | Pale brownish-yellow precipitate. | Deep brown red precipitate | Yellowish-brown precipitate |
| Potassium sulphocyanate. . . | ..... | Dark red color. | ..... | ..... | Color much intensified. | Green color slightly intensified. |
| Borax bead in oxidizing flame | ..... | Dark yellow to red, while hot | Violet. | ..... | Blue. | Red, while hot. |

Zinc sulphate forms small, colorless crystals, which are isomorphous with magnesium sulphate; it is easily soluble in water. It is so much like magnesium sulphate in appearance that it is sometimes taken in mistake for the latter salt. The tests given below will distinguish between the two salts.

**Antidotes.**—Soluble zinc salts (sulphate, chloride) have a poisonous effect. If the poison has not produced vomiting, this should be induced. Milk, white of egg, or, still better, some substance containing tannic acid (with which zinc forms an insoluble compound) should be given.

### Tests for Zinc.

(Use a 5 per cent. solution of zinc sulphate.)

1. Add to the solution some ammonium sulphide. A white precipitate of zinc sulphide, ZnS, is produced, which is soluble in mineral acids, but not in acetic acid. (Of the familiar metals, zinc is the only one of which the sulphide is white.)

If the zinc salt is not pure, the sulphide may appear more or less gray instead of white:

$$ZnSO_4 + (NH_4)_2S = (NH_4)_2SO_4 + ZnS.$$

2. Hydrogen sulphide passed into the solution gives a partial precipitate of zinc sulphide because of the solvent action of the acid liberated. In the presence of sodium acetate, however, the precipitate is complete because of the liberation of acetic acid, in which the sulphide is insoluble:

$$ZnSO_4 + 2Na(C_2H_3O_2) + H_2S = ZnS + Na_2SO_4 + 2H.C_2H_3O_2.$$

3. Addition of caustic alkali or ammonia water gives a white precipitate of zinc hydroxide, $Zn(OH)_2$. It is soluble in excess of the alkali, forming zincates:

$$Zn(OH)_2 + 2NaOH = Zn(ONa)_2 + 2H_2O.$$

The hydroxide is also soluble in excess of ammonia water, forming a complex compound, $Zn(NH_3)_4.(OH)_2$. In this respect zinc differs from magnesium. The ions of this compound are $Zn(NH_3)_4^{\cdot\cdot}$ and $2(OH)'$.

4. Addition of a solution of a carbonate or phosphate, gives a white precipitate of zinc carbonate or phosphate:

$$ZnSO_4 + Na_2HPO_4 = ZnHPO_4 + Na_2SO_4.$$

Zinc carbonate is soluble in excess of ammonium carbonate.

5. Solution of potassium ferrocyanide gives a white precipitate of zinc ferrocyanide. (Distinction from magnesium and aluminum, which give no precipitate.) The precipitate is $Zn_2Fe(CN)_6$, and is difficultly soluble in hydrochloric acid.

Tests 1, 3, and 5 together are conclusive for zinc salts. Practically

all the compounds of zinc are colorless. The oxide, carbonate, phosphate, ferrocyanide, and sulphide are insoluble in water; the chloride, bromide, iodide, nitrate, sulphate, and acetate are soluble in water. These are the common salts. The soluble zinc salts are hydrolyzed somewhat in water, and therefore show an acid reaction. This explains the solvent action of a zinc chloride solution when used on metal surfaces in soldering. The coat of metallic oxide is thus removed.

Zinc forms the divalent ion $Zn^{\cdot\cdot}$, which unites with acid radicals to form the zinc salts. The ionic equations for the above tests are of the same form as those given under the tests for calcium. $Zn(OH)_2$ has weak basic properties, and still weaker acid properties. Like aluminum and chromium hydroxides, it is slightly soluble and ionizes in two ways, thus:

$$Zn(OH)_2 \rightleftarrows Zn^{\cdot\cdot} + 2(OH)'.$$

With acids, zinc salts are formed by the union of $(OH)'$ and $H^{\cdot}$ ions to form water.

Also, $$Zn(OH)_2 \rightleftarrows ZnO_2'' + 2H^{\cdot},$$

and with considerable excess of alkali the hydroxide dissolves to form zincates by the union of $H^{\cdot}$ ions with $(OH)'$ ions of the alkali. The equation in simple form is written,

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O.$$

**Cadmium, Cd = 112.4.** Found in nature associated (though in very small quantities) with the various ores of zinc, with which metal it has in common a number of physical and chemical properties. Cadmium differs from zinc by forming a yellow sulphide (with hydrogen sulphide), insoluble in diluted acids. Cadmium and its compounds are of little interest here; the yellow sulphide is used as a pigment, the sulphate and iodide sometimes for medicinal purposes.

Cadmium is a constituent of many alloys distinguished by very low fusing points.

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QUESTIONS.—How is zinc found in nature, and by what process is it obtained? Mention the properties of metallic zinc, and what is it used for? Mention two processes for making zinc oxide. How does heat act on zinc oxide? Show by chemical symbols the action of hydrochloric and sulphuric acids on zinc. State the properties of chloride and of sulphate of zinc. What is white vitriol? Explain the formation of precipitated zinc carbonate, and state its composition. Mention tests for zinc compounds. How many pounds of crystallized zinc sulphate may be obtained from 21.7 pounds of metallic zinc?

## 30. LEAD. COPPER. BISMUTH.

**General Remarks Regarding the Metals of the Lead Group.**—The six metals belonging to this group (Pb, Cu, Bi, Ag, Hg, and Cd) are distinguished by forming sulphides which are insoluble in water, insoluble in dilute mineral acids, insoluble in ammonium sulphide; consequently they are precipitated from neutral, alkaline, or acid solutions by hydrogen sulphide or ammonium sulphide.

The metals themselves do not decompose water at any temperature, and are not acted upon by dilute sulphuric acid; heated with strong sulphuric acid, most of these metals are converted into sulphates with liberation of sulphur dioxide; nitric acid converts all of them into nitrates with liberation of nitric oxide.

The oxides, iodides, sulphides, carbonates, phosphates, and a few of the chlorides and sulphates of these metals are insoluble; all the nitrates, and most of the chlorides and sulphates are soluble.

In regard to valence, they show no uniformity whatever, silver being univalent, copper, cadmium, and mercury bivalent, bismuth trivalent, and lead either bivalent or quadrivalent.

### Lead, $Pb^{ii}$ = 207.1.

This element falls in the fifth column of the periodic table and in the family consisting of carbon, silicon, germanium, tin and lead. All of these elements show a maximum valence of four. Germanium, tin and lead also act with a valence of two, thus resembling carbon. Carbon and silicon have already been considered. They are acidic elements. Germanium is a rare element and need not be considered in this book. Tin and lead form oxides and hydroxides which have both basic and acidic properties.

Divalent lead is a fairly active basic element, while quadrivalent lead has feeble basic properties. The salts of divalent lead are somewhat hydrolyzed by water while those of quadrivalent lead are completely hydrolyzed. Plumbites and plumbates, such as $K_2PbO_2$ and $K_2PbO_3$ are considerably hydrolyzed. The most usual compounds of the element are those of divalent lead, as all the salts of quadrivalent lead readily give up half of the acid radical, the lead assuming the divalent state.

**Preparation and Properties.**—Lead is obtained chiefly from the native lead sulphide (*galena*), PbS, by first roasting it, whereby part is converted into oxide and sulphate. By heating this mixture with undecomposed sulphide to a higher temperature lead is formed, thus:

$$PbS + 2PbO = 3Pb + SO_2 \text{ and } PbS + PbSO_4 = 2Pb + 2SO_2.$$

Lead owes its usefulness in the metallic state chiefly to its softness, fusibility, and resistance to acids, which properties are of advantage in using it for tubes or pipes, or in constructing vessels to hold or manufacture sulphuric acid.

Lead is exceedingly malleable and somewhat ductile, but not very tenacious. It is a constituent of many alloys, as for instance of type metal, britannia metal, shot, etc. Common solder is an alloy of equal weights of lead and tin. The noble metals are rendered brittle and unworkable when alloyed with even a small quantity of lead.

*Experiment* 38.—Dissolve 1 gram of lead acetate or lead nitrate in about 200 c.c. of water, suspend in the centre of the solution a piece of metallic zinc, and set aside. Notice that metallic lead is deposited slowly upon the zinc in a crystalline condition, while zinc passes into solution, which may be verified by analytical methods. The chemical change taking place is this:

$$Pb(NO_3)_2 + Zn = Zn(NO_3)_2 + Pb.$$

**Electrolytic solution tension.** The precipitation of lead from solution by zinc in the experiment above is represented by the ionic equation:

$$Zn + Pb^{\cdot\cdot} + 2NO_3' = Zn^{\cdot\cdot} + 2NO_3' + Pb.$$

The lead ions lose their charges to zinc which becomes ionic, while metallic lead is precipitated. This action is pretty much like the liberation of hydrogen from acids by some metals:

$$Zn + 2H^{\cdot} + SO_4'' = Zn^{\cdot\cdot} + SO_4'' + H_2.$$

The explanation of this type of chemical change is found in the *theory of electrolytic solution tension* proposed by Nernst. According to this, a metal when immersed in water or a solution sends some positive ions into the solution, and itself assumes negative charges of electricity. This proceeds to a point where the metal is sufficiently charged negatively that it attracts its positive ions at the same rate at which they tend to be given off from the metal. An equilibrium between the two tendencies is reached. The tension or pressure that drives the ions into the solution differs for different metals, the order of decrease being the same as the order in the electrochemical series of the metals (page 152). Any metal in the series has a higher tension than those following, and will displace them from solutions of their salts, but not vice versâ. Zinc has a much greater solution tension than lead. When it is placed in the lead solution, it acquires a greater negative charge of electricity than does a piece of lead when it is placed in a solution. The result is that the lead ions are attracted to the zinc and discharged, and metallic lead is deposited. This process continues until all the lead has been deposited from the solution, which then contains an equivalent amount of zinc salt.

**Lead Oxide** (*Plumbi Oxidum*) **PbO = 223.1** (*Litharge*).—Obtained by exposing melted lead to a current of air, when the metal is gradually oxidized with the formation of a yellow powder, known as *massicot;* at a high temperature this fuses, forming reddish-yellow crystalline scales, known as *litharge;* by heating still further in contact with air, a portion of the oxide is converted into dioxide (or peroxide), $PbO_2$, and a red powder is formed, known as *red lead* (or *minium*), which probably is a mixture (or combination) of oxide and dioxide of lead, $PbO_2(PbO)_2$.

Lead oxide is used in the manufacture of lead salts, lead plaster, glass, paints, etc.

Nitric acid when heated with red lead combines with the oxide, while *lead dioxide*, $PbO_2$, is left as a dark brown powder, which, on heating with hydrochloric acid, evolves chlorine (similar to manganese dioxide). Lead dioxide is a conductor of electricity, differing thus from most oxides.

**Accumulator or storage battery.** This consists of two sets of lead plates made in the form of gratings. One set, which are all connected, have the spaces in the gratings filled up with spongy lead; the other set, likewise connected, are filled up with lead dioxide. When the plates are dipped into dilute sulphuric acid they show a difference of potential, and when connected a current flows. When in action or discharging, the $SO_4''$ ions of the sulphuric acid are attracted to the plates filled with spongy lead, give up their negative charges to the plate, and form lead sulphate. The $H^{\cdot}$ ions of the acid pass to the plates filled with $PbO_2$, give up their positive charges, and reduce $PbO_2$ to PbO, which combines with sulphuric acid and forms lead sulphate. The current flows in the outside circuit from the plates filled with $PbO_2$ to the plates filled with spongy lead, and has a voltage of about 2. Both plates ultimately become filled with $PbSO_4$, and the battery then is exhausted. Sulphuric acid is removed from the solution, and the specific gravity of the latter falls. By this means one can tell when the battery is approaching exhaustion.

Charging the battery consists in restoring the plates to their original state, and is accomplished by passing a current from a dynamo through it in a direction opposite to that of the current produced by the battery. By this action electrical energy is stored up in the battery as chemical energy, which is given back again as electrical energy when the battery is discharged. When the dynamo current passes, $H^{\cdot}$ ions of the acid solution pass to the plates originally filled with lead, and form sulphuric acid with $SO_4''$ ions of the lead sulphate, leaving the plate finally filled with reduced spongy lead. At the same time, $SO_4''$ ions of the acid solution pass to the other plates, where they are discharged and enter into reaction with the lead sulphate in the plates, thus:

$$PbSO_4 + SO_4 + 2H_2O = PbO_2 + 2H_2SO_4.$$

All the lead sulphate is ultimately converted into lead dioxide, and this set of plates are restored to the original state. All the sulphuric acid is restored to the liquid, and the battery is ready for use. The changes involved in the complete cycle may be written in one equation, thus:

$$2PbSO_4 + 2H_2O \underset{\text{charging} \rightarrow}{\overset{\leftarrow \text{discharging.}}{\rightleftharpoons}} Pb + 2H_2SO_4 + PbO_2.$$

**Lead Nitrate, $Pb(NO_3)_2$ = 331.12.**—Obtained by dissolving the oxide in nitric acid:

$$PbO + 2HNO_3 = H_2O + Pb(NO_3)_2.$$

Lead nitrate is the only salt of lead (with a mineral acid) which is easily soluble in water; it has a white color, and a sweetish, astringent, and afterward metallic taste. It is insoluble in strong nitric acid; hence lead is insoluble in this acid.

*Experiment* 39.—Heat 30 c.c. of dilute nitric acid, but not to the boiling-point, and dissolve in it, with stirring, small portions of lead oxide, until no more is taken up. Filter the solution if necessary, and let it cool to crystallize. If no crystals form, concentrate further. The crystals are octahedra. Examine their appearance and form. Which one of the methods of forming salts does this experiment illustrate?

Heat some of the dried and powdered crystals in a porcelain crucible moderately. Note the brown fumes of nitrogen tetroxide and residue of brown lead oxide, which becomes yellow on cooling. This experiment illustrates the instability of most nitrates when heated, and the method by which some oxides are obtained:

$$Pb(NO_3)_2 = PbO + N_2O_4 + O.$$

**Lead Carbonate, $PbCO_3$.**—Lead carbonate occurs in nature as the mineral *cerussite*, and may be obtained by precipitation of a lead acetate solution with sodium bicarbonate. While this normal salt is scarcely used, the *basic lead carbonate* or *white lead* of the approximate composition $2PbCO_3.Pb(OH)_2$ is used very largely as a constituent of paints. It is manufactured on a large scale directly from lead, by exposing it to the simultaneous action of air, carbon dioxide, and vapors of acetic acid. The latter combines with the lead, forming a basic acetate, which is converted into the carbonate (almost as soon as produced) by the carbon dioxide present.

The action of acetic acid on lead or lead oxide will be considered in connection with acetic acid.

Lead carbonate is a heavy, white, insoluble, tasteless powder; the white lead of commerce frequently is found adulterated with barium sulphate, gypsum or lead sulphate.

**Lead Iodide, $PbI_2$ = 460.94.**—Made by adding solution of potassium iodide to lead nitrate (Plate III, 6):

$$Pb(NO_3)_2 + 2KI = 2KNO_3 + PbI_2.$$

It is a heavy, bright yellow, almost insoluble powder, which may be distinguished from lead chromate by its solubility in ammonium chloride solution on boiling, lead chromate being insoluble in this solution.

**Poisonous properties and antidotes.** Compounds of lead are directly poisonous, and it happens, not infrequently, that water passing through leaden pipes or collected in leaden tanks becomes contaminated with lead. Water free from air and salts scarcely acts on lead; but if it contain air, oxide of lead is formed, which is either dissolved by the water or is decomposed by the nitrates or chlorides present in the water, the soluble nitrate or chloride of lead being formed.

If the water contains carbonates and sulphates, however, these will form insoluble compounds, producing a film or coating over the lead, preventing further contact with the water. Rain water, in consequence of its containing atmospheric constituents, and no sulphates, acts as a solvent on lead pipe; spring and river waters generally do not.

Water containing lead will show a dark color on passing hydrogen sulphide through it; if the quantity present be very small, the water should be evaporated to $\frac{1}{10}$ or even $\frac{1}{100}$ of its original volume before applying the test.

The constant handling of lead compounds is one of the causes of lead poisoning (painters' colic). As an antidote, magnesium sulphate should be used, which forms with lead an insoluble sulphate; the purgative action of magnesia is also useful. (In lead works workmen often drink water containing a little sulphuric acid.)

### Tests for Lead.

(Use a 5 per cent. solution of lead acetate or lead nitrate.)

1. Hydrogen sulphide or ammonium sulphide added to the solution produces a black precipitate of lead sulphide (Plate III, 1), insoluble in dilute acids or alkalies. A very delicate reaction:

$$Pb(NO_3)_2 + H_2S = PbS + 2HNO_3.$$

2. Dilute sulphuric acid or a solution of a sulphate gives a white precipitate of lead sulphate, $PbSO_4$. This is one of the four insoluble sulphates. (See test 2 for sulphates.)

3. Other reagents which give precipitates with solutions of lead salts are:

Hydrochloric acid or solution of a chloride, producing white lead chloride, $PbCl_2$. (See test 3 for hydrochloric acid.)

Potassium iodide, producing yellow lead iodide, $PbI_2$ (Plate III, 6). (See test 2 for iodides.)

Potassium chromate, producing yellow lead chromate (chrome-yellow), $PbCrO_4$ (Plate II, 6). (See test 2 for chromates.)

Alkali carbonates, producing white basic lead carbonate.

Alkali phosphates, producing white lead phosphate, $PbHPO_4$.

Solution of sodium hydroxide, producing white lead hydroxide, $Pb(OH)_2$, which dissolves in excess of the alkali, forming sodium plumbite, $Pb(ONa)_2$. (See comments on tests for zinc.)

4. When a charcoal reduction test (for which see directions in test 3 for sulphates) is made on any dry lead compound, a globule of metallic lead is obtained, which is recognized by its softness and malleability. Try its solubility in dilute hydrochloric, sulphuric, and nitric acids.

Tests 1, 2, and 4 are sufficient for recognition of a lead compound. Lead salts are mostly colorless. Lead nitrate has an acid reaction, due to hydrolysis in water.

## Copper, $Cu^{ii} = 63.57$.

This metal falls in the second column of the periodic table in the family consisting of copper, silver and gold. These three metals are in universal use for coins and ornaments, are the best conductors

of the electric current, and, since they occur in the free state in nature, were known in ancient times.

**Occurrence and Properties.**—Copper is found in nature in the free state in the Lake Superior region, China and Japan, but it occurs mostly in combination with sulphur or oxygen, or as basic carbonate, in Montana, England, Spain, Germany, Siberia, etc. The commonest copper-ore is *Copper pyrite*, a double sulphide of copper and iron, $CuFeS_2$ or $Cu_2S.Fe_2S_3$, having the color and lustre of brass or gold. Other ores are: *Copper glance*, cuprous sulphide, having a dark gray color and the composition $Cu_2S$; *malachite*, a beautiful green mineral, being a carbonate and hydroxide of copper, $CuCO_3.Cu(OH)_2$. Cuprous and cupric oxide also are found occasionally. Copper is obtained from the oxide by reducing it with coke; sulphides previously are converted into oxide by roasting.

Copper is the only metal showing a distinct red color; it is so malleable that, of the metals in common use, only gold and silver surpass it in that respect; it is one of the best conductors of heat and electricity, it does not change in dry air, but becomes covered with a film of green subcarbonate when exposed to moist air.

Copper frequently is used in the manufacture of alloys, of which the more important are:

| | Copper. | Zinc. | Tin. | Nickel. | Antimony. |
|---|---|---|---|---|---|
| Brass | 64 | 36 | .. | .. | |
| German silver | 51 | 31 | .. | 18 | |
| Bell-metal | 78 | .. | 22 | .. | . |
| Bronze | 80 | 16 | 4 | .. | .. |
| Gun-metal | 90 | .. | 10 | .. | .. |
| Babbitt-metal | 43 | .. | 43 | .. | 14 |

Copper frequently is alloyed with gold and silver.

Copper forms two oxides, and corresponding to these are two series of salts, known as cupr*ous* and cupr*ic* compounds. The principal cuprous compounds are $Cu_2O$, CuCl, CuBr, CuI, Cu(CN), $Cu_2S$. All these, except $Cu_2O$ and $Cu_2S$, are white and insoluble in water. Cupric iodide, ($CuI_2$), and cyanide, ($Cu(CN)_2$), cannot be obtained, as they decompose into the cuprous salt and free iodine or cyanogen, $CuI_2 = CuI + I$. These are obtained when potassium iodide or cyanide solution is added to solution of cupric sulphate:

$$CuSO_4 + 2KI = CuI + I + K_2SO_4.$$

Cuprous salts of oxygen acids are unusual and not well known. Some that have been made are the sulphite, sulphate, ammoniated sulphate, carbon monoxide compound of the sulphate, and acetate.

Cupric compounds are more numerous, as they embrace the salts of oxygen acids as well as salts of some of the halogen acids. The anhydrous salts are usually white or yellow, but the solutions as well as the hydrated crystals are usually blue or greenish blue. The

cupric compounds are more important and familiar than the cuprous salts, and those most frequently employed are the sulphate, acetate, and oxide. The valence of copper in cupric compounds is 2. Some facts indicate that in the cuprous compounds the valence of copper is 1, while others indicate that it is 2. Some writers assign the valence of 2 to copper in all its compounds, and use double formulas for the cuprous salts to account for the apparent univalence of copper, thus, $Cu_2Cl_2$ or Cl-Cu—Cu-Cl, assuming that two atoms of copper are united by one bond. The behavior of the cuprous salts can very readily be represented by the simple formulas and univalence of copper, and there is no need for using double formulas.

**Cupric Oxide, CuO** (*Black Oxide or Monoxide of Copper*).—Heated to redness, copper becomes covered with a black scale, which is cupric oxide; it is obtained also by heating cupric nitrate or carbonate, both compounds being decomposed with formation of the oxide; finally, it may be made by adding sodium or potassium hydroxide to the solution of a cupric salt, when a bulky, pale blue precipitate of *cupric hydroxide*, $Cu(OH)_2$, is formed, which, upon boiling, is decomposed into water and cupric oxide, a heavy dark brown powder (Plate III, 2):

$$CuSO_4 + 2KOH = K_2SO_4 + Cu(OH)_2;$$
$$Cu(OH)_2 = H_2O + CuO.$$

**Cuprous Oxide, $Cu_2O$** (*Red Oxide or Suboxide of Copper*).—When cupric oxide is heated with metallic copper, charcoal, or organic matter, the cupric oxide is decomposed, and cuprous oxide is formed. (Excess of carbon or organic matter reduces the oxide to metallic copper.)

$$CuO + Cu = Cu_2O;$$
$$2CuO + C = Cu_2O + CO.$$

Some organic substances, especially grape-sugar, decomposes alkaline solutions of cupric sulphate with precipitation of cuprous oxide, which is a red, insoluble powder.

*Experiment* 40.—To 5 c.c. of a 5 per cent. solution of copper sulphate add about 20 c.c. of the reagent solution of sodium hydroxide. Note the blue precipitate of copper hydroxide, $Cu(OH)_2$. Add to the mixture about 2 grams of Rochelle salt (sodium potassium tartrate) and shake. The precipitate dissolves to a deep blue solution, which is essentially Fehling's solution (see Index). The copper enters the negative tartaric acid radical or ion, and while in the cupric state is not precipitated by alkali. If the copper is reduced to the cuprous state, it can no longer remain in solution and is precipitated as the reddish cuprous oxide, $Cu_2O$.

Heat the blue solution to boiling and add a little dilute glucose solution and heat again a few minutes. A precipitate of cuprous oxide is produced, due to the reducing action of the glucose. This is usually employed as a test for glucose in urine.

**Cupric Sulphate** (*Cupri Sulphas*) $CuSO_4.5H_2O$ = **249.72** (*Sulphate of Copper, Blue Vitriol, Blue-stone*).—This is the most important compound of copper. It is manufactured on a large scale, either from copper pyrite, or by dissolving cupric oxide in sulphuric acid, evaporating and crystallizing the solution.

Cupric sulphate forms large, transparent, deep-blue crystals, which are easily soluble in water, and have a nauseous, metallic taste. By heating it to about 200° C. (392° F.) all water of crystallization is expelled, and the *anhydrous cupric sulphate* formed, which is a white powder. By further heating this is decomposed, sulphuric and sulphurous oxides are evolved, and cupric oxide is left.

*Experiment* 41.—Boil about 5 grams of fine copper with 15 c.c. of concentrated sulphuric acid until the action ceases and most of the copper is dissolved. Dilute with about 15 c.c. of hot water, filter, and set aside for crystallization. State the exact quantities of copper and $H_2SO_4$ required to make 100 pounds of crystallized cupric sulphate.

**Cupric Carbonate.**—Cupric carbonate is obtained by the addition of sodium carbonate to solution of cupric sulphate, when a bluish-green precipitate is formed, which is cupric carbonate with hydroxide (Plate III, 4); by dissolving this in the various acids, the different cupric salts are obtained.

**Ammonio-copper Compounds.**—A number of compounds are known which are either double salts of ammonia and copper, or are derived from ammonium salts and contain copper. Thus, cupric chloride forms with ammonia the compounds: $CuCl_2(NH_3)_2$, $CuCl_2(NH_3)_4$, and $CuCl_2(NH_3)_6$. Cupric sulphate forms in like manner, cupric-diammonium sulphate, $CuSO_4(NH_3)_2$, and cupric tetrammonium sulphate, $CuSO_4(NH_3)_4$, which is a deep azure-blue compound taking up one molecule of water during crystallization.

It is this formation of soluble ammonio-copper compounds which causes the deep blue color in solutions of cupric salts on the addition of ammonia water.

All copper salts, except the sulphide, are soluble in ammonia water. Hence, copper cannot be precipitated from ammoniacal solution by any reagent except hydrogen sulphide or alkali sulphides. Copper hydroxide with excess of ammonia water forms the deep-blue soluble compound, $Cu(NH_3)_4.(OH)_2$, in which the copper is held in the complex radical or ion, $Cu(NH_3)_4^{\cdot\cdot}$. The ammonio-copper salts are derived from the hydroxide above, and also contain the radical $Cu(NH_3)_4^{\cdot\cdot}$, which is the cause of the blue color. The sulphate has the formula $Cu(NH_3)_4.SO_4.H_2O$.

With excess of alkali cyanides, copper also forms complex double cyanides, from which copper cannot be precipitated by any reagent, not even hydrogen sulphide.

**Poisonous properties and antidotes.** The use of copper for culinary vessels is frequently the cause of poisoning by this metal. A perfectly clean surface of metallic copper is not affected by any of the substances used in the preparation

of food, but as the metal is very apt to become covered with a film of oxide when exposed to the air, and as the oxide is easily dissolved by the combined action of water, carbonic or other acids, such as are found in vinegar, the juice of fruits, or rancid fats, the use of copper for culinary vessels is always dangerous. Actual adulterations of food with compounds of copper have been detected.

In cases of poisoning by copper the stomach-pump should be used, vomiting induced, and albumen (white of egg) administered, which forms an insoluble compound with copper. Reduced iron, or a very dilute solution of potassium ferrocyanide, may be of use as antidotes.

### Tests for Copper.

(Use a 5 per cent. solution of copper sulphate.)

1. Add to the solution hydrogen sulphide or ammonium sulphide: a black precipitate of cupric sulphide is formed. (Plate III, 1):

$$CuSO_4 + H_2S = H_2SO_4 + CuS.$$

2. Add solution of sodium or potassium hydroxide: a bluish precipitate of cupric hydroxide, $Cu(OH)_2$, is formed, which is converted into dark brown cupric oxide, CuO, by boiling. (See equation above.) (Plate III, 2.)

3. Add ammonia water: a bluish precipitate of cupric hydroxide is formed which readily dissolves in an excess of the reagent, forming a deep azure-blue solution containing an ammonio-copper compound. (See explanation above.) (Plate III, 3.)

The delicacy of this test is shown by diluting the solution of the copper salt until its color is no longer visible, and then adding ammonia.

4. Add solution of potassium ferrocyanide: a reddish-brown precipitate of cupric ferrocyanide, $Cu_2Fe(CN)_6$, is obtained. (Plate III, 5.)

This is a very delicate test, and should also be made on a highly diluted solution made as directed in test 3.

5. Add solution of sodium or potassium carbonate: green cupric carbonate with hydroxide is precipitated. (Plate III, 4.)

6. Immerse a piece of iron or zinc, showing a bright surface, in an acidified solution of copper: the latter is precipitated upon the iron, an equivalent amount of iron passing into solution. (See page 294.)

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

7. Most compounds of copper color the flame green, cupric chloride, blue. The cupric chloride flame can be made very striking by dissolving the copper salt in a little concentrated hydrochloric acid, pouring this solution on the corner of a piece of iron-wire gauze, and holding it in the Bunsen flame.

8. Cupric compounds give a blue, cuprous compounds a red, borax bead.

Tests 3, 4, 6, and 8 are sufficient to identify copper compounds. The insoluble ones are made soluble by treating with mineral acids. The sulphate, nitrate, chloride, acetate, and ammonio-salts of copper are soluble in water, most of the other compounds are insoluble. The soluble normal salts redden litmus, due to hydrolysis.

The ionic equations for the tests are of the same form as those given under the tests for calcium.

## Bismuth, $Bi^{iii}$ = 208.

This metal falls in the sixth column of the periodic table in the family embracing the elements nitrogen, phosphorus, arsenic, antimony and bismuth. The first two have already been discussed; they and the element arsenic are decidedly acid-forming elements, antimony is both acid-forming and base-forming, while bismuth is almost exclusively a base-forming element. Bismuth does not form a compound with hydrogen, but the other members of the family do.

**Occurrence and Properties.**—Bismuth is found free in nature and to a lesser extent as trioxide and sulphide. The extraction of the metal is a mere mechanical process, the earthy matter containing it being heated in iron cylinders, and the melted bismuth collected in suitable receivers. It melts at about 270° C.

Bismuth is grayish-white, with a pinkish tinge, very brittle, generally showing a distinct crystalline structure. Occasionally it is used in alloys and in the manufacture of a few medicinal preparations.

Bismuth has the property of expanding while passing from the liquid to the solid state, and of greatly lowering the fusing-point of other metals. These properties make it a useful constituent of many alloys. The presence of bismuth in dental amalgams renders them sticky and adhesive and causes them to require a larger proportion of mercury.

Bismuth is trivalent, as a rule, as shown in the chloride, $BiCl_3$, or oxide, $Bi_2O_3$, but it is also quinquivalent, as shown by the oxide, $Bi_2O_5$, corresponding to $P_2O_5$, $Sb_2O_5$, $I_2O_5$, or $N_2O_5$. In fact, bismuth forms, besides the two oxides mentioned, two others of the composition $Bi_2O_2$ and $Bi_2O_4$, corresponding to the respective nitrogen oxides. A characteristic property of this metal is decomposition of the concentrated solution of any of its normal salts by the addition of much water, with the formation and precipitation of so-called oxysalts or subsalts of bismuth, while some bismuth with a large quantity of acid remains in solution. This is due to the very weak basic character of $Bi(OH)_3$.

The true constitution of these subsalts is as yet doubtful, but a comparison of them has led to the assumption of a radical *Bismuthyl*, BiO, which behaves like an atom of a univalent metal.

The relation between the normal or bismuth salts, and the subsalts

or bismuthyl salts, will be shown by the composition of the following compounds:

| | | | |
|---|---|---|---|
| Bismuth chloride, | $BiCl_3$. | Bismuthyl chloride, | $(BiO)Cl$. |
| " bromide, | $BiBr_3$. | " bromide, | $(BiO)Br$. |
| " iodide, | $BiI_3$. | " iodide, | $(BiO)I$. |
| " nitrate, | $Bi(NO_3)_3$. | " nitrate, | $(BiO)NO_3$. |
| " sulphate, | $Bi_2(SO_4)_3$. | " sulphate, | $(BiO)_2SO_4$. |
| " carbonate, | $Bi_2(CO_3)_3$ not known. | " carbonate, | $(BiO)_2CO_3$. |

The nature of normal bismuth salts and bismuthyl salts may be explained by saying that the first are derived from the triacid base $Bi(OH)_3$, the latter from the monacid base BiO.OH. These two hydroxides are related to one another thus:

$$Bi(OH)_3 = Bi\begin{matrix}=O\\ \diagdown OH\end{matrix} + H_2O.$$

**Bismuth Subnitrate** (*Bismuthi Subnitras*) $\mathbf{BiONO_3.H_2O}$ (?) (*Oxynitrate of Bismuth*).—By dissolving metallic bismuth in nitric acid, a solution of bismuth nitrate is obtained, nitric oxide escaping:

$$Bi + 4HNO_3 = Bi(NO_3)_3 + NO + 2H_2O.$$

Upon evaporation of the solution, colorless crystals of *bismuth nitrate*, $Bi(NO_3)_35H_2O$, are obtained.

If, however, the solution (or the dissolved crystals) be poured into a large quantity of water, the salt is decomposed with the formation of bismuthyl nitrate and nitric acid, which latter keeps in solution some bismuth:

$$Bi(NO_3)_3 + 2H_2O = BiONO_3.H_2O + 2HNO_3.$$

Subnitrate of bismuth is a heavy, white, tasteless powder, of a somewhat varying chemical composition; it is almost insoluble in water, soluble in most acids.

*Experiment* 42.—Dissolve by the aid of heat about 1 gram of metallic bismuth in a mixture of 2 c.c. of nitric acid and 1 c.c. of water. Evaporate the clear solution to about one-half its volume, in order to remove excess of acid, and pour into this solution of normal bismuth nitrate 100 c.c. of water. Collect the precipitate of bismuthyl nitrate on a filter, wash and dry it. Prove the presence of bismuth in the filtrate by tests mentioned below.

**Bismuth Subcarbonate** (*Bismuthi Subcarbonas*) $\mathbf{(BiO)_2CO_3.H_2O}$ (?) (*Oxycarbonate of bismuth, Pearl-white*).—Made by adding sodium carbonate to solution of bismuth nitrate, when the subcarbonate is precipitated, some carbon dioxide escaping:

$$2Bi(NO_3)_3 + 3Na_2CO_3 + H_2O = 6NaNO_3 + 2CO_2 + (BiO)_2CO_3.H_2O.$$

A white, or pale yellowish-white powder, resembling the subnitrate. It readily loses water and carbon dioxide on heating, when the *yellow oxide*, $Bi_2O_3$, is left.

A mixture of bismuth subnitrate, sodium bicarbonate, and water is often prescribed, but, as such a mixture gives off carbon dioxide, it is better to substitute the subcarbonate for the subnitrate.

### Tests for Bismuth.

Use a solution made by dissolving bismuth subnitrate or subcarbonate in the least possible quantity of dilute nitric acid, with gentle heat. Dilute cautiously with water, adding a few drops more of the acid if there is any tendency to precipitation.

1. Add to the solution hydrogen sulphide or ammonium sulphide: a dark brown (almost black) precipitate of bismuth sulphide, $Bi_2S_3$, is produced (Plate III, 8):

$$2BiCl_3 + 3H_2S = 6HCl + Bi_2S_3.$$

2. Add solution of ammonium or sodium hydroxide, or carbonate: a white precipitate of bismuth hydroxide, $Bi(OH)_3$, or of bismuthyl carbonate is produced. (See explanation above.)

3. Solution of potassium iodide precipitates brown bismuth iodide, $BiI_3$, soluble in excess of the reagent.

4. Solution of potassium dichromate precipitates yellow bismuthyl dichromate $(BiO)_2Cr_2O_7$.

5. A small quantity of bismuth or of any bismuth compound, mixed with equal quantities of sulphur and potassium iodide, and heated moderately upon charcoal before the blowpipe, forms a scarlet-red incrustation of bismuthyl iodide, BiOI.

6. Apply the reduction test on charcoal (see directions in test 3 for sulphuric acid) to any dry bismuth compound. A hard, brittle bead of metallic bismuth is produced, which, if dissolved in a little concentrated hydrochloric acid, aided by a few drops of nitric acid, and the solution then be strongly diluted with water, gives a dense white precipitate of bismuth subchloride,

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

Tests 1, 5, and 6 together are sufficient to identify a bismuth compound. The insoluble or sub-salts are the most stable, and can be dissolved by acids, forming the normal salts. The latter cannot exist in aqueous solution, except in the presence of an acid. The decomposition of normal salts of bismuth by water into insoluble sub-salts is the most characteristic property of bismuth. One other metal resembles it in this respect, namely, antimony, but its sulphide has an orange color.

The most readily obtained sub-salt of bismuth is the subchloride, BiOCl. If no precipitate occurs when diluting the nitrate solution

(because of too much acidity), addition of solution of ammonium or sodium chloride produces a precipitate of the subchloride immediately.

## 81. SILVER. MERCURY.

**Silver, Ag = 107.88 (Argentum**

This metal falls in the second column of the periodic table in the copper, silver, gold family, which has already been referred to under Copper. In contrast to copper, the oxide of silver is a strong base, the salts of silver are normal rather than basic, and as a rule they are not hydrolyzed by water and are neutral to litmus. Like copper, silver enters into complex radicals, and its halogen salts, like cuprous halides, are insoluble in water. Silver oxide, like that of gold and platinum, but unlike that of copper, is decomposed by heat into silver and oxygen.

**Occurrence.**—Silver is found to some extent in the free state in nature, and contains gold and copper. Native copper always contains some silver. Silver also occurs as silver sulphide, either alone or associated with lead sulphide (argentiferous galena). To a small extent it is found as silver sulphantimonite (pyrargyrite), $Ag_3SbS_3$, and silver sulpharsenite (proustite), $Ag_3AsS_3$, and also as chloride (horn-silver), AgCl.

**Preparation and Properties.**—Silver contained in crude copper is recovered from the sediment of impurities that accumulates in the tanks during the electrolytic refining of copper, in which process a slab of impure copper as anode in a bath of copper sulphate is gradually dissolved and deposited as pure copper on a thin sheet of copper serving as cathode. In the case of lead obtained from silver-bearing galena, the silver is recovered by Parke's process in which the principle of extraction by immiscible solvents is employed. Molten zinc and lead do not alloy or mix except to a very small extent. Molten lead dissolves 1.6 per cent. of zinc, and zinc 1.2 per cent. of lead. Silver is much more soluble in zinc than in lead. The silver-bearing lead is melted and thoroughly stirred with some zinc, which dissolves nearly all of the silver. After a time the zinc collects on the surface and, as it solidifies before the lead, can easily

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QUESTIONS.—What are the properties of lead, and from what ore is it obtained? What is litharge, and how does it differ from red lead? Give the composition of nitrate, carbonate, and iodide of lead; how are they made? State the analytical reactions for lead. How is copper found in nature? How many oxides of copper are known; what is their composition, and under what conditions are they formed? What is "blue vitriol;" how is it made, and what are its properties? How does ammonium hydroxide act on cupric solutions? Mention tests for copper. What is the composition of subnitrate and subcarbonate of bismuth; how are they made from metallic bismuth, and what explanation is given in regard to their constitution?

be removed. Any lead adhering to the zinc is removed by careful heating whereby the lead melts and runs off. The zinc is removed by distillation, and the small amount of lead remaining in the silver is removed by oxidizing it to lead oxide in a current of air in a furnace.

Silver is the whitest of all metals, and takes the highest polish; it is the best conductor of heat and electricity, and melts at about 1000° C. (1832° F.); it is univalent, and forms but one series of salts; it is not affected by the oxygen of the air at any temperature, but is readily acted upon by traces of hydrogen sulphide, which forms a black film of sulphide upon the surface of metallic silver. Hydrochloric acid scarcely acts on silver, nitric and sulphuric acids dissolve it. Heated caustic alkalies have no action on silver, whereas platinum is attacked by them.

While many of the non-metallic elements have long been known to exist in allotropic forms, none of the metals had been obtained in such a condition until quite recently, when it was shown that silver is capable of assuming a number of allotropic modifications. These are obtained chiefly by precipitating silver from solutions by different reducing agents. While normal silver is white, the allotropic forms have distinct colors—blue, bluish-green, red, purple, yellow—and differ also in many other respects. Thus they are converted into silver chloride by highly diluted hydrochloric acid, which does not act on common silver; they are soluble in ammonia water, and act as reducing agents upon a number of substances, such as permanganates, ferricyanides, etc. Allotropic silver can be converted into the common form by different forms of energy—for instance, by heat, electricity, and the action of strong acids.

This allotropic form of silver is known as *colloidal silver*, and its solution in water is not a true, but a *colloidal solution*. Such a solution has the same freezing- and boiling-point as water itself, and it has been shown that the colloid is simply suspended in the liquid, although it is in too fine a state of division to be retained by a filter-paper. Colloidal solutions of silver, gold, or platinum result when electric discharges pass between wires of these metals held under water.

**Collargol** (**Argentum Credé**) is a preparation of colloidal (soluble) silver, said to contain 85.87 per cent. of silver and a small amount of albumin. It is bluish-black, scale-like, soluble in 20 parts of water. Albumin is added to prevent precipitation of silver from its solution by acids and salts, or by heating. It is incompatible with the usual silver reagents.

*Collargol Ointment* (*Unguentum Credé*) is an ointment containing 15 per cent. of collargol, of a dark, bluish-gray color.

Silver is too soft for use as coin or silverware, and therefore is alloyed with from 5 to 25 per cent. of copper, which causes it to become harder, and consequently gives it more resistance to the wear and tear by friction.

Pure silver may be obtained by dissolving silver coin in nitric acid, when a blue solution, containing the nitrates of copper and silver, is

formed. By the addition of sodium chloride to the solution a white, curdy precipitate of *silver chloride*, AgCl, forms, while cupric nitrate remains in solution. The silver chloride is washed, dried, mixed with sodium carbonate, and heated in a crucible, when sodium chloride is formed, carbon dioxide escapes, and a button of silver is found at the bottom of the crucible:

$$2AgCl + Na_2CO_3 = 2NaCl + CO_2 + 2Ag + O.$$

*Experiment* 43. Dissolve a small silver coin in nitric acid, dilute with water, and precipitate the clear liquid with an excess of solution of sodium chloride. The washed precipitate of silver chloride may be treated with sodium carbonate, as stated above, or may be converted into metallic silver by the following method: Place the dry chloride in a small porcelain crucible and apply a gentle heat until the chloride has fused; when cold, place a piece of sheet zinc upon the chloride, cover with water, to which a few drops of sulphuric acid have been added, and set aside for a day, when the silver chloride will be found to have been decomposed with liberation of metallic silver and formation of zinc chloride.

A simpler method is to heat the silver chloride with a solution of formaldehyde and a few drops of alkali, or with glucose and alkali. Metallic silver in a finely divided state is obtained, which, after washing, may be fused into a lump.

**Silver Nitrate** (*Argenti Nitras*) **$AgNO_3$ = 169.89.**—Pure silver is dissolved in nitric acid:

$$3Ag + 4HNO_3 = NO + 2H_2O + 3AgNO_3.$$

The solution is evaporated to dryness with the view of expelling all free acid, the dry mass dissolved in hot water and crystallized.

If the silver used should contain copper, the latter may be eliminated from the mixture of silver and cupric nitrate by evaporating to dryness and fusing, when the latter salt is decomposed, insoluble cupric oxide being formed. The fused mass is dissolved in water, filtered, and again evaporated for crystallization.

When silver nitrate, after the addition of 4 per cent. of hydrochloric acid, is fused and poured into suitable moulds it yields the white cylindrical sticks which are known as *moulded silver nitrate caustic*, *lunar caustic*, or *lapis infernalis*.

Silver nitrate forms colorless, transparent, tabular, rhombic crystals, or, when fused, a white, hard substance; it is soluble in less than its own weight of water, the solution having a neutral reaction. Exposed to the light, especially in the presence of organic matter, silver nitrate blackens in consequence of decomposition; when brought in contact with animal matter, it is readily decomposed into free nitric acid and metallic silver, which produces the characteristic black stain; it is this decomposition, and the action of the free nitric acid, to which the strongly caustic properties of silver nitrate are due.

Silver nitrate is used for various kinds of indelible inks and hair-dyes, and very largely in the manufacture of those silver compounds employed for photographic purposes.

**Photography.**—Photography is the art of obtaining images of objects by means of chemical changes produced in certain substances (chiefly compounds of silver or platinum) by the action of light. Three separate operations are required to obtain the image: they are exposure, developing, and fixation.

The *exposure* of a light-sensitive surface to a projected image of the object to be photographed is made in the camera, which is so arranged that the image can be thrown upon the surface by means of a lens. The surface used is generally that of a glass plate or a gelatine film, sensitized with the bromide or iodide of silver.

On the exposed plate a chemical change has taken place in the silver salt wherever light has acted on it. The exact nature of this change is not understood, and nothing can be detected on the plate with the eye after exposure. But when the exposed plate is treated with certain solutions, called *developers*, that portion of the silver salt which has been acted upon by light is decomposed with the formation of a deposit of metallic silver, forming the visible image. The acting constituent of developers are deoxidizing agents, such as pyrogallol, hydroquinone, ferrous sulphate, etc.

After the silver image has appeared there yet remains on the plate that portion of the silver salt which has not been acted on by light, and consequently not by the developer. This portion of the undecomposed silver salt must be removed before the plate can be taken to the light, and this removal, called *fixation*, is accomplished by immersion of the plate in a fixing solution of sodium thiosulphate, $Na_2S_2O_3$ (hyposulphite), which dissolves the salt in consequence of the formation of a double salt of the composition $Ag_2S_2O_3.2Na_2S_2O_3$; this is eliminated by washing in water.

The image thus obtained is called a *negative*, because it shows dark what ought to be light, and *vice versa*. By placing this negative upon sensitized material (generally paper) and permitting light to pass through the negative to the underlying paper the light-sensitive material is chemically affected most where the silver deposit in the negative is the thinnest, and *vice versa*. By developing and fixing the exposed paper the positive picture is obtained.

**Silver Oxide** (*Argenti Oxidum*), **$Ag_2O$ = 231.76.** Made by the addition of an alkali hydroxide to silver nitrate:

$$2AgNO_3 + 2KOH = 2KNO_3 + H_2O + Ag_2O.$$

A dark brown, almost black, powder, but very sparingly soluble in water, imparting to the solution a weak alkaline reaction. It is a strong base, and easily decomposed into silver and oxygen.

**Antidotes.**—Sodium chloride, white of egg, or milk, followed by emetic.

**Complex Silver Compounds.**—A great many combinations of silver with organic substances have been introduced and a few are extensively employed in medicine. These compounds usually differ in properties from the inorganic salts of silver. They are antiseptic and less irritating than silver nitrate.

*Argonin, silver-casein,* is a soluble casein compound containing 4.28 per cent. of silver. It is a nearly white powder, soluble in water, from which the silver is not precipitated by sodium chloride or hydrogen sulphide. It is also soluble in alkalies, egg-albumin, blood-serum, etc.

*Argyrol, silver vitellin,* is a compound of a derived proteid and silver oxide, containing from 20 to 25 per cent. of silver. It occurs as black, glistening hygroscopic scales, freely soluble in water and glycerin, insoluble in oils and alcohol. It is said to be incompatible with acids and most of the neutral and acid salts in strong solution.

*Protargol* is a compound of albumin and silver, containing 8.3 per cent. of silver. It is a yellow powder, soluble in 2 parts of cold water. The silver is not precipitated by the usual reagents, such as alkalies, sulphides, chlorides, bromides, iodides, nor by heat. It is compatible with picric acid and its salts and with most metallic salts, but is precipitated by cocaine hydrochloride, which, however, may be prevented by addition of boric acid. It is a non-irritant bactericide and antiseptic, extensively used as a substitute for silver nitrate.

### Tests for Silver.

(Use a 1 per cent. solution of silver nitrate in distilled water.)

1. Add to the solution hydrogen sulphide or ammonium sulphide: a dark brown precipitate of silver sulphide is produced:

$$2AgNO_3 + H_2S = 2HNO_3 + Ag_2S.$$

2. Add hydrochloric acid, or solution of any soluble chloride: a white, curdy precipitate of silver chloride is produced, which is insoluble in dilute acids, but soluble in ammonium hydroxide and in potassium cyanide:

$$AgNO_3 + NaCl = NaNO_3 + AgCl.$$

3. Add potassium chromate or dichromate solution: a red precipitate of silver chromate, $Ag_2CrO_4$, is formed (Plate II, 7).

4. Add sodium phosphate solution: a pale yellow precipitate of silver phosphate, $Ag_3PO_4$, is formed, which is soluble in ammonia and in nitric acid. Free phosphoric acid does not give a precipitate.

5. Solutions of alkali hydroxides precipitate dark brown silver oxide, soluble in ammonia water, forming a complex hydroxide, $Ag(NH_3)_2.OH$.

6. Solution of potassium iodide or bromide gives a pale yellow precipitate.

7. Metallic copper or zinc precipitates metallic silver from solutions of silver in any form of combination. (See page 294.)

Test 2 is sufficient to identify silver in ordinary solutions, for, although mercurous and lead chloride are insoluble in water and dilute acids, silver chloride alone of these three insoluble chlorides is soluble in ammonia water. Silver forms a number of complex combinations with organic compounds from which it is not easily

precipitated, but by reduction of the silver to the metallic state and solution of the metal in nitric acid, the tests may be applied. The same procedure applies also to inorganic insoluble silver compounds, as AgCl, AgBr, AgI, $Ag_2S$.

All silver salts are soluble in ammonia water, except the iodide and sulphide; hence the latter alone can be precipitated from an ammoniacal solution. In these solutions complex combinations, as $Ag(NH_3)_2.NO_3$, $Ag(NH_3)_2Cl$, are formed, which are salts of the hydroxide, $Ag(NH_3)_2.OH$. In this respect silver acts very much like copper. These compounds dissociate thus:

$$Ag(NH_3)_2NO_3 \rightleftarrows Ag(NH_3)_2^{\cdot} + NO_3'.$$

The $Ag(NH_3)_2^{\cdot}$ ions yield a slight amount of $Ag^{\cdot}$ ions, but not enough to be precipitated by any of the reagents except iodide and sulphide. The concentration of $Ag^{\cdot}$ ions given by the latter precipitates is less than that given by the $Ag(NH_3)_2^{\cdot}$ ions, hence precipitation takes place. (See page 148.)

Solutions of alkali cyanides and thiosulphates dissolve all silver compounds, giving complex substances of the form $KAg(CN)_2$ and $Na_3Ag(S_2O_3)_2$. The ions of these are $K^{\cdot} + Ag(CN)_2'$, and $3Na^{\cdot} + Ag(S_2O_3)_2'''$. Such a slight amount of $Ag^{\cdot}$ ions are formed from these compounds that no reagent will give a precipitate. That there are some $Ag^{\cdot}$ ions, however, is shown by the fact that active metals, like zinc, separates the silver from the solutions. Also that in electroplating silver is deposited from cyanide solution.

Soluble silver salts are not hydrolyzed, and are, therefore, neutral.

## Mercury, Hydrargyrum, Hg = 200.6 (Quicksilver).

This element falls in the third column of the periodic table as was stated in chapter 24 on Magnesium. It is a member of the family which consists of glucinum, magnesium, zinc, cadmium and mercury, all of which have a valence of 2, but mercury also has a valence of 1. Mercurous halides, like cuprous and silver halides, are insoluble in water, and decomposed when exposed to light. Mercury, like silver, does not form hydroxides. The oxides act exclusively as bases, although weak ones. The soluble mercurous and mercuric salts are considerably hydrolyzed by water and basic salts are easily formed.

**Occurrence and Properties.**—Mercury is found sometimes in small globules in the metallic state, but generally as mercuric sulphide or *cinnabar*, a dark red mineral. The chief supply was formerly obtained from Spain and Austria; now, however, large quantities are obtained from California; it is also imported from Peru and Japan.

Mercury is obtained from cinnabar either by roasting it, whereby the sulphur is converted into sulphur dioxide, or by heating it with lime, which combines with the sulphur, while the metal volatilizes, and is condensed by passing the vapors through suitable coolers.

Mercury is the only metal showing the liquid state at the ordinary temperature; it solidifies at —40° C. (—40° F.), and boils at 357° C.

(675° F.); but is slightly volatile at all temperatures; it is almost silver-white, and has a bright metallic lustre; its specific gravity is 13.56 at 15° C. (59° F.).

Pure mercury should present a bright surface even after agitation with air; when dropped on paper it should form globules which roll about freely, retain their globular form and leave no streaks. Commercial mercury is often contaminated with tin, lead, bismuth, and zinc. Such impurities cause a trail of dross when globules are made to roll over paper.

Mercury can be purified by repeated distillation, or by covering it with dilute nitric acid and agitating the mass frequently during two days. The total of the base metals, with some mercury, pass in solution, which is washed out with water, after which the mercury is dried by setting it in a warm place.

Mercury is peculiar in that its molecule contains but one atom, at least when in the state of a gas; in the liquid and solid states it may contain two atoms, like most other elements, but we have as yet no means of proving this fact.

Mercury forms, like copper, two series of compounds, distinguished as mercuric and mercurous compounds. In the former, mercury is bivalent, while in mercurous compounds the atom exerts a valence of one. It was long supposed that this was due to the fact that two mercury atoms were joined together, each atom thereby losing one of its points of affinity, leaving but one point for combining with another atom or radical. This view necessitated the existence of two mercury atoms in the molecule of every mercurous compound, the composition, for instance, of mercurous chloride being ClHg–HgCl or $Hg_2Cl_2$. There are, however, good reasons to believe that mercury is univalent in mercurous compounds, the composition of mercurous chloride being, consequently, HgCl. Similarly, copper is assumed to be univalent in cuprous compounds.

Mercury is not affected by the oxygen of the air, nor by hydrochloric acid, while chlorine, bromine, and iodine combine with it directly, and warm sulphuric and nitric acids dissolve it.

Mercury is used in the metallic state for many scientific instruments (thermometer, barometer, etc.); for making amalgams; for extracting gold from the ore; for manufacturing from it all of the various mercury compounds, and those official preparations in which mercury exists in the metallic state.

These latter preparations are: *Mercury with chalk, mass of mercury,* or *blue pill, mercurial ointment,* and *mercurial plaster.* Mercury exists in a metallic, but highly subdivided, state in these preparations, which are made by intimately mixing (triturating) metallic mercury with the different substances used (viz., chalk, pill-mass, fat, lead-plaster). It is most probable that the action of these agents upon the animal system is chiefly due to the conversion of small quantities of mercury into mercurous oxide, which, in contact with the acids of the gastric juice or with perspiration, are converted into soluble compounds capable of being absorbed.

**Amalgams.** Alloys containing mercury are termed amalgams. Mercury unites with most metals, and with some of them it forms definite compounds. Dental alloys used for amalgamation are composed chiefly of silver and tin with one or more of the following metals: gold, platinum, copper, zinc. Dental amalgams are made by reducing the alloy ingot to fine shavings or filings, which are triturated with the necessary quantity of mercury to form a plastic mass, which becomes hard or sets.

The properties most essential for a good amalgam are strength, immutability as to volume, freedom from discoloration, and resistance to the action of the oral secretions. Many formulas have been suggested to obtain these results.

The addition of either gold, platinum, copper or zinc to a silver-tin alloy facilitates setting, while this is retarded by an excess of mercury or by the employment of an alloy that has been long exposed to the air or has been annealed. The change in form—*i. e.*, expansion or contraction—which an amalgam undergoes in hardening is very objectionable and difficult to completely overcome.

The discoloration of amalgams is in great measure due to the formation of sulphides, particularly upon those amalgams in which there is not complete chemical union of the metallic constituents. A proper proportion of zinc in an alloy prevents discoloration considerably, making, however, the alloy difficult to amalgamate, while the presence of copper greatly increases the tendency to discolor.

**Mercurous Oxide, $Hg_2O$** (*Black Oxide or Suboxide of Mercury*).—An almost black, insoluble powder, made by adding an alkaline hydroxide to a solution of mercurous nitrate:

$$2HgNO_3 + 2KOH = 2KNO_3 + H_2O + Hg_2O.$$

A similar decomposition takes place when alkaline hydroxides are added to insoluble mercurous chloride. A mixture of lime-water and mercurous chloride (calomel) is known as *black-wash;* when the two substances are mixed, calomel is converted into mercurous oxide, while calcium chloride is formed:

$$2HgCl + Ca(OH)_2 = CaCl_2 + H_2O + Hg_2O.$$

**Mercuric Oxide, HgO = 216.60.**—There are two mercuric oxides which are official; they do not differ in their chemical composition, but in their molecular structure.

The *yellow mercuric oxide, Hydrargyri oxidum flavum,* is made by pouring a solution of mercuric chloride into a solution of sodium hydroxide, when an orange-yellow, heavy precipitate is produced, which is washed and dried at a temperature not exceeding 30° C. (86° F.) (Plate IV, 3):

$$HgCl_2 + 2NaOH = HgO + 2NaCl + H_2O.$$

The *red mercuric oxide, Hydrargyri oxidum rubrum,* is made by heating mercuric nitrate, either by itself or after it has been intimately mixed with an amount of metallic mercury equal to the mercury in the nitrate used (Plate IV, 4). In the first case, nitrous fumes and oxygen are given off, mercuric oxide remaining:

$$Hg(NO_3)_2 = HgO + 2NO_2 + O.$$

In the other case, no oxygen is evolved:

$$Hg(NO_3)_2 + Hg = 2HgO + 2NO_2.$$

The red oxide of mercury differs from the yellow oxide in being more compact, and of a crystalline structure; while the yellow oxide is in a more finely divided state, and consequently acts more energetically when used in medicine. Yellow oxide, when digested on a water-bath with a strong solution of oxalic acid, is converted into white mercuric oxalate within fifteen minutes, while red oxide is not acted upon by oxalic acid under the same conditions.

When mercuric chloride is added to lime-water, a mixture is formed holding in suspension yellow mercuric oxide; this mixture is known as *yellow-wash*.

*Experiment* 44. Shake a *small* knifepointful of mercurous chloride (calomel) with 50 c.c. of lime-water. Note that the chloride instantly turns dark, due to formation of mercurous oxide (see reaction in text). The lime-water must be in excess.

Add about 1 c.c. of reagent solution of mercuric chloride to 50 c.c. of lime-water and stir. Yellow mercuric oxide is formed at once (see reaction in text). If the lime-water is not in excess, the precipitate will not be pure yellow, but whitish, due to formation of an oxychloride, $Hg_2OCl_2$.

Caustic alkalies produce the same results as above, but any excess of these stronger alkalies is objectionable for the purposes for which these "washes" are used.

*Experiment* 45. Heat some mercuric nitrate in a porcelain dish, placed in a fume chamber, until red fumes no longer escape. The remaining red powder is mercuric oxide, which, by further heating, may be decomposed into its elements.

**Mercurous Chloride** (*Hydrargyri Chloridum Mite*) **HgCl = 236.06** (*Calomel, Mild Mercurous Chloride, Subchloride or Protochloride of Mercury*).—Mercurous chloride, like mercurous oxide, may be made by different processes, but the article used medicinally is the one obtained (except it be otherwise stated) by sublimation and the rapid condensation of the vapor in the form of powder.

It is made either by subliming a mixture of mercuric chloride and mercury:

$$HgCl_2 + Hg = 2HgCl.$$

or by thoroughly mixing with mercuric sulphate a quantity of mercury equal to that contained in the sulphate; by this operation mercurous sulphate is obtained, which is mixed with sodium chloride, and sublimed from a suitable apparatus into a large chamber, so that the sublimate may fall in powder to the floor:

$$HgSO_4 + Hg + 2NaCl = Na_2SO_4 + 2HgCl.$$

Precipitated calomel, being in a finer state of subdivision, acts more energetically when used medicinally. It is obtained by precipitation of a soluble mercurous salt by any soluble chloride:

$$HgNO_3 + NaCl = NaNO_3 + HgCl.$$

Mercurous chloride, made by either process, generally contains traces of mercuric chloride, and should therefore be washed with hot water until the washings are no longer acted upon by ammonium sulphide or silver nitrate.

Mercurous chloride is a white, impalpable, tasteless powder, insoluble in water and alcohol; it volatilizes without fusing previously; when given internally, it should not be mixed with either mineral acids, alkali bromides, iodides, hydroxides, or carbonates, except the action of the decomposition products be desired.

**Mercuric Chloride** (*Hydrargyri Chloridum Corrosivum*) **$HgCl_2$ = 271.52** (*Corrosive Mercuric Chloride, Corrosive Sublimate, Perchloride or Bichloride of Mercury*).—Made by thoroughly mixing mercuric sulphate with sodium chloride, and subliming the mixture, when mercuric chloride is formed, and passes off in white fumes which are condensed in the cooler part of the apparatus, while sodium sulphate is left:

$$HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2.$$

Mercuric chloride is a heavy, white powder, or occurs in heavy, colorless, rhombic crystals or crystalline masses; it is soluble in 16 parts of cold and 2 parts of boiling water, and in about 3 parts of alcohol, in 4 parts of ether, and in about 14 parts of glycerin; when heated, it fuses and is volatilized; it has an acrid, metallic taste, an acid reaction, and strongly poisonous and antiseptic properties.

**Poison Tablets of Corrosive Mercuric Chloride** (*Toxitabellæ Hydrargyri Chloridi Corrosivi*), (*Corrosive Sublimate Tablets, Bichloride Tablets*), have the following specifications in the U. S. P.: Angular shape, each tablet having the word "Poison" and the skull and cross-bones design stamped upon it. Each tablet, weighing about 1 gram, contains 0.45 to 0.55 gram of mercuric chloride, the rest consisting chiefly of sodium chloride. The tablets should be colored blue, preferably with sodium indigotin-disulphonate.

The halogen salts of mercury are very little ionized in solution. On this account, mercuric chloride is much less hydrolyzed than mercuric nitrate, that is, there is not so much tendency to precipitate a basic salt. Mercuric chloride also has the tendency to form complex salts. Thus sodium chloride increases its solubility in water and causes the solution to become neutral, because of the formation of the salt, $HgCl_2.NaCl$ or $NaHgCl_3$. Mercuric chloride tablets are made up with sodium chloride, because the latter prevents the formation of insoluble chlorides and facilitates solution, although the activity of the mercury compound is somewhat lessened. Mercuric chloride is sometimes used as a preservative of specimens. It forms insoluble compounds with albumin and

prevents its decay. On this principle, albumin is given as an antidote in mercuric chloride poisoning.

**Mercurous Iodide** (*Hydrargyri Iodidum Flavum*) **HgI = 327.52** (*Yellow Iodide, Green Iodide or Protiodide of Mercury*).—Both iodides of mercury may be obtained either by rubbing together mercury and iodine in the proportions represented by the respective atomic weights, or by precipitation of soluble mercurous or mercuric salts by potassium iodide.

According to the U. S. P., mercurous iodide is made by the precipitation of a solution of mercurous nitrate, to which some nitric acid has been added, by a solution of potassium iodide:

$$HgNO_3 + KI = KNO_3 + HgI.$$

The precipitate is collected on a filter, well washed with water and alcohol, and dried between paper at a temperature not exceeding 40° C. (104° F.). During the whole operation light should be excluded as much as possible, as it decomposes the compound.

Mercurous iodide is a yellow, tasteless powder, almost insoluble in water. It is easily decomposed into mercuric iodide and mercury, becoming darker and assuming a greenish-yellow to green tint, due to the admixture of metallic mercury, which, in a finely divided state, is blue, and consequently causes a greenish mixture with the yellow iodide. (Plate IV, 5.)

**Mercuric Iodide** (*Hydrargyri Iodidum Rubrum*), **$HgI_2$ = 454.44** (*Red Iodide or Biniodide of Mercury*).—Made by mixing solutions of potassium iodide and mercuric chloride, when a pale yellow precipitate is formed, turning red immediately (Plate IV, 6):

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

Mercuric iodide is soluble both in solution of potassium iodide and mercuric chloride, for which reason an excess of either substance will cause a loss of the salt when prepared. It is a scarlet-red, tasteless powder, almost insoluble in water and but slightly soluble in alcohol; on heating or subliming it turns yellow in consequence of a molecular change which takes place; on cooling, and, more quickly, on pressing or rubbing the yellow powder, it reassumes the original condition and the red color.

When mercuric iodide is dissolved in potassium iodide solution, a complex salt is formed, $HgI_2.2KI$, or $K_2HgI_4$, from which many of the usual reagents fail to precipitate the mercury. For example, caustic potash has no effect on the compound, and such an alkaline solution is known as Nessler's reagent. This reagent gives a yellow color with traces of ammonia, and a brown precipitate with larger amounts:

$$2HgI_2 + 4NH_3 = Hg_2NI + 3NH_4I.$$

Nessler's reagent is used in water analysis for detecting traces of ammonia. The compound, $Hg_2NI$, is called dimercur-ammonium iodide.

**Mercuric Sulphate, $HgSO_4$.**—When mercury is heated with strong sulphuric acid (the presence of nitric acid facilitates the formation) chemical action takes place between the two substances, sulphur dioxide being liberated and mercuric sulphate formed, which upon evaporation of the solution is obtained as a heavy, white, crystalline powder:

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2.$$

**Yellow Mercuric Subsulphate $HgSO_4.(HgO)_2$** (*Basic Mercuric Sulphate, Turpeth Mineral, Mercuric Oxysulphate*).—When mercuric sulphate, prepared as directed above, is thrown into boiling water, it is decomposed into an acid salt which remains in solution, and a basic salt which is precipitated. As shown by its composition, it may be looked upon as mercuric sulphate in combination with mercuric oxide. It is a heavy, lemon-yellow, tasteless powder, almost insoluble in water.

*Mercurous sulphate*, $Hg_2SO_4$. When mercuric sulphate is triturated with a sufficient quantity of mercury, direct combination takes place, and the mercurous salt is formed:

$$HgSO_4 + Hg = Hg_2SO_4.$$

**Nitrates of Mercury.**—*Mercurous nitrate*, $HgNO_3$, and *Mercuric nitrate*, $Hg(NO_3)_2$, may both be obtained as white salts by dissolving mercury in nitric acid. The relative quantities of the two substances present determine whether mercurous or mercuric nitrate be formed. If mercury is present in excess the mercurous salt, if nitric acid is present in excess the mercuric salt, is formed, the latter especially on heating. Both salts are white and soluble in water containing free acid. Water alone causes decomposition of the nitrates, similar to that of the sulphates, resulting in the formation of insoluble basic salts, the composition of which depends on the relative proportions of the mercury salt and water used.

*Experiment* 46.—Heat gently a small globule (about 1 gram) of mercury with 2 c.c. of nitric acid until red fumes cease to escape. If some of the mercury remains undissolved, the solution will deposit crystals of mercurous nitrate on cooling. Use some of the solution, after being diluted with much water, for mercurous tests. Use another portion as follows: Heat the solution, or some of the crystals, with about an equal weight of nitric acid until no more red fumes escape. Add to a few drops of the diluted liquid a little hydrochloric acid, which, if the conversion of the mercurous into mercuric salt has been complete, will give no precipitate. If, however, one should be formed, the solution is heated with more nitric acid until no precipitate is formed by hydrochloric acid, when the solution is evaporated and set aside for crystallization.

The respective changes may be represented by the following equations:

$$3Hg + 4HNO_3 = 3HgNO_3 + 2H_2O + NO;$$
$$3HgNO_3 + 4HNO_3 = 3Hg(NO_3)_2 + 2H_2O + NO.$$

**Mercuric Sulphide, HgS.**—This compound has been mentioned as the chief ore of mercury, occurring crystallized as *cinnabar*, which has a *red* color (Plate IV, 2). The same compound may, however, be obtained by passing hydrogen sulphide through mercuric solutions, when at first a white precipitate is formed (a double compound of the sulphide of mercury in combination with the mercuric salt), which soon turns *black* (Plate IV, 1):

$$HgCl_2 + H_2S = 2HCl + HgS.$$

The black, amorphous, mercuric sulphide may be converted into the red, crystallized variety by sublimation, and is then the preparation known as *red sulphide of mercury, cinnabar, or vermilion*. It forms brilliant dark red crystalline masses, or a fine bright scarlet powder, which is insoluble in water, hydrochloric or nitric acid, but soluble in nitrohydrochloric acid.

Mercuric and mercurous sulphides may be made also by triturating the elements mercury and sulphur in the proper proportions, when they combine directly.

**Ammoniated Mercury** (*Hydrargyrum Ammoniatum*), **$NH_2HgCl$ = 252.09** (*White Precipitate, Mercurammonium Chloride*).—This compound is made by pouring solution of mercuric chloride into ammonia-water, when a white precipitate falls, which is washed with highly diluted ammonia-water and dried at a low temperature:

$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O.$$

As shown by the composition of this compound, it may be regarded as ammonium chloride, $NH_4Cl$, in which two atoms of hydrogen have been replaced by one atom of the bivalent mercury. The mercurammonium salts are of a different type from those combinations formed when copper, silver, zinc, etc., salts are dissolved in ammonia-water. The former are all insoluble in water.

Ammoniated mercury is a white, tasteless, insoluble powder.

*Mercurous salts* with ammonia-water give black insoluble precipitates consisting of a mixture of mercurammonium salts and mercury which causes the black appearance. For mercurous chloride and nitrate the reactions are:

$$2HgCl + 2NH_3 = HgNH_2.Cl + Hg + NH_4Cl.$$
$$2HgNO_3 + 2NH_3 = HgNH_2.NO_3 + Hg + NH_4NO_3.$$

It should be noted that in the case of mercury salts, ammonia-water does not precipitate hydroxides, as it does in other cases.

Ammoniated mercury and calomel are both white and insoluble in water; the former is poisonous while the latter is not. They may be distinguished chemically as follows: Ammoniated mercury is soluble in dilute nitric or acetic acid, and silver nitrate added to the solution gives a white precipitate (AgCl), while calomel is insoluble; ammonia-water added to ammoniated mercury does not change its appearance, but when added to calomel, the latter becomes black; with caustic alkalies, ammoniated mercury gives off ammonia, and a yellow compound is formed.

## Summary of analytical characters of metals of the lead group.

| | *Lead.* | *Copper.* | *Bismuth.* | *Silver.* | *Mercuric salts.* | *Mercurous salts.* | *Cadmium.* |
|---|---|---|---|---|---|---|---|
| Hydrogen sulphide . . . | Black precipitate. | Black precipitate. | Dark-brown precipitate | Black precipitate. | Black precipitate. | Black precipitate. | Yellow precipitate. |
| Sodium hydroxide . . . . | White precipitate. | Blue precipitate turning brown on boiling | White precipitate. | Brown precipitate. | Yellow precipitate. | Black precipitate. | White precipitate. |
| Ammonia water . . . . | White precipitate. | Pale-blue precipitate | White precipitate. | Brown precipitate. | White precipitate. | Black precipitate. | White precipitate. |
| In excess of reagent . . | Insoluble | Dark blue solution. | Insoluble. | Colorless solution. | Insoluble. | Insoluble. | Colorless solution. |
| Sodium carbonate . . . . | White precipitate. | Greenish-blue precipitate. | White precipitate. | Pale-yellow precipitate. | Reddish-brown precipitate. | Yellowish precipitate. | White precipitate. |
| Potassium iodide . . . . | Yellow precipitate. | Yellow precipitate. | Brown precipitate. | Pale-yellow precipitate | Scarlet-red precipitate. | Yellowish-green precipitate. | ..... |
| In excess of reagent . . | Sparingly soluble. | Insoluble. | Insoluble | Insoluble. | Soluble. | Partly soluble. | ..... |
| Potassium chromate . . . | Yellow precipitate | Orange precipitate. | ..... | Dark-red precipitate. | Orange precipitate. | Brick-red precipitate. | ..... |
| Hydrochloric acid . . . . | White precipitate, soluble in hot water. | ..... | ..... | White precipitate, soluble in ammonia water. | ..... | White precipitate, turning dark with ammonia. | ..... |
| Sulphuric acid . . . . . | White precipitate. | ..... | ..... | ..... | ..... | White precipitate. | ..... |

**Tests for Mercury.**

| | *Mercurous salts.* (Mercurous nitrate, $HgNO_3$ may be used.) | *Mercuric salts.* (Mercuric chloride, $HgCl_2$, may be used.) |
|---|---|---|
| 1. Hydrogen sulphide, or ammonium sulphide. | Black precipitate of mercuric sulphide, with mercury. $2HgNO_3 + H_2S = 2HNO_3 + HgS + Hg.$ | Black precipitate of mercuric sulphide. (Precipitate may be white or gray, with an insufficient quantity of the reagent.) (See above.) (Plate IV., 1.) |
| 2. Potassium iodide. | Green precipitate of mercurous iodide (Plate IV., 7): $HgNO_3 + KI = KNO_3 + HgI.$ | Red precipitate of mercuric iodide (See above.) (Plate IV., 6.) |
| 3. Potassium or sodium hydroxide. | Dark-brown precipitate of mercurous oxide, $Hg_2O$ (Plate IV., 5). | Yellow precipitate of mercuric oxide HgO. (See above.) (Plate IV., 3.) |
| 4. Ammonium hydroxide. | Black precipitate of a mixture of mercury and mercuric-ammonium chloride (see explanation above). | White precipitate of a mercuric ammonium salt is formed. (See explanation above.) |
| 5. Potassium or sodium carbonate. | Yellowish precipitate of mercurous carbonate, which is unstable. | Brownish-red precipitate of basic mercuric carb., mixed with mercuric oxychloride. |
| 6 Hydrochloric acid or soluble chlorides. | White precipitate of mercurous chloride is produced: $HgNO_3 + HCl = HNO_3 + HgCl.$ | No change. |

7. Stannous chloride produces, in solutions of mercury, a white precipitate, which turns dark gray on heating with an excess of the reagent. The reaction is due to the strong reducing or deoxidizing property of the stannous chloride, which itself is converted into stannic chloride, while the mercury salt is first converted into a mercurous salt and afterward into metallic mercury:

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4;$$
$$2HgCl + SnCl_2 = 2Hg + SnCl_4.$$

8. Dry mercury compounds, when mixed with sodium carbonate and potassium cyanide, and heated in a narrow test-tube, are decomposed with liberation of metallic mercury, which condenses in small globules in the cooler part of the tube.

9. A piece of bright metallic copper when placed in a slightly acid mercury solution becomes coated with a dark film of metallic mercury, which by rubbing becomes bright and shining, and may be volatilized by heat. (See Solution Tension, page 294.)

10. All compounds of mercury are completely volatilized by heat, either with or without decomposition.

Tests 2, 4, 7, 8, and 9 will show the presence of mercury in any of its compounds. Those that are insoluble in water may be dissolved by a little concentrated hydrochloric with a few drops of nitric acid, forming mercuric chloride. Excess of acid is removed by evaporation before applying reagents.

**Antidotes.**—Albumen (white of egg), of which, however, not too much should be given at one time, lest the precipitate formed by the mercuric salt and albumin be redissolved. The antidote should be followed by an emetic to remove the albuminous mercury compound.

*Ionic conditions.* The simple mercury compounds give mercurous ions, $Hg^{\cdot}$, and mercuric ions, $Hg^{\cdot\cdot}$, which show different behaviors toward reagents, as seen in the tests above. The mercury ions are colorless, and are not formed extensively from any compound. The disinfecting and poisonous properties of mercury compounds depend upon the presence of the ions. Mercuric chloride in the dry state is inactive, and its solution in alcohol or ether is almost inert as a disinfectant, because there are practically no mercury ions formed.

Salts in general have a high degree of ionization, but salts of mercury and cadmium are remarkable exceptions. For this reason mercury salts show some peculiar behaviors. For example, the halogen salts of mercury dissociate so little (the bromide and iodide less than the chloride) that they are scarcely affected by sulphuric or nitric acid. Sodium chloride with sulphuric acid gives hydrochloric acid, and with nitric acid it gives chlorine Mercuric cyanide, $Hg(CN)_2$, is so minutely dissociated, that the presence of either $Hg^{\cdot\cdot}$ ions or $(CN)'$ ions cannot be shown by precipitation with many reagents. Thus, silver nitrate does not precipitate the $(CN)'$ ions, as AgCN, nor do alkalies precipitate $Hg^{\cdot\cdot}$ ions, as HgO. But hydrogen sulphide precipitates mercury from any of its soluble compounds, because mercuric sulphide is practically completely insoluble and unionized. It is for this reason that the sulphide is not dissolved by any acid, even when concentrated and heated, except nitrohydrochloric.

Mercury is deposited from all its compounds, whether soluble in water or not, by the metals higher up in the electrochemical series. Hence, it is not advisable to use vermilion in paint to be applied to metallic surfaces. Red lead is better for this purpose.

The complex salts which mercuric chloride forms with alkali chlorides dissociate in part so that mercury is contained in the complex negative ion, and to this extent loses its disinfectant property. The ionization equation for this type of compound is illustrated in the case of the sodium compounds, $NaCl.HgCl_2$ or $NaHgCl_3$, and $2NaCl.HgCl_2$ or $Na_2HgCl_4$:

$$NaHgCl_3 \rightleftarrows Na^{\cdot} + HgCl_3';$$
$$Na_2HgCl_4 \rightleftarrows 2Na^{\cdot} + HgCl_4''.$$

But there is considerable dissociation also into $Hg^{\cdot\cdot}$ ions and $Cl'$ ions. Hence with not too much sodium chloride present and in very dilute solution, the mercuric chloride tablets containing sodium or ammonium chloride do not lose materially in germicidal power, since a relatively large proportion of the ions are the active $Hg^{\cdot\cdot}$ ions.

The complex potassium mercuric iodide, $K_2HgI_4$, gives $K^{\cdot}$ ions and $HgI_4''$ ions, but very few $Hg^{\cdot\cdot}$ ions. Hence the failure of some reagents, as alkalies and carbonates, to give a precipitate in a solution of the compound.

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QUESTIONS.—How is silver obtained from the native ores, and how may it be prepared from silver coin? State of silver nitrate: its composition, mode of preparation, properties, and names by which it is known. Give analytical reactions for silver. How is mercury found in nature; how is it obtained from the native ore; what are its physical and chemical properties? Mention the

## 32. ARSENIC.

As = 74.96.

**General Remarks Regarding the Metals of the Arsenic Group.**—The metals belonging to either of the five groups, considered heretofore, show much resemblance to each other in their chemical properties, and consequently in their combinations. This is much less the case among the six metals (As, Sb, Sn, Au, Pt, Mo) which are classed together in this group. In fact the chief resemblance which unites these metals is the insolubility of their sulphides in dilute acids and the solubility of these sulphides in ammonium sulphide (or alkali hydroxides), with which they form soluble double compounds; the oxides have also a tendency to form acids. In most other respects no general resemblance exists between these metals. On the other hand, arsenic and antimony have many properties in common, and resemble in many respects the non-metallic elements phosphorus and nitrogen, as may be shown by a comparison of their hydrides, oxides, acids, and chlorides.

| | | | | |
|---|---|---|---|---|
| $NH_3$ | $N_2O_3$ | $N_2O_5$ | | $NCl_3$. |
| $PH_3$ | $P_2O_3$ | $P_2O_5$ | $H_3PO_4$ | $PCl_3$. |
| $AsH_3$ | $As_2O_3$ | $As_2O_5$ | $H_3AsO_4$ | $AsCl_3$. |
| $SbH_3$ | $Sb_2O_3$ | $Sb_2O_5$ | | $SbCl_3$. |

### Arsenic.

Found in nature sometimes in the native state, but generally as sulphide or arsenide. One of the most common arsenic ores is the arseniosulphide of iron, or *mispickel*, FeSAs. *Realgar* is the native red sulphide, $As_2S_2$, and *orpiment* or *auripigment*, the native yellow sulphide, $As_2S_3$. Arsenides of cobalt, nickel, and other metals are not infrequently met with in nature. Certain mineral waters contain traces of arsenic compounds.

Arsenic may be obtained easily by heating arsenous oxide with charcoal, or by allowing vapors of arsenous oxide to pass over charcoal heated to redness:

$$As_2O_3 + 3C = 3CO + 2As.$$

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three oxides of mercury; how are they made, what is their composition, what is their color and solubility? State of the two chlorides of mercury: their names, composition, mode of preparation, solubility, color, and other properties. Mention the same of the two iodides, as above, for the chlorides. State the difference between mercuric sulphate, basic mercuric sulphate, and mercurous sulphate. What is formed when ammonium hydroxide, calcium hydroxide, potassium or sodium hydroxide is added to either mercurous or mercuric chloride? Give tests answering for any mercury compound, and tests by which mercuric compounds may be distinguished from mercurous compounds.

In both cases the arsenic, when liberated by the reducing action of the charcoal, exists in the form of vapor, which condenses in the cooler part of the apparatus as a steel-gray metallic mass, which when exposed to the atmospheric air, loses the metallic lustre in consequence of the formation of a film of oxide.

*Experiment* 47.—Rub together in a mortar a small quantity of arsenous oxide and about ten times as much charcoal. Heat the mixture in a covered porcelain crucible with a small flame. After a time examine the cover for a dark deposit of arsenic.

When pure, arsenic is odorless and tasteless; it is very brittle, and volatilizes unchanged and without melting when heated to 180° C. (356° F.), without access of air. Heated in air, it burns with a bluish-white light, forming arsenous oxide. Although insoluble in water, yet water digested with arsenic soon contains some arsenous acid in solution, the oxide of arsenic being formed by oxidation of the metal by the oxygen absorbed in the water.

Arsenic is used in the metallic state as fly poison, and in some alloys, chiefly in shot, an alloy of lead and arsenic.

The molecule of arsenic contains four atoms, and not two, like most elements. It is trivalent in some compounds, quinquivalent in others.

Although arsenic is grouped with the metals in the analytical system of classification, in nearly all respects it behaves like a non-metal and should properly be classed as such. The oxides have only acidic character, and do not form salts with acids, as nitrates, sulphates, etc. The chloride, $AsCl_3$, can be obtained, but it decomposes at once in water, giving arsenous acid. It exists in solution only in the presence of excess of hydrochloric acid. When the solution is evaporated to dryness, arsenous oxide remains.

**Arsenic Trioxide** (*Arseni Trioxidum*) $\mathbf{As_2O_3}$ **= 197.92** (*Arsenous Oxide, White Arsenic, Arsenous Anhydride,* improperly *Arsenous Acid*). —This compound is frequently obtained as a by-product in metallurgical operations during the manufacture of metals from ores containing arsenic. Such ores are roasted (heated in a current of air), when arsenic is converted into arsenous oxide, which at that temperature is volatilized and afterward condensed in chambers or long flues.

Arsenous oxide is a heavy, white solid, occurring either as an opaque, slightly crystalline powder, or in transparent or semitransparent masses which frequently show a stratified appearance; recently sublimed arsenous oxide exists as the amorphous, semitransparent, glassy mass known as vitreous arsenous oxide, which gradually becomes opaque and ultimately resembles porcelain. This change is due to a rearrangement of the molecules into crystals which can be seen under the microscope.

The two modifications of arsenous oxide differ in their solubility in water, the amorphous or glassy variety dissolving more freely than

the crystallized. One part of arsenous oxide dissolves in from 30 to 80 parts of cold and in 15 parts of boiling water, the solution having at first a faint acrid and metallic, and afterward a sweetish taste. This solution contains the arsenous oxide not as such, but as *arsenous acid*, $H_3AsO_3$, which compound, however, cannot be obtained in an isolated condition, but is known in solution only:

$$As_2O_3 + 3H_2O = 2H_3AsO_3.$$

A second arsenous acid, termed *metarsenous acid* or *meta-arsenous acid*, $HAsO_2$, is known in some salts, as, for instance, in sodium metarsenite, $NaAsO_2$, which salt may be obtained by the action of arsenous oxide on the carbonate, bicarbonate, or hydroxide of sodium:

$$As_2O_3 + 2NaOH = 2NaAsO_2 + H_2O.$$

When heated to about 218° C. (424° F.) arsenous oxide is volatilized without melting; the vapors, when condensed, form small, shining, eight-sided crystals; when heated on charcoal, it is deoxidized, giving off, at the same time, an odor resembling that of garlic.

Arsenous oxide is frequently used in the arts and for manufacturing purposes, as, for instance, in the manufacture of green colors, of opaque white glass, in calico-printing, as a powerful antiseptic for the preservation of organic objects of natural history, and, finally, as the substance from which all arsenic compounds are obtained.

The official *Solution of arsenous acid*, *Liquor acidi arsenosi*, is a 1 per cent. solution of arsenous oxide in water to which 5 per cent. of diluted hydrochloric acid has been added.

The official *Solution of potassium arsenite*, *Liquor potasii arsenitis*, or *Fowler's solution*, is made by dissolving 1 part of arsenous oxide and 2 parts of potassium bicarbonate in 94 parts of water and adding 3 parts of compound tincture of lavender; the solution contains the arsenic as potassium metarsenite.

**Arsenic Oxide, $As_2O_5$** (*Arsenic Pentoxide, Arsenic Acid Anhydride*). —When arsenous oxide is heated with nitric acid, it becomes oxidized and is converted into *arsenic acid*, $H_3AsO_4$, from which the water may be expelled by further heating, when arsenic oxide is left:

$$2H_3AsO_4 = As_2O_5 + 3H_2O.$$

Arsenic oxide is a heavy, white, solid substance which, in contact with water, is converted into arsenic acid. This acid resembles phosphoric acid in composition, but differs from it in not forming pyro- and metarsenic acids. Arsenic acid when moderately heated loses all its water and leaves the pentoxide, which at higher heat is decomposed into the trioxide and oxygen. Phosphoric acid, however, when heated is converted into metaphosphoric which can be volatilized, and phosphorus pentoxide does not decompose by heating. Sodium pyro-arsenate, perhaps, is formed when sodium arsenate is heated, but when the mass is dissolved in water arsenate is formed at once, whereas the pyrophosphate can be crystallized from water.

Arsenic oxide and arsenic acid are used largely as oxidizing agents in the manufacture of aniline colors.

**Disodium Hydrogen Arsenate** (*Sodii Arsenas*), **$Na_2HAsO_4.7H_2O$ = 312.08** (*Sodium Arsenate*).—This salt is made by fusing arsenous oxide with carbonate and nitrate of sodium.

$$As_2O_3 + 2NaNO_3 + Na_2CO_3 = Na_4As_2O_7 + N_2O_3 + CO_2.$$

Sodium pyro-arsenate is formed, nitrogen trioxide and carbon dioxide escaping. By dissolving in water and crystallizing, the official salt is obtained in colorless, transparent crystals:

$$Na_4As_2O_7 + 15H_2O = 2(Na_2HAsO_4.7H_2O).$$

*Exsiccated sodium arsenate, Sodii arsenas exsiccatus*, $Na_2HAsO_4$, is the product obtained by driving off all the water of crystallization at 150° C. (302° F.). *Liquor sodii arsenatis* is a 1 per cent. solution of exsiccated sodium arsenate in water, corresponding to 1.68 per cent. of the crystallized salt.

**Lead arsenate,** $Pb_3(AsO_4)_2$, is used for spraying plants to exterminate moths. It is a white, fusible powder, insoluble in water, ammonia, and ammonium salts. It is obtained by precipitation of basic lead acetate (subacetate) with sodium arsenate, or lead nitrate with excess of sodium arsenate:

$$3Pb(NO_3)_2 + 4Na_2HAsO_4 = Pb_3(AsO_4)_2 + 6NaNO_3 + 2NaH_2AsO_4.$$

**Hydrogen Arsenide, $AsH_3$** (*Arsine, Arsenetted or Arseniuretted Hydrogen*).—This compound is formed always when either arsenous or arsenic oxides or acids, or any of their salts, are brought in contact with nascent hydrogen, for instance, with zinc and diluted sulphuric acid, which evolve hydrogen:

$$As_2O_3 + 12H = 2AsH_3 + 3H_2O.$$
$$As_2O_5 + 16H = 2AsH_3 + 5H_2O.$$
$$AsCl_3 + 6H = AsH_3 + 3HCl.$$

Hydrogen arsenide is a colorless, highly poisonous gas, having a strong garlic odor. Ignited, it burns with a bluish flame, giving off white clouds of arsenous oxide:

$$2AsH_3 + 6O = As_2O_3 + 3H_2O.$$

When a cold plate (porcelain answers best) is held in the flame of arsenetted hydrogen, a dark spot of element arsenic (arsenic spots) is produced upon the plate (in a similar manner as a deposit of carbon is produced by a common luminous flame). The formation of this dark deposit may be explained by the fact that the heat of the flame decomposes the gas, and that, furthermore, of the two liberated elements, arsenic and hydrogen, the latter has the greater affinity for oxygen. In the centre of the flame, to which but a limited amount of oxygen penetrates, the latter is taken up by the hydrogen, arsenic being present in the free state until it burns in the outer cone of

the flame. It is this liberated arsenic which is deposited upon a cold substance held in the flame.

Arsenetted hydrogen, when heated to redness, is decomposed into its elements; by passing the gas through a glass tube heated to redness, the liberated arsenic is deposited in the cooler part of the tube, forming a bright metallic-looking ring.

**Sulphides of Arsenic.**—Three sulphides of arsenic are known. Two have been mentioned above as the native *disulphide* or *realgar*, $As_2S_2$, and the *trisulphide* or *orpiment*, $As_2S_3$. Disulphide of arsenic is an orange-red, fusible, and volatile substance, used as a pigment; it may be made by fusing together the elements in the proper proportions. Trisulphide is a golden-yellow, fusible, and volatile substance, which also may be obtained by fusing the elements, or by precipitating an arsenic solution by hydrogen sulphide (Plate V, 1).

The pentasulphide, $As_2S_5$, has the same color as the trisulphide, and is most readily obtained by acidifying a solution of a sulpharsenate:

$$2(NH_4)_3AsS_4 + 6HCl = 2H_3AsS_4 + 6NH_4Cl.$$
$$2H_3AsS_4 = 3H_2S + As_2S_5.$$

The tri- and pentasulphide of arsenic have acid properties, similar to the corresponding oxides. They unite with alkali sulphides to form soluble metasulpharsenites and sulpharsenates:

$$As_2S_3 + (NH_4)_2S = 2NH_4AsS_2.$$
$$As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3AsS_4.$$

When the trisulphide is dissolved in a solution of a polysulphide (yellow ammonium sulphide), a sulpharsenate is formed.

$$As_2S_3 + 3(NH_4)_2S + S_2 = 2(NH_4)_3AsS_4.$$

from which acids precipitate the pentasulphide. Both sulphides are also soluble in solutions of alkali hydroxides or carbonates, forming a mixture of metarsenite and metasulpharsenite, and arsenate and sulpharsenate respectively.

**Arsenous Iodide** (*Arseni Iodidum*), **$AsI_3$ = 455.72** (*Iodide of Arsenic*).—Arsenous iodide may be obtained by direct combination of the elements, and forms orange-red crystalline masses, soluble in water and alcohol, but decomposed by boiling with either of these liquids. It is used in the official preparation, *Solution of arsenous* and *mercuric iodides, Donovan's solution*, which is made by dissolving one part each of arsenous iodide and mercuric iodide in 98 parts of water.

### Tests for Arsenic.

(For arsenous compound, use a solution of arsenous oxide made by dissolving 0.5 gram in 100 c.c. of hot water and allowing to cool; for arsenic compound, use a 5 per cent. solution of sodium arsenate.)

1. Hydrogen sulphide produces in the solution of arsenous acid a yellowish coloration, but no precipitate. This is due to the fact that

the arsenic trisulphide remains in solution in the colloidal state and is precipitated only after a long time. Addition of some hydrochloric acid causes precipitation immediately of the yellow trisulphide (Plate V, 1):

$$2H_3AsO_3 + 3H_2S = 6H_2O + As_2S_3.$$

When a rapid stream of hydrogen sulphide is passed into a hot acidified solution of an arsenate, a yellow precipitate of arsenic pentasulphide is gradually formed:

$$2H_3AsO_4 + 5H_2S = 8H_2O + As_2S_5.$$

Solution of ammonium sulphide or caustic alkali readily dissolves both sulphides of arsenic. Addition of acid reprecipitates the sulphides.

2. Add 1 or 2 c.c. of silver nitrate solution to about 5 c.c. of the arsenous acid solution; no preciptate results. Now pour carefully upon the surface of the mixture a little very dilute ammonia-water; a *yellow* precipitate of silver arsenite (Plate V, 3) is formed at the line of contact of the two liquids, which may be increased by cautiously mixing the liquids. The precipitate is soluble in excess of ammonia or in nitric acid. When solution of an arsenite instead of free arsenous acid is used, silver nitrate gives a precipitate at once, without addition of ammonia water:

$$H_3AsO_3 + 3AgNO_3 + 3NH_4OH = Ag_3AsO_3 + 3NH_4NO_3 + 3H_2O.$$
$$Na_3AsO_3 + 3AgNO_3 = Ag_3AsO_3 + 3NaNO_3.$$

Dissolve the precipitate in a slight excess of ammonia-water, add a few drops of caustic soda, and apply heat; a mirror of metallic silver is formed, due to the reducing action of the arsenite, which becomes arsenate.

When silver nitrate is added to the sodium arsenate solution (about 3 c.c.), a *reddish-brown* precipitate of silver arsenate is formed, which is soluble in ammonia-water or nitric acid (Plate V, 4):

$$Na_2HAsO_4 + 3AgNO_3 = Ag_3AsO_4 + 2NaNO_3 + HNO_3.$$

3. Add 2 or 3 drops (avoid excess) of copper sulphate solution to about 5 c.c. of the arsenous acid, and overlay the mixture with very dilute ammonia-water as in test 2 (if an arsenite is used, ammonia-water is unnecessary); a green precipitate of copper arsenite, *Scheele's green*, $CuHAsO_3$, is produced (Plate V, 2). Add some caustic alkali solution to the precipitate and boil; red cuprous oxide is formed, due to reduction by the arsenite, which becomes arsenate. (*Schweinfurt green*, copper aceto-arsenite, $3Cu(AsO_2)_2.Cu(C_2H_3O_2)_2$, is obtained by adding solution of copper acetate to a boiling solution of arsenite. This and Scheele's green are often called *Paris green.*)

When copper sulphate solution is added to the sodium arsenate solution, a greenish-blue precipitate of copper arsenate, $CuHAsO_4$, is

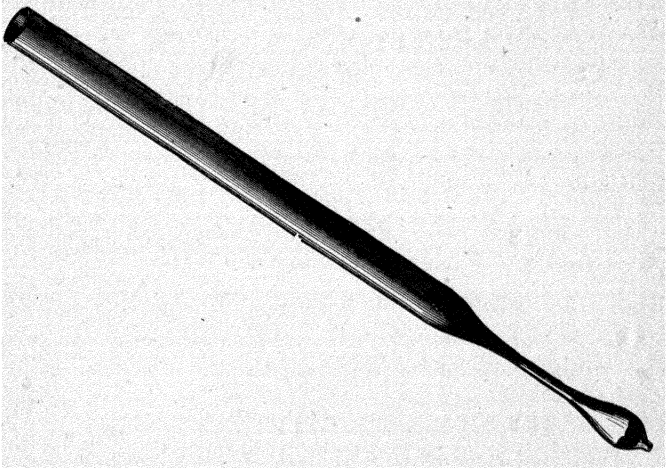
formed. All these precipitates are soluble in ammonia-water and in acids.

4. Add to a little of the arsenate solution, a clear mixture of magnesium sulphate, ammonium chloride and ammonia-water, and shake; a white precipitate of ammonium magnesium arsenate is formed, $NH_4MgAsO_4$ (see test 1 under Phosphoric Acid).

Magnesium arsenite is insoluble in water, but soluble in ammonia-water and in ammonium chloride solution.

5. Add to a few drops of the arsenate solution, excess of ammonium molybdate solution (about 5 c.c.) and warm gently; a yellow precipitate of ammonium arsenomolybdate is formed, similar in all respects to the corresponding phosphorus compound. (Arsenic is the only other element which behaves like phosphorus toward the molybdate reagent.) Arsenites give no precipitate with the reagent.

FIG. 18.



6. Heat any dry arsenic compound, after being mixed with some charcoal and dry potassium carbonate in a very narrow test-tube (or, better, in a drawn-out glass tube having a small bulb on the end): the arsenic compound is decomposed and the element arsenic deposited as a metallc ring in the upper part of the contraction. (Fig. 18.)

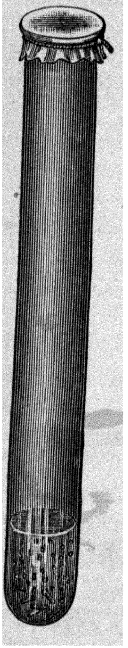
7. Heat arsenous or arsenic oxide upon a piece of charcoal by means of a blow-pipe: a characteristic odor of garlic is perceptible.

8. *Reinsch's Test.*—A thin piece of copper, having a bright metallic surface, placed in a solution of arsenic, strongly acidified with concentrated hydrochloric acid, becomes, upon heating the solution, coated with a dark steel-gray deposit of arsenic, which can be vaporized by application of heat. Antimony also responds to this test.

9. *Bettendorf's Test,* U. S. P. Add to any arsenic compound, dissolved in concentrated hydrochloric acid, an equal volume of freshly prepared satuated solution of stannous chloride in concentrated hydrochloric acid, and heat in boiling water for fifteen minutes; a brown color or precipitate is formed, due to separation of the arsenic. Antimony does not respond to this test.

10. *Gutzeit's Test.* Place a small piece (about 1 gram) of pure zinc in a test-tube, add about 5 c.c. of dilute (5 per cent.) sulphuric acid and a few drops of any arsenic solution, which should not be alkaline. Fasten over the mouth of the test-tube a cap made of three thicknesses of pure filter-paper, and moisten the upper paper with a drop of a saturated solution of silver nitrate in water acidulated with about 1 per cent. of nitric acid. (Fig. 19.) Place the tube in a box so as to exclude all light, and examine the paper cap after awhile. Upon it will appear a bright yellow stain, rapidly if the quantity of arsenic be considerable, slowly if it be small. Upon moistening the yellow stain with water the color changes to brown or black. The action of hydrogen arsenide upon silver nitrate in the absence of water takes place with the formation of a yellow compound, thus:

FIG. 19.



$$AsH_3 + 6AgNO_3 = 3HNO_3 + Ag_3As.(AgNO_3)_3.$$

In the presence of water metallic silver is separated, showing a black or brown color:

$$AsH_3 + 6AgNO_3 + 3H_2O = 6HNO_3 + H_3AsO_3 + 6Ag.$$

Compounds of antimony treated in the above manner produce a dark spot upon the paper, but cause no previous yellow color.

*Modified Gutzeit's Test.* This was employed in nearly all instances in the U. S. P., VIII, where traces of arsenic were tested for in official products. It cannot be used in the case of bismuth or antimony compounds, for which Bettendorf's test is employed. The test is carried out as follows:

All the tests for arsenic bearing proper names are intended to be applied for the detection of minute quantities of arsenic. If arsenic compounds themselves are used, only very dilute solutions should be tested, in order to appreciate the delicacy of the tests. The arsenic should be in the form of an arsen*ous* compound for the above test, as in this condition it is more readily reduced to arsine. This is insured by adding to 5 c.c. of a 10 per cent. aqueous solution of the chemical to be tested (in some instances special previous treatment is necessary, which may be seen in the U. S. P.) 1 c.c. of a mixture of equal volumes of concentrated sulphuric acid and water, and 10 c.c. of fresh saturated solution of sulphur dioxide. The liquid is evaporated over boiling water until it is free from sulphur dioxide and has been

reduced to 5 c.c. in volume. It is then introduced into a 75 c.c. flask containing 2 or 3 grams of granular zinc and 20 c.c. of 8 per cent. hydrochloric acid, a small wad of clean dry gauze is inserted into the lower end of the neck of the flask, followed by a wad moistened with lead acetate solution. The mouth of the flask is then covered by folding over it a filter-paper, the center of which has previously been three times successively wet with a saturated alcoholic solution of mercuric chloride and dried. After one-half to one hour, the paper cap is examined for a yellow stain, which indicates arsenic. The presence of arsenic much in excess of the permissible limit of the U. S. P. (1 in 100,000) is shown by a distinct yellow to orange spot. All the reagents used must be free from arsenic, which is determined by making a blank test, omitting the chemical to be tested. The student should carry out the test on 2 or 3 c.c. of a $\frac{1}{5000}$ per cent. solution of arsenic trioxide, which need not be submitted to the reduction with sulphur dioxide. Antimony gives a dark coloration.

The test for traces of arsenic adopted in the present U. S. P., IX, while embracing the same chemical principles as in the modified Gutzeit's test, is too involved in apparatus and execution for description in this book.

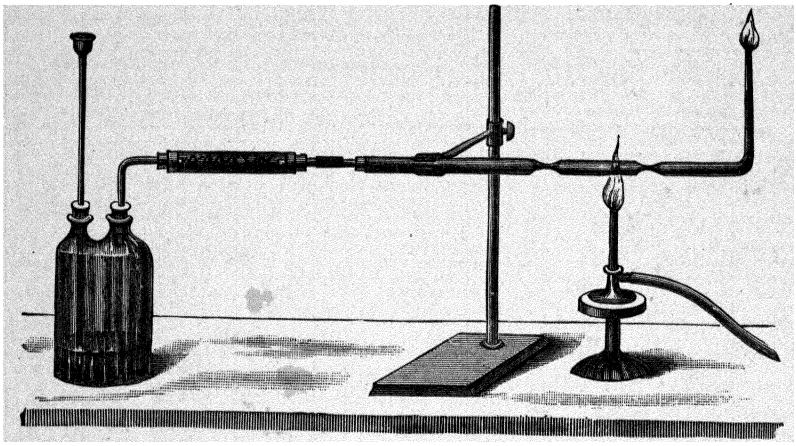
11. *Fleitmann's Test.* This is similar to the Gutzeit's test, the chief difference being that hydrogen is evolved in alkaline solution, which has the advantage that the presence of antimony does not interfere, because this metal does not form antimonetted hydrogen in alkaline solutions.

Place about 1 gram of pure zinc in a test-tube, add about 5 c.c. of potassium hydroxide solution and a few drops of the arsenic solution, which should not be acid. Provide paper cap as described in Gutzeit's test, and set the test-tube in a box containing sand heated to about 90° C. (194° F.). A brown or black stain of metallic silver will appear upon the paper.

12. *Marsh's Test.* While this test is not used now for qualitative determinations as much as formerly, it is of great value because it may serve for collecting the total amount of arsenic present in a specimen, thus permitting quantitative estimation. The apparatus (Fig. 20) used for performing this test consists of a glass vessel (flask or Woulf's bottle) provided with a funnel-tube and delivery-tube (bent at right angles), which is connected with a wider tube, filled with pieces of calcium chloride or plugs of asbestos; this drying-tube is again connected with a piece of hard-glass tube, about one foot long, having a diameter of $\frac{1}{4}$ inch, drawn out at intervals of about 3 inches, so as to reduce its diameter to $\frac{1}{8}$ inch. Hydrogen is generated in the flask by the action of sulphuric acid on zinc, and examined for its purity by heating the glass tube to redness at one of its wide parts for at least thirty minutes; if no trace of a metallic mirror is formed at the constriction beyond the heated point, the gas and

the substances used for its generation may be pronounced free from arsenic. (Both zinc and sulphuric acid often contain arsenic.)

FIG. 20.



Marsh's apparatus for detection of arsenic.

After having thus demonstrated the purity of the hydrogen, the suspected liquid, which must contain the arsenic either as oxide or chloride (not as sulphide), is poured into the flask through the funnel-tube. If arsenic is present in not too small quantities, the gas ignited at the end of the glass tube shows a flame decidedly different from that of burning hydrogen. The flame becomes larger, assumes a bluish tint, and emits an odor of garlic, while above it a white cloud appears which is more or less dense; a cold test-tube held inverted over the flame will be covered upon its walls with a white deposit of minute octahedral crystals of arsenous oxide; a piece of cold porcelain held in the flame becomes coated with a brown stain (arsenic spot) of arsenic. (See explanation above in connection with arsenetted hydrogen.)

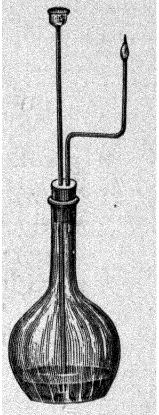
The glass tube heated, as above mentioned, at one of its wide parts, will show a bluish-black metallic mirror at the constriction beyond.

If quantitative determination is desired, the glass tube is heated in two places so as to cause all hydrogen arsenide to be decomposed. To collect, however, the arsenic from any gas that might escape, the end of the tube is inverted and placed into solution of nitrate of silver, which is decomposed by the hydrogen arsenide, silver and arsenous acid being formed. The arsenic solution should be introduced into the hydrogen generator in small portions, so as not to produce more hydrogen arsenide at a time than can be decomposed by the method given.

The only element which, under the same conditions, forms spots and mirrors similar to arsenic, is antimony; there are, however, sufficiently reliable tests to distinguish arsenic spots from those of antimony.

Arsenic spots treated with solution of hypochlorites (solution of bleaching-powder) dissolve readily; antimony spots are not affected. When nitric acid is added to an arsenic spot and evaporated to dryness and the spot moistened with a drop of silver nitrate, it turns brick-red; antimony spots treated in like manner remain white. Arsenic spots dissolved in ammonium sulphide and evaporated to dryness show a bright-yellow, antimony spots an orange-red, residue. Fig. 21 represents a simpler form of Marsh's apparatus, which generally will answer for students' tests.

FIG. 21.



Students' apparatus for making arsenic spots.

**Preparatory treatment of organic matter for arsenic analysis.** If organic matter is to be examined for arsenic (or for any other metallic poison), it ought to be treated as follows: The substance, if not liquid, is cut into pieces, well mashed and mixed with water; the liquid or semi-liquid substance is heated in a porcelain dish over a steam bath with hydrochloric acid and potassium chlorate until the mass has a uniform light yellow color and has no longer the odor of chlorine. By this operation all poisonous metals (lead and silver excepted, because insoluble silver chloride and possibly insoluble lead sulphate are formed) are rendered soluble even when present as sulphides, and may now be separated by filtration from the remaining solid matter The clear solution is heated and treated with hydrogen sulphide gas for several hours, when arsenic and all metals of the arsenic and lead groups are precipitated as sulphides, a little organic matter also being precipitated generally.

The precipitate is collected upon a small filter and treated with warm ammonium sulphide, which dissolves the sulphides of arsenic and antimony, leaving behind the sulphides of the lead group, which may be dissolved in nitric, or, if mercury be present, in nitro-hydrochloric acid, and the solution tested by the methods mentioned for the respective metals. The ammonium sulphide solution is evaporated to dryness, this residue mixed with nitrate and carbonate of sodium, and the mixture fused in a small porcelain crucible. By the oxidizing action of the nitrate, both sulphides are converted into the higher oxides, arsenic forming sodium arsenate, antimony forming antimonic oxide. By treating the mass with warm water, sodium arsenate is dissolved and may be filtered off, while antimonic oxide remains undissolved, and may be dissolved in hydrochloric acid. Both solutions may now be used for making the respective tests for arsenic or antimony.

*Comments.* Tests 1, 6, and 3 are sufficient to identify arsenic compounds. Test 3 will detect an arsenite in presence of an arsenate, and tests 4 and 5 an arsenate in presence of an arsenite. Test 10, especially in the modified form, and Test 12 are most often used to detect traces of arsenic.

Alkali arsenites are soluble in water; all others are either insoluble or difficultly soluble in water. Alkali arsenates and acid arsenates of the alkaline earths are soluble in water. All the salts are soluble in mineral acids.

Arsenous acid dissociates very slightly, and is therefore a weak acid. Its soluble salts are hydrolyzed to a considerable extent, and show an alkaline reaction. Boiling a solution of arsenous acid or its salts in hydrochloric acid results in a loss of arsenic by volatilization as arsenous chloride. Solutions of arsenic acid or its salts suffer no loss of arsenic in this manner.

Arsenic acid dissociates very much like phosphoric acid, but to a little less extent than the latter in solutions of equal concentration. Even in high dilution the dissociation is mainly thus:

$$H_3AsO_4 \rightleftarrows H^{\cdot} + H_2AsO_4'.$$

Further dissociation into $HAsO_4''$ and $AsO_4'''$ ions is very slight.

**Antidotes.** Moist, recently prepared ferric hydroxide or dialyzed iron are the best antidotes. Vomiting should be induced by tickling the fauces or by administering zinc sulphate, but not tarter emetic.

## 33. ANTIMONY. TIN. GOLD. PLATINUM. MOLYBDENUM.

### Antimony, Sb = 120.2 (Stibium).

This metal is found in nature chiefly as the trisulphide, $Sb_2S_3$, an ore which is known as *black antimony, crude antimony,* or *stibnite.*

The metal is obtained from the sulphide by roasting, when it is converted into oxide, which is reduced by charcoal. Antimony is a brittle, bluish-white metal, having a crystalline structure; it fuses at 450° C. (842° F.), and may at a higher temperature be distilled without change, provided air is excluded; heated in air it burns brilliantly.

Antimony is used in a number of important alloys, for instance, in type-metal, an alloy of lead, tin, and antimony.

The best solvent for antimony is hydrochloric acid, containing a little nitric acid, whereby antimonous or antimonic chloride is formed. Nitric acid converts it into antimonous or antimonic oxide, which are almost insoluble in the liquid.

Three oxides of antimony are known, namely, trioxide, $Sb_2O_3$, pentoxide, $Sb_2O_5$, and tetroxide, $Sb_2O_4$. Antimony differs from arsenic in that the trioxide is more basic than acidic, forming salts with mineral and organic acids. The salts with mineral acids, however, are decomposed by water, and require the presence of free acid for solution. Antimony pentoxide is exclusively acidic in character,

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QUESTIONS.—Which metals belong to the arsenic group; what are their characteristics? Which non-metallic elements does arsenic resemble? Mention some of the compounds showing this analogy. How is arsenic obtained in the free state; what are its physical and chemical properties; how does heat act upon it? What is white arsenic? State its composition, mode of manufacture, appearance, solubility, and other properties. Which three solutions, containing arsenic, are official, and what is their composition? How is arsenic acid obtained from arsenous oxide, and which arsenate is official? State composition and properties of arsenetted hydrogen, and explain its formation. What use is made of it in testing for arsenic? State the composition of realgar, orpiment, Scheele's green, and Schweinfurth green. Give a detailed description of the process by which arsenic can be detected in organic matter. Describe in detail the principal tests for arsenic.

forming metantimonates and pyro-antimonates with caustic alkalies. The tetroxide is neither basic nor acidic. It is formed when either of the other oxides is heated in air to a dull redness for a long time.

The compounds of antimony commonly met with are the chloride, sulphide, and double tartrate (tartar emetic).

**Antimony Trisulphide, $Sb_2S_3$** (*Antimonous Sulphide*).—The above-mentioned native sulphide, the black antimony, is found generally associated with other ores or minerals, from which it is freed by heating the masses, when the antimony sulphide fuses and is made to run off into suitable vessels for cooling. Thus obtained it forms steel-gray masses of a metallic lustre, and a striated, crystalline fracture, forming a grayish-black, lustreless powder, which is insoluble in water, but soluble in hydrochloric acid with liberation of hydrogen sulphide.

Antimonous sulphide found in nature is crystallized and *steel-gray* (Plate V, 6), but it may be obtained also in an amorphous condition as an *orange-red* (Plate V, 5) powder by passing hydrogen sulphide through an antimonous solution. By heating the orange-red sulphide, it is converted into the black variety.

The sulphides and oxides of antimony, like those of arsenic, combine with many metallic sulphides or oxides to form sulpho-salts or oxy-salts. Thus the sodium sulph-antimonite, $Na_3SbS_3$, and the sodium antimonite, $NaSbO_2$, are formed when antimonous sulphide is boiled with sodium hydroxide.

$$Sb_2S_3 + 4NaOH = Na_3SbS_3 + NaSbO_2 + 2H_2O.$$

By the addition of sulphuric acid, both salts are decomposed, sodium sulphate is formed, and antimonous sulphide is precipitated:

$$Na_3SbS_3 + NaSbO_2 + 2H_2SO_4 = Sb_2S_3 + 2Na_2SO_4 + 2H_2O.$$

While the above is the principal reaction, there is formed also some antimony oxide.

*Experiment* 48.—Intimately mix about 0.5 gram of finely powdered black antimony sulphide with some sodium carbonate and potassium cyanide. Heat this mixture with a blowpipe flame on charcoal till it fuses thoroughly and a bead of metallic antimony is obtained. Drop the molten antimony from the height of about a foot upon a sheet of paper and notice that characteristic grayish-white streaks are formed, radiating in all directions. Test the crust (left on the charcoal) on a silver coin for sulphur. Examine another bead of antimony for color, hardness, malleability, etc.; then try its solubility in acids in the order of hydrochloric, dilute sulphuric, nitric, and nitrohydrochloric acids.

**Antimony Pentasulphide, $Sb_2S_5$** (*Golden Sulphuret of Antimony*).—A red powder, which, like antimonous sulphide, forms sulpho-salts. It may be obtained by precipitation of acid solutions of antimonic acid by hydrogen sulphide.

**Antimonous Chloride, $SbCl_3$** (*Antimony Terchloride, Butter of Anti-*

*mony*).—Obtained by boiling the native sulphide with hydrochloric acid:

$$Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3.$$

The clear solution is evaporated and the remaining chloride distilled, when it is obtained as a white, crystalline, semitransparent mass.

By passing chlorine over antimonous chloride it is converted into *antimonic chloride*, $SbCl_5$, which is a fuming liquid.

*Experiment* 49.—Boil about 2 grams of black antimony with 10 c.c. of hydrochloric acid until most of the sulphide is dissolved. Set aside for subsidence, pour off the clear solution of antimonous chloride, evaporate to about half its volume and use solution for next experiment.

**Antimonous Oxide** (*Antimony Trioxide*).—When antimonous chloride is added to water decomposition takes place similar to the one which normal bismuth salts undergo by the action of water, viz., a white precipitate of oxychloride of antimony (antimonyl chloride), SbOCl, is formed, which, however, is mixed with antimonous oxide, as the following two reactions take place:

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$
$$2SbCl_3 + 3H_2O = Sb_2O_3 + 6HCl.$$

The relative proportions of the two constituents depend on the mode of manipulating and on the quantity of water used.

The white precipitate was formerly known as *powder of Algaroth*. It is completely converted into oxide by treating it with sodium carbonate:

$$2SbOCl + Na_2CO_3 = Sb_2O_3 + 2NaCl + CO_2.$$

The precipitate when washed and dried is a heavy, grayish-white, tasteless powder, insoluble in water, soluble in hydrochloric acid, and also in a warm solution of tartaric acid. Antimonous oxide, while yet moist, dissolves readily in potassium acid tartrate, forming the *double tartrate of potassium and antimony*, or *tartar emetic*, which salt will be more fully considered hereafter.

*Experiment* 50. Pour the antimonous chloride solution (obtained by Experiment 49), which should have been boiled sufficiently to expel all hydrogen sulphide, into 100 c.c. of water, wash by decantation the white precipitate of oxychloride thus obtained, and add to it an aqueous solution of about 1 gram of sodium carbonate. After effervescence ceases, collect the precipitate on a filter, wash well and treat some of the precipitate, while yet moist, with a solution of potassium acid tartrate, which dissolves it readily, forming tartar emetic. (For the latter compound see Index.)

**Antidotes.**—Poisonous doses of any preparation of antimony are generally quickly followed by vomiting: if this, however, has not occurred, the stomach-pump must be applied. Tannic acid in any form, or recently precipitated ferric hydroxide, should be administered.

### Tests for Antimony.

(Use a solution of antimony chloride prepared as in Experiment 49, and diluted to about 30 c.c. by adding, first, 2 or 3 c.c. of dilute hydrochloric acid, and then water cautiously. Also a 5 per cent. solution of tartar emetic, $K(SbO)C_4H_4O_6$, in water. Note that the latter dissolves easily and without decomposition.)

1. Add hydrogen sulphide to some of the solution of antimony chloride: an orange-red precipitate of antimonous sulphide ($Sb_2S_3$) is produced (Plate V, 5).

Hydrogen sulphide produces the same precipitate in the solution of tartar emetic.

2. Add yellow ammonium sulphide to the precipitated sulphide of antimony: this is dissolved and may be reprecipitated by neutralizing with an acid. The same results are obtained with caustic alkalies.

3. Produce a concentrated solution of antimonous chloride by evaporation or by dissolving the sulphide in hydrochloric acid, and pour it into water: a white precipitate of oxychloride is formed. (See explanation above.)

Add a few drops of dilute hydrochloric acid to some of the solution of tartar emetic: a white precipitate of oxychloride is also formed. In analysis, this might be mistaken for a chloride of silver, lead, or mercury, but it differs from the latter by being soluble in excess of the acid.

4. Add sodium hydroxide, ammonium hydroxide, or sodium carbonate to the antimony chloride solution: in either case white antimonous hydroxide, $Sb(OH)_3$, is produced, which is soluble in excess of sodium hydroxide.

The same reagents added to the solution of tartar emetic produce scarcely any precipitate, due to the solvent effect of the organic (tartaric) acid.

5. Boil a piece of bright metallic copper in the solution of antimonous chloride: a black deposit of antimony is formed upon the copper. By heating the latter in a narrow test-tube, the antimony is volatilized and deposited as a white incrustation of antimonous oxide upon the glass.

6. Use Gutzeit's or Marsh's test as described under Tests for Arsenic.

### Tin, Sn = 119 (Stannum).

This metal is found in nature chiefly as stannic oxide or *tin-stone*, $SnO_2$, from which the metal is easily obtained by heating with coal:

$$SnO_2 + 2C = Sn + 2CO.$$

Tin is an almost silver-white, very malleable metal, fusing at the comparatively low temperature of 228° C. (440° F.). It is used in many alloys, and chiefly in the manufacture of tin-plate, which is sheet-iron covered with a thin layer of tin.

Tin is bivalent in some compounds, quadrivalent in others. These combinations are distinguished as stannous and stannic compounds.

**Stannous Hydroxide, $Sn(OH)_2$,** is not known.—When a solution of sodium hydroxide or carbonate is added to a solution of stannous chloride, a precipitate, $H_2Sn_2O_3$, is formed, which is derived from $Sn(OH)_2$. When it is heated in an atmosphere of carbon dioxide, black stannous oxide, SnO, is formed, which ignites when heated in air, giving stannic oxide.

**Stannic Hydroxide, $H_2SnO_3$** (*Stannic Acid*).—Stannic hydroxide is formed when a solution of stannic chloride is boiled:

$$SnCl_4 + 3H_2O = H_2SnO_3 + 4HCl.$$

It is also formed when sodium hydroxide or carbonate is added to a solution of stannic chloride, or when just enough of an acid is added to a solution of a stannate to effect decomposition:

$$Na_2SnO_3 + 2HCl = 2NaCl + H_2SnO_3.$$

It is a white substance insoluble in water, but easily soluble in hydrochloric, nitric, or sulphuric acid, forming the corresponding salt, and in caustic alkalies, forming stannates.

*Metastannic acid* is formed when tin is treated with concentrated nitric acid. It is a white powder insoluble in water and acids, but seems to have the same composition as stannic acid. It forms salts with alkalies which are entirely different in properties and composition from the stannates, and are known as *metastannates*. Two sodium salts are known, $Na_2Sn_5O_{11}$ and $Na_2Sn_9O_{19}$. When the acid is heated, stannic oxide, $SnO_2$, is formed.

**Stannous Chloride, $SnCl_2$** (*Protochloride of Tin*).—Obtained by dissolving tin in hydrochloric acid by the aid of heat:

$$Sn + 2HCl = SnCl_2 + 2H.$$

Sufficiently evaporated, the solution yields crystals of the composition $SnCl_2.2H_2O$. Stannous chloride is a strong deoxidizing agent, frequently used as a reagent for arsenic, mercury, and gold, which metals are precipitated from their solutions in the metallic state. It is used also in calico printing.

**Stannic Chloride, $SnCl_4$** (*Perchloride of Tin*).—Stannous chloride may be converted into stannic chloride either by passing chlorine through its solution or by heating with hydrochloric and nitric acids.

### Tests for Tin.

(Stannous chloride, $SnCl_2$, and stannic chloride, $SnCl_4$, may be used.)

1. Add hydrogen sulphide to solution of a stannous salt: brown stannous sulphide is precipitated (Plate V, 7):

$$SnCl_2 + H_2S = 2HCl + SnS.$$

The precipitate is soluble in yellow ammonium sulphide.

2. Add hydrogen sulphide to a solution of a stannic salt: yellow stannic sulphide is precipitated (Plate V, 8):

$$SnCl_4 + 2H_2S = 4HCl + SnS_2.$$

The precipitate is soluble in ammonium sulphide.

3. Sodium or potassium hydroxide added to a stannous salt produces a white precipitate of stannous hydroxide, $H_2Sn_2O_3$. The same reagents added to a stannic salt produce white stannic acid, $H_2SnO_3$. Both precipitates are soluble in excess of the alkali, forming stannite, $Na_2SnO_2$, and stannate, $Na_2SnO_3$.

## Gold, Au = 197.2 (Aurum).

Gold occurs in nature chiefly in the free state, generally associated with silver, copper, and possibly with other metals, sometimes also in combination with selenium and tellurium. This impure gold is separated from most of the adhering sand and rock by a mechanical process of washing, in which advantage is taken of the high specific gravity of the metallic masses. The remaining mixture of heavy material is treated with mercury, which dissolves gold and silver, leaving behind most other impurities. The gold amalgam is placed in a retort and heated, when the mercury distils over, while the gold is left behind.

From ores containing but little gold the metal is now extracted largely by treating the finely powdered material with a solution of potassium cyanide, which forms a soluble double cyanide of gold and potassium, $AuK(CN)_2$. From the solution gold is precipitated electrolytically or by adding metallic zinc.

**Refining gold.** Gold obtained by either of the above processes is not pure, but has to be purified or *refined* by methods which differ according to the nature or quantity of the impurities present, or according to the use to be made of the gold. The methods employed may be divided into two classes, viz., dry and wet processes. In the dry or crucible methods the operation is conducted at a temperature sufficiently high to melt the gold, while in the wet processes the dissolving action of acids is made use of.

Of dry methods may be mentioned the following: The gold is fused in a clay or graphite crucible which has been glazed on the inside with borax, and a stream of chlorine is passed through the molten mass. The chlorides of zinc, bismuth, arsenic, and antimony, when present, are volatilized, while the chlorides of silver and copper rise to the top, forming, with some of the borax, a layer over the purified gold. Another method consists in melting the gold in a crucible, prepared as before mentioned, and adding gradually a mixture of potassium nitrate and carbonate with borax. All base metals are converted into oxides which become dissolved in the borax; but silver is not eliminated by this method. It may, however, be gotten rid of by heating to a temperature just below fusion, the granulated gold with about one-sixth of its weight of sulphur. The mixture should be protected with a layer of fine charcoal. Silver sulphide is formed during the operation and the gold, after being fused, may be cast into an ingot mold.

Another dry method, used, however, more for assaying gold ores or gold alloys than for purifying gold on a large scale, is the *cupellation process.* It depends on the solubility of gold in molten lead and the readiness with which lead takes up oxygen when heated in an oxidizing flame. In carrying out the process the material to be operated on is fused with a quantity of lead amply sufficient to dissolve the metals present. The resulting alloy, called the *lead button,* is then submitted to fusion on a very porous support, made of bone-ash, and called a *cupel.* All metals except gold and silver are oxidized; the lead oxide, which is fusible, takes up all other oxides, and the whole of this mass is absorbed by the porous bone-ash, on the surface of which is finally left a button of gold and silver.

Of *wet processes* for the separation of gold and silver is to be mentioned the method known as *parting.* It depends on the extraction of the silver (and copper, if present) by treating the granulated alloy with nitric acid of a specific gravity of 1.32. This dissolves silver and copper, but does not act on the gold. The process, however, is not applicable to an alloy containing more than 33 per cent. of gold, and it was believed that it should not exceed 25 per cent. In order to subject to this process an alloy which is richer in gold, the alloy is first fused with silver, and as it was customary to use 3 parts of silver for 1 part of impure gold the process became known as *quartation* or *inquartation.* In place of nitric acid, sulphuric acid of a specific gravity of 1.84 may be used. Gold which has been freed from base metals and silver by any of the above-described methods is known as *refined gold,* but it is rarely absolutely pure. It retains traces of base metals or silver and all of the platinum if originally present.

*Chemically pure gold,* or as it is termed by the mints gold 1000 fine, may be obtained by the following process. Nitro-hydrochloric acid, consisting of one part of nitric acid and two parts of hydrochloric acid, is added in small portions to the granulated gold, refined by one of the ordinary processes, until its solution, with the aid of heat, has been effected. This solution of gold chloride is evaporated nearly to dryness at a moderate heat. If platinum be suspected the remaining mass is dissolved in very little water, and to the solution is added an equal volume of alcohol and some ammonium chloride. If platinum be present it is precipitated as ammonium platinic chloride and separated by filtration. The filtrate is diluted with four parts of water and permitted to stand for several days in order to cause complete precipitation of any silver chloride present. To the filtrate a clear solution of ferrous sulphate is added which causes the precipitation of gold. After decanting the supernatant liquid and thoroughly washing the precipitate with distilled water it is treated with hot concentrated acid, to eliminate traces of iron or copper. The purified gold is again washed, dried, fused in a borax-lined crucible and poured into an ingot mold. The chemical reaction which occurs in the precipitation of gold with ferrous sulphate is this:

$$AuCl_3 + 3FeSO_4 = FeCl_3 + Fe_2(SO_4)_3 + Au.$$

Many other reducing agents may be used in place of ferrous sulphate for the precipitation of gold. Thus it is precipitated in a spongy or crystalline condition by gently heating the gold solution with oxalic acid:

$$2AuCl_3 + 3H_2C_2O_4 = 6HCl + 6CO_2 + 2Au.$$

Sulphurous acid precipitates gold in scales:

$$2AuCl_3 + 3H_2SO_3 + 3H_2O = 6HCl + 3H_2SO_4 + 2Au.$$

Zinc and many other base metals precipitate gold as a brown powder:

$$2AuCl_3 + 3Zn = 3ZnCl_2 + 2Au.$$

Elementary phosphorus, and many other organic and inorganic reducing agents, may be used similarly for the precipitation of gold from its solutions, or this precipitation may be effected electrolytically.

*Cohesive gold*, used in dentistry, may be obtained by heating gold foil to redness, by which is restored its cohesiveness, which is greatly diminished during the conversion of pieces of gold into foil by beating.

Gold is orange-yellow by reflected light, and green by transmitted light; it fuses at 1200° C. (2192° F.), has a specific gravity of 19.36, and is a good conductor of heat and electricity. It is so malleable and ductile that 1 grain can be hammered into a film covering 54 square inches, and can be drawn into a wire, if protected by some more tenacious metal such as silver, so fine that 1 grain will measure 550 feet.

Tin, lead, antimony, arsenic, and bismuth destroy the ductility and malleability of gold, making it very brittle. A small proportion of platinum confers upon gold elasticity and increases its hardness.

Pure gold is too soft for general use, and therefore is alloyed with various proportions of silver and copper. It is customary to express the purity or fineness of gold in *carats*, an old term meaning a twenty-fourth part. Pure gold is 24 carats, while an alloy containing 75 per cent. of gold is said to be of 18 carats fineness. American coin is an alloy of 90 parts of gold and 10 parts of copper; jeweller's gold contains generally 75 per cent. or more of gold, the other metals being copper and silver; the varying proportions are well indicated by the color.

Gold is not affected by either hydrochloric, nitric, or sulphuric acid, but is dissolved by nitrohydrochloric acid, by free chlorine and bromine, and by mercury, with which it forms an amalgam.

Gold is trivalent generally, as in auric chloride, $AuCl_3$, but also univalent in some compounds, as in aurous chloride, AuCl.

**Gold Chloride, $AuCl_3$** (*Auric Chloride*).—Obtained by dissolving pure gold in nitrohydrochloric acid and evaporating the solution to dryness. A mixture of equal parts by weight of gold chloride and sodium chloride is official under the name of *gold and sodium chloride*. It is an orange-yellow, very soluble powder, containing about 30 per cent. of metallic gold.

### Tests for Gold.

(Solution of auric chloride, $AuCl_3$, may be used.)

1. Add hydrogen sulphide to the solution: brown auric sulphide, $Au_2S_3$, is precipitated, which is soluble in yellow ammonium sulphide.

2. Add ferrous sulphate to the solution and set aside for a few hours—metallic gold is precipitated as a dark powder:

$$AuCl_3 + 3FeSO_4 = Fe_2(SO_4)_3 + FeCl_3 + Au.$$

3. Many other reagents cause the separation of metallic gold from its solution, as, for instance, oxalic acid, sulphurous and arsenous acids, potassium nitrite, etc.

## Platinum, Pt = 195.2.

Platinum, like gold, is found in nature in the free state, the chief supply being derived from the Ural mountains, where it is associated with a number of metals (iridium, ruthenium, osmium, palladium, rhodium) resembling platinum in their properties.

While the solubility of platinum in molten lead is sometimes used for its separation by the cupellation process (see refining of gold) the abstraction of platinum is usually accomplished by the wet process. The material containing it is treated with nitro-hydrochloric acid under slight pressure, when platinic chloride is formed. The solution is evaporated to dryness and the mass heated to a temperature of 125° C. in order to decompose the higher chlorides of iridium and palladium, which metals, if present, would otherwise accompany the platinum. After dissolving the residue in water, ammonium chloride is added, which precipitates platinum as ammonium platinic chloride, $PtCl_4.2NH_4Cl$. The washed precipitate when heated to redness is completely decomposed, metallic platinum being left as a gray, spongy mass, which may be fused by means of the oxy-hydrogen flame or in an electric furnace.

Platinum is of great importance and value on account of its high fusing-point and its resistance to the action of most chemical agents for which reason it is used in the manufacture of vessels serving in chemical operations. While sulphuric, nitric, hydrochloric, and hydrofluoric acids have no action on platinum, it is readily attacked by chlorine, and at a red heat by caustic alkalies, sulphur, and phosphorus.

Platinum is of a silver-white color with a tinge of blue; it is very malleable and ductile; its rate of expansion by heat is low, about that of glass. This property is of value in the use of the metal for the pins of artificial teeth, and as a base for continuous gum work. Addition of iridium renders platinum harder, more rigid and more elastic, all of which properties platinum confers upon silver and gold.

The property of platinum to condense oxygen upon its surface and to dissolve hydrogen is made very conspicuous in *platinum sponge* and *platinum black*. The former is made by heating precipitated ammonium chloroplatinate, by which a gray mass of finely divided platinum is left; the latter is obtained as a black powder by adding zinc to chloroplatinic acid. Either of these forms of platinum, when thrown into a mixture of oxygen and hydrogen, causes instant explosion. This is an example of catalytic action, in which the speed of a chemical change is enormously increased. The gases condensed in the pores of the finely divided metal unite rapidly with production of sufficient heat to cause the rest of the gases to unite with explosion.

**Chloroplatinic Acid, $H_2PtCl_6.6H_2O$** (often called *Platinic Chloride*). —Chloroplatinic acid is obtained as reddish-brown deliquescent

crystals when platinum is dissolved in aqua regia and the solution evaporated. It serves as a valuable reagent for potassium and ammonium, as explained in connection with the analytical reactions of these bodies. In the acid and its salts platinum is in the anion, as $PtCl_6''$. The chloride, $PtCl_4$, is obtained by heating the chloroplatinic acid in a current of chlorine at 360° C. Its solution in water gives red, non-deliquescent crystals of the composition, $H_2PtCl_4O.4H_2O$.

*Chloroplatinous acid*, $H_2PtCl_4$, results when platinous chloride $PtCl_2$, is dissolved in hydrochloric acid. The potassium salt, $K_2PtCl_4$, is used in making platinum prints in photography. The corresponding barium platinocyanide, $BaPt(CN)_4.4H_2O$, forms light yellow crystals. Screens coated with this salt become luminous when Roentgen rays (*x*-rays) fall upon them. Such fluorescent screens are used for observing *x*-ray pictures. Ultra-violet and radium rays also affect the screens.

**Iridium, Ir = 193.1.** This element has been mentioned as one of the metals which accompany platinum in nature. It is obtained from the material left in the working of platinum ores.

Iridium has a grayish-white color and resembles polished steel; it is harder, more brittle, specifically heavier and less fusible than platinum. The increased hardness, rigidity and elasticity which iridium imparts to platinum makes the alloy a valuable dental material. Gold pens are often tipped with iridium which renders them more durable.

Compact pieces of iridium are insoluble in all acids; when finely divided it dissolves in nitro-hydrochloric acid. It is for these reasons that most of the iridium is left in the residue of the material from which platinum has been extracted. Several oxides, hydroxides and chlorides of iridium are known.

**Molybdenum, Mo = 96.** This metal is found in nature chiefly as sulphide, $MoS_2$, from which, by roasting, molybdic oxide. $MoO_3$, is obtained. The oxide, when dissolved in water, forms an acid which combines with metals, forming a series of salts termed molybdates. Of interest is *ammonium molybdate*, a solution of which in nitric acid is an excellent reagent for phosphoric acid, with which it forms a yellow precipitate, insoluble in acids, soluble in ammonium hydroxide.

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QUESTIONS.—How is antimony found in nature, and what are the properties of this metal? State the composition of antimonous sulphide, and its color when crystallized and amorphous. How do hydrochloric acid and alkali hydroxides act upon antimonous sulphide? Mention the two chlorides of antimony and state their properties. How is antimonous oxide made, and for what is it used? Give tests for antimony. State the use made of tin in the metallic state; mention the two chlorides of tin, and the use of stannous chloride. Describe processes for refining gold by the dry and wet methods. How are gold and platinum found in nature; by what acid may they be dissolved, and what is the composition of the compounds formed? Which is the most important compound of molybdenum, and what is its use?

**Summary of Analytical Characters of Metals of the Arsenic Group.**

| | *Arsenic.* | *Antimony.* | *Tin.* | *Gold* | *Platinum.* |
|---|---|---|---|---|---|
| Hydrogen sulphide . | Yellow precipitate. | Orange precipitate | Yellow or brown precipitate | Black precipitate | Dark-brown precipitate |
| Precipitate heated in strong hydrochloric acid . . | Insoluble. | Soluble. | Soluble. | Insoluble. | Insoluble. |
| Potassium hydroxide | ..... | White precipitate, soluble in excess. | White precipitate, soluble in excess. | Brownish precipitate, soluble in excess. | With excess of hydrochloric acid a yellow precipitate. |
| Ammonia water . . | ..... | White precipitate | White precipitate. | Brownish yellow precipitate | |
| Gutzeit's test . . . | Yellow stain, turning dark with water. | Dark stain. | ..... | ..... | ..... |
| Fleitmann's test . . | Dark stain. | ..... | ..... | ..... | ..... |

# III.

# ANALYTICAL CHEMISTRY.

## 34. INTRODUCTORY REMARKS AND PRELIMINARY EXAMINATION.

**General Remarks.**—Analytical chemistry is that part of chemistry which treats of the different analytical methods by which substances are recognized and their chemical composition determined. This determination may be either qualitative or quantitative, and, accordingly, a distinction is made between a *qualitative analysis*, by which simply the nature of the elements (or groups of elements) present in the substance under examination is determined, and a *quantitative analysis*, by which also the exact amount of these elements is ascertained.

In this book qualitative analysis will be considered chiefly, as the methods for quantitative determinations of the different elements are so numerous and so varied that a detailed description of them would occupy more space than can be devoted to analytical chemistry in this work. Some brief directions concerning quantitative determinations, especially by volumetric methods, are given in chapter 38. Everyone studying analytical chemistry should do it practically, that is, should perform for himself in a laboratory all those reactions which have been mentioned heretofore as characteristic of the different elements and their compounds, and, furthermore, should make himself acquainted with the methods by which substances are recognized when mixed with others, by analyzing various complex substances.

Such a course of practical work in a suitable laboratory is of the greatest advantage to all studying chemistry, and students cannot be too strongly advised to avail themselves of any facilities offered in performing chemical experiments, analytically or otherwise.

### Apparatus Needed for Qualitative Analysis.

1. Iron stand. (Fig. 22.)
2. Bunsen lamp with flexible tube (Fig. 22) or (where without gas-supply) spirit-lamp and alcohol.
3. Test-tube stand and one dozen assorted test-tubes. (Fig. 23.)

4. Three beakers from 100 to 150 c.c. capacity. (Fig. 24, *A*.)
5. Two flasks of 100 to 150 c.c. capacity. (Fig. 24, *B*.)

FIG. 22.

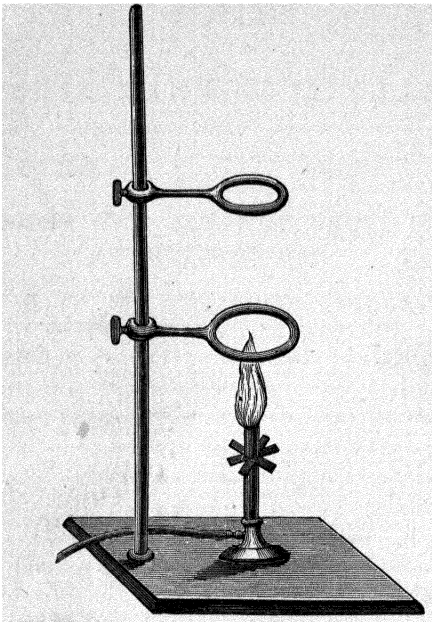


FIG. 23.

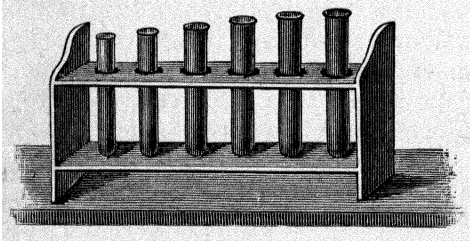
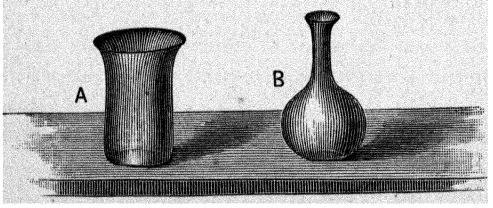


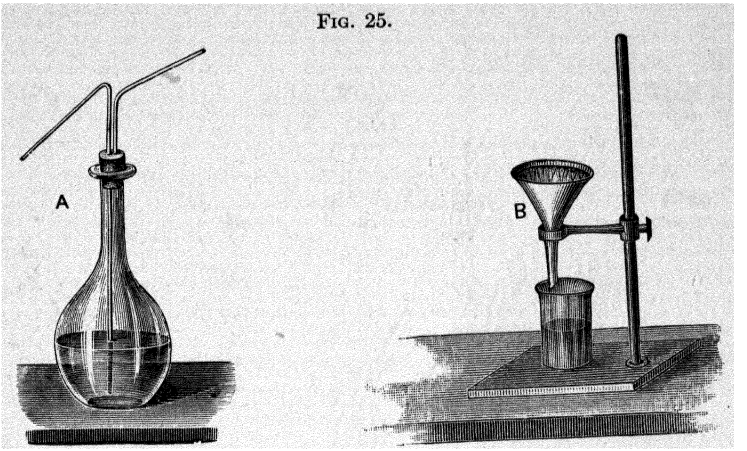
FIG. 24.




6. Wash-bottle of about 400 c.c. capacity. (Fig. 25, *A*.)
7. Three small glass funnels, about one and a half or two inches in diameter. (Fig. 25, *B*.)

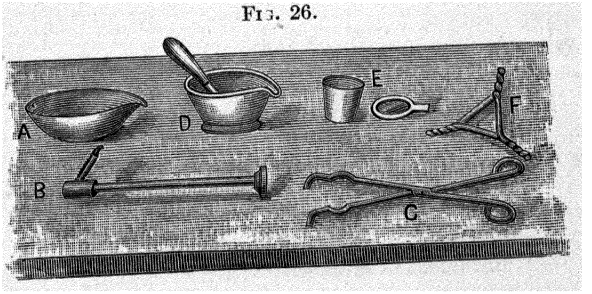
8. A few pieces of glass tubing about ten inches long, and some India-rubber tubing to fit the glass tubing.
9. Three glass rods.

FIG. 25.




10. Three small porcelain evaporating dishes, about two inches in diameter. (Fig. 26, *A*.)
11. Blowpipe. (Fig. 26, *B*.)
12. Crucible tongs. (Fig. 26, *C*.)

FIG. 26.




13. Round and triangular file.
14. Wire gauze, about six inches square, or sand tray.
15. On square inch of platinum foil (not too light), and six inches of platinum wire.
16. Filter-paper.
17. Pair of scissors.
18. One or two dozen assorted corks.
19. Sponge and towel.
20. Two watch-glasses.
21. Small pestle and mortar. (Fig. 26, *D*.)
22. Small porcelain crucible.
23. Small platinum crucible. (Fig. 26, *E*.)
24. Wire triangle to support the crucible. (Fig. 26, *F*.)

## Reagents Needed in Qualitative Analysis.

*a. Liquids.*

1. Sulphuric acid, sp. gr. 1.84, $H_2SO_4$.
2. Sulphuric acid diluted, sp gr 1.068 (1 part sulphuric acid, 9 parts water).
3. Hydrochloric acid, sp. gr. 1 16, HCl.
4. Hydrochloric acid diluted, sp gr. 1.049 (6 parts hydrochloric acid, 13 parts water).
5. Nitric acid, sp. gr. 1.42, $HNO_3$.
6. Acetic acid, sp. gr. 1.048, $C_2H_4O_2$.
7. Hydrogen sulphide, either the gas or its solution in water, $H_2S$.
8. Ammonium sulphide, $(NH_4)_2S$
9. Ammonium hydroxide (ammonia water), $NH_4OH$.
10. Ammonium carbonate, $(NH_4)_2CO_3$. A solution of one part of the commercial salt in a mixture of four parts of water and one part of ammonia water.
11. Ammonium chloride, $NH_4Cl$; ten per cent solution.
12. Ammonium oxalate, $(NH_4)_2C_2O_4$; five per cent. solution.
13. Ammonium molybdate, $(NH_4)_2MoO_4$ A five per cent solution of the salt in a mixture of equal parts of water and nitric acid.
14. Sodium hydroxide, NaOH.
15. Sodium carbonate, $Na_2CO_3$.
16. Sodium phosphate, $Na_2HPO_4$.
17. Sodium acetate, $NaC_2H_3O_2$.
18. Potassium chromate, $K_2CrO_4$.
19. Potassium dichromate, $K_2Cr_2O_7$.

} Ten per cent. solutions.

20. Potassium iodide, KI
21. Potassium ferrocyanide, $K_4Fe(CN)_6$.
22. Potassium ferricyanide, $K_6Fe_2(CN)_{12}$.
23. Potassium sulphocyanate, KCNS.

} Five per cent. solutions.

24. Magnesium sulphate, $MgSO_4$.
25. Barium chloride, $BaCl_2$.
26. Calcium chloride, $CaCl_2$.

} Ten per cent. solutions.

27. Calcium hydroxide, $Ca(OH)_2$ (lime-water).
28. Calcium sulphate, $CaSO_4$.

} Saturated solutions.

29. Ferric chloride, $FeCl_3$.
30. Lead acetate, $Pb.(C_2H_3O_2)_2$.
31. Silver nitrate, $AgNO_3$.
32. Mercuric chloride, $HgCl_2$.
33. Platinic chloride, $H_2PtCl_6$.

} Five per cent. solutions.

34. Stannous chloride, $SnCl_2.2H_2O$; ten per cent. solution.
35. Solution of indigo
36. Alcohol, $C_2H_5OH$.

37. Sodium cobaltic nitrite solution, $Co_2(NO_2)_6.6NaNO_2 + H_2O$. Four grams of cobaltous nitrate, $Co(NO_3)_2.6H_2O$, and 10 grams of sodium nitrite, $NaNO_2$, are dissolved in about 50 c.c. of water, 2 c.c. of acetic acid are added, and then water to make 100 c.c.
38. Alkaline mercuric-potassium iodide solution (Nessler's solution). Five grams of potassium iodide are dissolved in hot water, and to this is added a hot solution, made by dissolving 2.5 grams of mercuric chloride in 10 c.c. of water. To the turbid red mixture is added a solution made by

dissolving 16 grams of potassium hydroxide in 40 c.c. of water, and the whole diluted to 100 c.c. Some mercuric iodide deposits on cooling, and may be left in the bottle, the clear solution being decanted as needed.

*b. Solids.*

1. Litmus or blue and red litmus paper.
2. Turmeric paper.
3. Sodium carbonate, dried, $Na_2CO_3$
4. Sodium biborate, borax, $Na_2B_4O_7.10H_2O$.
5. Sodium-ammonium-hydrogen phosphate (microcosmic salt), $Na(NH_4)HPO_4.4H_2O$.
6. Potassium carbonate, $K_2CO_3$.
7. Potassium nitrate, $KNO_3$.
8. Potassium chlorate, $KClO_3$.
9. Potassium permanganate, $KMnO_4$.
10. Potassium cyanide, KCN.
11. Calcium hydroxide, $Ca(OH)_2$.
12. Ferrous sulphide, FeS.
13. Ferrous sulphate, $FeSO_4.7H_2O$.
14. Manganese dioxide, $MnO_2$
15. Zinc, granulated, Zn.
16. Copper, Cu
17. Cupric oxide, CuO.
18. Cupric sulphate, $CuSO_4\ 5H_2O$.
19. Tartaric acid, $H_2C_4H_4O_6$.
20. Tannic acid, $H\ C_{14}H_9O_9$
21. Pyrogallic acid, $C_6H_3(OH)_3$.
22. Diphenylamine, $(C_6H_5)_2NH$.
23. Starch, $C_6H_{10}O_5$

While the apparatus and reagents here enumerated are the more important ones, the analyst will occasionally require others not mentioned in the above list.

**General Mode of Proceeding in Qualitative Analysis.**—Every step taken in analysis should be properly written down in a note-book, and these remarks should be made *directly after a reaction has been performed*, and not after the nature of the substance has been revealed by perhaps numerous reactions.

Not only the reactions by which *positive* results have been obtained should be noted, but also those tests and reagents mentioned which have been applied with *negative* results—that is, which have been applied without revealing the presence of any substance, or any group of substances. Such negative results are, however, positive insofar as they prove the absence of a certain substance, or certain substances, for which reason they are of direct value, and should be noted.

In comparing, finally, the result obtained by the analysis with the notes taken during the examination, none of them should be contradictory to the conclusions drawn. If, for instance, the preliminary examination showed the substance to have been volatilized by heating upon platinum foil *with the exception of a very slight residue*, and

if, afterward, other tests show the presence of ammonia and hydrochloric acid and the absence of everything else, and if, then, the conclusion be drawn that the substance is *pure* ammonium chloride, this conclusion must be incorrect, because pure ammonium chloride is wholly volatile, and does not leave a residue. It will then be the task of the operator to find where the mistake occurred, and to correct it.

**Use of Reagents.**—A mistake made by most beginners in analyzing is the use of too large quantities both of the substance applied for testing and of the reagents added. This excessive use of material is not only a waste of money, but, what is of greater importance, a waste of time. Some experience in analyzing will soon convince the student of the truth contained in this remark, and will also enable him to select the correct quantities of materials to be used, which rarely exceed 0.2–1.0 gram. A smaller amount—in fact, as little as a few milligrams—frequently may answer, and a much larger quantity may occasionally be needed, as, for instance, in cases where highly diluted reagents, such as calcium sulphate solution, lime-water, hydrogen sulphide-water, etc., are applied.

**Preliminary Examination.**—This examination includes the following points:

1. *Physical Properties.*—Solid or liquid; crystallized or amorphous; color, odor, hardness, gravity, etc. (On account of possible poisonous properties, the greatest care should be exercised in tasting a substance.)

2. *Action on Litmus.*—Examined by holding litmus-paper in the liquid, or by placing the powdered solid upon red and blue litmus-paper, moistened with water. (It should be remembered that many normal salts, as, for instance, aluminum sulphate, ferrous sulphate, etc., have an acid reaction to litmus-paper, and that such a reaction consequently is not conclusive of the presence of a free acid, nor even of an acid salt.)

3. *Heating on Platinum Foil or in a Dry Glass Tube, Open at Both Ends.*—(If the substance to be examined be a liquid, it should be evaporated in a small porcelain dish to see whether a solid residue be left or not. If a residue be left, it should be treated like a solid.) The heating of a small quantity of a solid substance upon platinum foil, or upon a piece of mica, held over the flame of a Bunsen burner, is a test which should *never* be omitted, as it discloses in most cases the fact whether the substance is of an organic or inorganic nature.

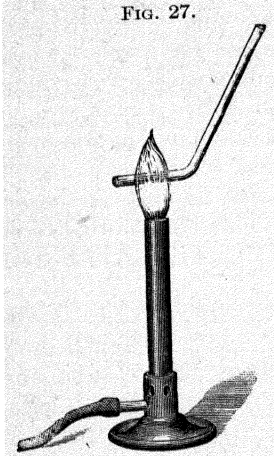
Most organic (non-volatile) substances when thus heated will burn with a luminous flame, leaving in many cases a black residue of carbon, which upon further heating disappears. In cases where the organic nature of a compound is not clearly demonstrated by heating on platinum foil, the substance is heated with an excess of cupric oxide in a test-tube or other glass tube, provided with a delivery-tube which passes into lime-water. Upon heating the mixture the

carbon of the organic matter is converted into carbon dioxide, which renders lime-water turbid.

The analytical processes by which the nature of an organic substance is determined are not considered in this part of the book, but will be mentioned when considering the carbon compounds. Some substances ruin platinum when heated on it. Thus, salts of easily reducible metals, as lead, bismuth, antimony, tin, especially their organic salts, are apt to do so, because these metals form fusible alloys with the platinum. Thiosulphates corrode and hypophosphites destroy platinum. Should the presence of any of the substances be suspected, heating on *platinum* should be omitted. Indeed, tests 4 and 5 can be applied first, as they may show the presence of these objectionable substances.

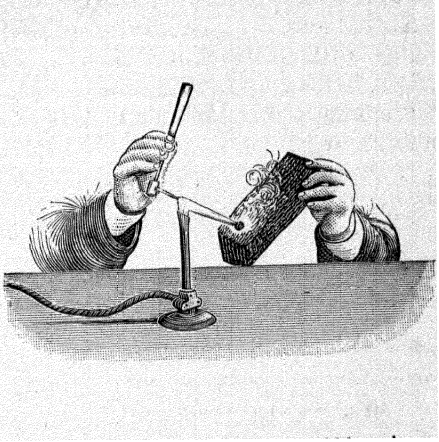
An inorganic substance heated on platinum foil may either be volatilized, change color, become oxidized, suffer decomposition, or remain unchanged. (See Table I., page 352.)

FIG. 27.



Heating of solids in bent glass tubes.

FIG. 28.



Heating on charcoal by means of blowpipe.

Some substances, containing small quantities of water enclosed between the crystals (common salt, for instance), *decrepitate* when heated, the small fragments being thrown from the foil; such substances should be heated in a dry test-tube to expel the water and then be examined on platinum foil.

In many cases it is preferable to heat the substance in a bent glass tube, as shown in Fig. 27, instead of on platinum foil, because volatile products evolved during the process of heating may become recondensed in the cooler part of the tube, and thus saved for further examination.

The presence of water, sulphur, mercury, arsenic, etc., may often be readily demonstrated by this mode of operating.

4. *Heating on Charcoal by Means of the Blowpipe.*—This test reveals the presence of chlorates and nitrates by the vivid combustion of the charcoal (known as *deflagration*), which takes place in consequence of the oxidizing action of these substances.

Arsenic is indicated by a characteristic odor of garlic.

5. *Heating on Charcoal with Sodium Carbonate and Potassium Cyanide.*—A small quantity of the finely powdered substance is mixed with twice its weight of potassium cyanide and dry sodium carbonate. This mixture is placed in a small hole made in a piece of charcoal, and heat applied by means of the blowpipe. (See Fig. 28.) Many metallic compounds may be recognized by this test, the metals being liberated and found as metallic globules or shining particles in the fused mass after this has been removed from the charcoal and washed with water in a small mortar. (See Fig. 29.)

FIG. 29.

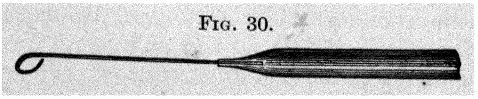


A characteristic incrustation is formed by some metals, due to the precipitation of a metallic oxide around the heated spot on the charcoal.

If sulphur as such, or in any form of combination, be present in the substance examined by this test, the fused mass contains a sulphide of the alkali (*hepar*), which may be recognized by placing it on a piece of bright silver (coin) moistened with a drop of water, when the silver will be stained black in consequence of the formation of silver sulphide. The presence of the alkali sulphide may also be demonstrated by the addition of a few drops of hydrochloric acid to the fused mass, when hydrogen sulphide is evolved and may be recognized by its odor.

6. *Flame Tests.*—Many substances impart a characteristic color to a non-luminous flame. The best mode of performing this test is as follows: A platinum wire is cleaned by washing in hydrochloric acid and water, and heating it in the flame until the latter is no longer colored. One end of the wire is fused in a short piece of glass tubing (see Fig. 30), the other end is bent so as to form a small

FIG. 30.



loop, which is heated, dipped into the substance to be examined, and again held in the lower part of the flame, which then becomes colored.

Some substances show the color-test after being moistened with hydrochloric or sulphuric acid.

A second method of showing flame reactions is to mix the substance with alcohol in a small dish; the alcohol, upon being ignited, shows a colored flame, especially in the dark.

7. *Colored Borax Beads.*—The compounds of some metals when fused with glass, impart to it characteristic colors. For analytical purposes not the silica-glass, but borax-glass is generally used. This latter is made by dipping the loop of a platinum wire in powdered borax and heating it in the flame (directly, or by means of the blowpipe) until all water has been expelled and a colorless, transparent bead has been formed. To this colorless bead a little of the finely powdered substance is added and the bead strongly heated. The metallic compound is chemically acted upon by the boric acid, a borate being formed which colors the bead more or less intensely, according to the quantity of the metallic compound used.

Some metals (copper, for instance) forming two series of compounds give different colors to the bead when present in either the higher or the lower state of oxidation.

By modifying the blowpipe flame so as either to oxidize (by supplying an excess of atmospheric oxygen), or deoxidize (by allowing some unburnt carbon in the flame), the metallic compound in the head may be made to assume the higher or lower state of oxidation. A copper bead may thus be changed from blue to red, or red to blue, the blue bead containing the copper in the cupric, the red bead in the cuprous form. In some cases *microcosmic salt*, $NaNH_4HPO_4$, is used for making the bead.

8. *Liquefaction of Solid Substances.*—Most solid substances have to be dissolved for analysis. The solution obtained may be either a simple or chemical solution. In a *simple solution* the dissolved body retains all of its original properties, with the exception of its shape, and may be reobtained by evaporation. Sodium chloride and sugar dissolved in water form simple solutions. A *chemical solution* is one in which the chemical composition of the substance has been changed during the process of dissolving, as, for instance, when calcium carbonate is dissolved in hydrochloric acid; this solution now contains and leaves on evaporation calcium chloride. The solvents used are water, or the mineral acids for substances insoluble in water, especially dilute, or, if necessary, strong hydrochloric acid. The dissolving action of the acid should be facilitated by the aid of heat. Nitric or even nitrohydrochloric acid may have to be used in some cases.

*Three mistakes are frequently made by beginners in dissolving substances in acids, viz.: The substance is not powdered as finely as it should be; sufficient time is not given for the acid to act; too large an excess of the acid is used.*

If a substance is partly dissolved by water and partly by one or more other solvents, it may be well to examine the different solutions separately.

Substances insoluble in water and in acids have to be rendered

## TABLE I.—Preliminary examination.

| | |
|---|---|
| Heat the solid substance upon platinum foil, or in a dry, narrow glass tube open at both ends. | *Combustible* are: All **organic compounds, carbon, sulphur, phosphorus,** etc.<br>*Easily volatilized* are: All compounds of **ammonium** and **mercury,** some of **arsenic,** some of **antimony, etc.**<br>(Heat in a glass tube as directed on page 349.)<br>*Fusible* are: Most of the salts of the **alkalies,** and some of those of the **alkaline earths,** many metals, etc.<br>*Infusible* are: Salts of the **earths,** and most salts of the **alkaline earths** and **heavy metals,** most **silicates,** etc.<br>*Assume a darker color:* Many **oxides of the heavy metals** and **their salts** (oxides of zinc, antimony, lead, etc.).<br>*Evolve water:* Many **salts containing water of crystallization,** some **hydroxides,** etc.<br>*Decrepitate:* Some **salts,** sodium chloride, for instance. |
| Heat the solid substance on charcoal. | *Deflagrate:* **Nitrates, chlorates, iodates, bromates,** etc.<br>Give *garlic odor:* Most compounds of **arsenic.** |
| Heat the substance, mixed with sodium carbonate and potassium cyanide, on charcoal. | Give *hepar:* **Sulphur** and all **its compounds.**<br>Give *bright metallic grains without incrustation:* Compounds of **gold, silver, copper, tin.**<br>Give *bright metallic grains with incrustation:* Compounds of **lead, bismuth, antimony.**<br>Give *gray infusible powder:* Compounds of **iron, cobalt, nickel, platinum.** |
| Heat the substance on platinum wire in a non-luminous flame. | *Yellow* flame, compounds of **sodium.**<br>*Violet* flame, compounds of **potassium.**<br>*Crimson* flame compounds of **lithium** or **strontium.**<br>*Orange* flame, compounds of **calcium**<br>*Yellowish-green* flame, compounds of **barium** or **molybdenum.**<br>*Green* flame, compounds of **copper, phosphoric** or **boric acids.**<br>*Blue* flame, compounds of **arsenic, antimony, lead,** or **cupric chloride.** |
| Heat a colorless borax bead with very little of the substance. | *Green* bead, compounds of **chromium.**<br>*Blue* bead, compounds of **cobalt** or **copper** in the oxidizing flame.<br>*Red* bead, compounds of **copper** in the reducing flame.<br>*Violet* bead, compounds of **manganese.**<br>*Yellow* to *brown* bead, compounds of **iron.**<br>*Colorless* bead, compounds of the **light metals** and those of the **arsenic group**; also **silver, bismuth, lead,** etc. |

soluble by fusion with a mixture of potassium and sodium carbonate, or with potassium acid sulphate, or by the action of hydrofluoric acid.

The insoluble sulphates of the alkaline earths, when fused with the alkaline carbonates, are converted into carbonates, while the sulphates of the alkalies are formed. The latter compounds may be eliminated by washing the fused mass with water and filtering: the solid residue upon the filter contains the carbonates of the alkaline earths, which may be dissolved in hydrochloric acid.

Insoluble silicates may be decomposed by the methods mentioned on page 186.

## 35. SEPARATION OF METALS INTO DIFFERENT GROUPS.

**General Remarks.**—The preliminary examination will, in most cases, decide whether or not a metal or metals are present in the substance to be examined. If there be metals, the solution should be treated according to Table II, page 356, in order to find the group or groups to which these metals belong, and also to separate them into these groups, the individual nature of the metals themselves being afterward demonstrated by special methods.

The simplest method of separating from each other the 57 metals known, if all were in one solution, would be to add successively 57 different reagents, each of which should form an insoluble compound with but *one* of the metals. By separating this insoluble compound from the metals remaining in solution (by filtration), and by thus precipitating one metal after the other, they all could be easily separated. We have, however, no such 57 reagents, and are, consequently, compelled to precipitate a number of metals together, and the reagents used for this purpose are known as *group reagents.*

They are:

1. *Hydrogen sulphide,* added to the solution previously acidified by hydrochloric acid. Precipitated are: the metals of the arsenic and lead groups as sulphides.

2. *Ammonium sulphide,* added after supersaturating with *ammo-*

QUESTIONS.—What is analytical chemistry, and what is the object of qualitative and of quantitative analysis? What properties of a substance should be noticed first in making a qualitative analysis? By what tests may organic compounds be distinguished from inorganic compounds? Explain the terms decrepitation and deflagration. Mention some substances which are completely volatilized by heat, some which are fusible, and some which are not changed by heating them. What is meant by "hepar," and which element is indicated by the formation of hepar? Mention some metals which may be liberated from their compounds by heating on charcoal with potassium cyanide and carbonate. Which metallic compounds and which acids are capable of coloring a non-luminous flame? Name the colors imparted. State the metals which impart characteristic colors to a borax bead. Which solvents are used for liquefying solids, and what precautions should be observed in this operation?

*nium hydroxide.* Precipitated are: the metals of the iron group and of the earths as sulphides or hydroxides.

3. *Ammonium Carbonate.* Precipitated are: the metals of the alkaline earths as carbonates.

4. *In solution are left:* the metals of the alkalies and magnesium.

The order in which these group-reagents are added cannot be reversed or changed, because ammonium sulphide added first would precipitate not only the metals of the iron group and the earths, but also the metals of the lead group; ammonium carbonate would precipitate also most of the heavy metals.

For the same reasons, in separating metals of the different groups, the group-reagents must be added in *excess*, that is, enough of them must be added to precipitate the total quantity of the metals of one group, before it is possible to test for metals of the next group. Suppose, for instance, a solution to contain a salt of bismuth only. Upon the addition of hydrogen sulphide to the acidified solution, a dark-brown precipitate (of bismuth sulphide) is produced, indicating the presence of a metal of the lead group. Suppose, further, that hydrogen sulphide has not been added in sufficient quantity to precipitate the whole of the bismuth, then ammonium sulphide, as the next group-reagent, would produce a further precipitation in the filtrate, which fact would lead to the assumption that a metal of the iron group was present, which, however, would not be the case.

If the solution contain but one metal, the group-reagents are added successively in small quantities to the same solution, until the reagent is found which causes a precipitation, which reagent is then added in somewhat larger quantity in order to produce a sufficient amount of the precipitate for further examination.

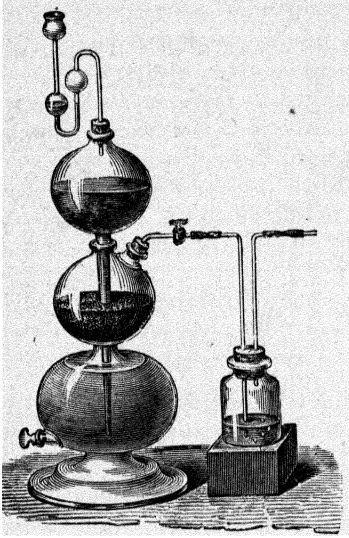
**Acidifying the Solution.**—Hydrogen sulphide has to be added to the *acidified* solution for two reasons, viz.: In a neutral or alkaline solution some metals of the arsenic group (which are to be precipitated) would not be precipitated by hydrogen sulphide; some of the metals of the iron group (which are not to be precipitated) would be thrown down.

The best acid to be used in acidifying is dilute hydrochloric acid; but this acid forms insoluble compounds with a few of the metals of the lead group, causing them to be precipitated. Completely precipitated by hydrochloric acid are mercurous and silver compounds; partially precipitated are compounds of lead, chloride of lead being somewhat soluble in water. The precipitate formed by hydrochloric acid may be examined by Table III, page 358.

Hydrochloric acid added to a solution may, in a few cases (other than those just mentioned), cause a precipitate, as, for instance, when added to solutions containing certain compounds of antimony or bismuth (the precipitated oxychlorides of these metals are soluble in excess of the acid), to metallic oxides or hydroxides which have been dissolved by alkali hydroxides (for instance, hydroxide of zinc dissolved in potassium or ammonium hydroxide), to solutions of alkali silicates, when silica separates, etc.

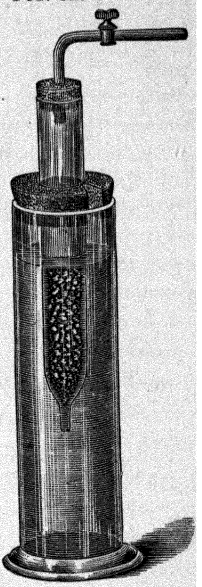
**Addition of Hydrogen Sulphide.**—This reagent is employed either in the gaseous state (by passing it through the heated solution) or as hydrogen sulphide water. The latter reagent answers in those cases where but one metal is present; if, however, metals of the arsenic and lead groups are to be separated from metals of other groups, the gas must be used.

FIG. 31.



Apparatus for generating hydrogen sulphide.

FIG. 32.



Apparatus for generating hydrogen sulphide.

For generating hydrogen sulphide the directions given on page 167 may be followed. In place of the apparatus there mentioned for generating the gas, others may be used which have the advantage to the analyst that the supply of gas may be better regulated. Fig. 31 shows such an apparatus for the continuous preparation of the gas. It consists of three glass bulbs; the upper bulb, prolonged by a tube reaching to the bottom of the lowest one, is ground air-tight into the neck of the second. Ferrous sulphide is introduced into the middle bulb through the tubulure, which is then closed by a perforated cork through which connection is made with the wash-bottle. Acid poured in through the safety tube, runs into the bottom globe and rises to the ferrous sulphide in the second bulb. Upon closing the delivery tube, the pressure of the generated gas forces the liquid from the second bulb through the lower to the upper, thus preventing contact of acid and ferrous sulphide until the gas is used again.

A convenient and cheaper apparatus is shown in Fig. 32. A glass tube, drawn at its lower end to a small point and partly filled with pieces of ferrous sulphide, is suspended through a cork (not air-tight) in a cylinder containing the acid. The gas supply is regulated by closing or opening the stop-cock, and also by raising or lowering the tube in the acid.

## TABLE II.—Separation of metals into different groups.

Add the following reagents successively to the same solution. Every time a precipitate is formed an excess of the precipitant is to be used; the precipitate is collected upon a filter, well washed, and treated by the tables mentioned. To the clear filtrate the next group-reagent is added If the solution contains but one metal, generally it is sufficient to find by means of this table the group to which it belongs, and then to use the original solution for testing according to Tables III.–VIII.

| **Dilute hydrochloric acid** precipitates: | **Hydrogen sulphide** precipitates: | | **Ammonium chloride, hydroxide, and sulphide** precipitate: | **Ammonium carbonate** precipitates: | In **solution** are left: |
|---|---|---|---|---|---|
| Metals of the **lead group.** | | **Arsenic group.** | **Iron group and earths.** | **Alkaline earths.** | **Alkalies and magnesium.** |
| | Insoluble in ammonium sulphide. | Soluble in ammonium sulphide. | | | |
| **Silver** chloride, **Mercurous** chloride, **Lead** chloride, } White. | **Lead** sulphide, **Mercuric** sulphide, **Bismuth** sulphide, **Cupric** sulphide, } Black. **Cadmium** sulphide, yellow. | **Arsenous** sulphide, yellow. **Antimonous** sulphide, orange. **Stannous** sulphide, brown. **Stannic** sulphide, yellow. **Auric** sulphide, brown. **Platinic** sulphide, brown. | **Ferrous** sulphide, black. **Cobaltous** sulphide, black. **Nickelous** sulphide, black. **Manganous** sulphide, flesh-colored. **Zinc** sulphide, white, **Chromic** hydroxide, green **Aluminum** hydroxide, white. A precipitate may be caused by other substances than those mentioned. See page 345. | **Calcium** carbonate, **Barium** carbonate, **Strontium** carbonate, } White. | **Magnesium.** **Potassium.** **Sodium.** **Lithium.** **Ammonium.** |
| A precipitate may be caused by other substances than those mentioned. See page 342. | | | | | |
| See Table III. | See Table IV. | See Table V. | See Table VI | See Table VII. | See Table VIII. |

In some cases sulphur is precipitated on the addition of hydrogen sulphide, while a change in color may take place. This change is due to the deoxidizing action of hydrogen sulphide, the hydrogen of this reagent becoming oxidized and converted into water, while sulphur is liberated. Thus, brown ferric compounds are converted into pale green ferrous compounds; red solutions of acid chromates become green; and red permanganates or green manganates are decolorized.

The same deoxidizing action of hydrogen sulphide is the reason why this reagent cannot be employed in a solution containing free nitric acid, which latter compound oxidizes the hydrogen sulphide.

**Separation of the Metals of the Arsenic from those of the Lead Group.**—The precipitate produced by hydrogen sulphide in acid solution contains the metals of the arsenic and lead groups. They are separated by means of ammonium sulphide, which dissolves the sulphides of the arsenic group, but does not act on those of the lead group.

**Addition of Ammonium Sulphide.**—This reagent should never be added to the acid solution, but the solution should be previously supersaturated by ammonium hydroxide, as, otherwise, a precipitate of sulphur may be formed. The yellow ammonium sulphide is almost invariably a polysulphide of ammonium, that is, ammonium sulphide which has combined with one or more atoms of sulphur. If an acid be added to this compound, an ammonium salt is formed, hydrogen sulphide is liberated, and sulphur precipitated:

$$(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S + S.$$

Ammonium sulphide precipitates the metals of the iron group as sulphides, with the exception of chromium, which is precipitated as hydroxide; aluminum is precipitated in the same form of combination.

Ammonium sulphide (or ammonium hydroxide) causes also the precipitation of metallic salts which have been dissolved in acids, as, for instance, of the phosphates, borates, silicates, or oxalates of the alkaline earths, magnesium, and others. The processes by which the nature of some of these precipitates is to be recognized are found in Table VI, page 360.

**Addition of Ammonium Carbonate.**—The reagent used is the commercial salt, dissolved in water, to which some ammonia-water has been added. Heating facilitates complete precipitation of the carbonates of the alkaline earths.

---

QUESTIONS.—State the three groups of heavy, and the three groups of light metals. By which two reagents may all heavy metals be precipitated? Why is a solution acidified before the addition of hydrogen sulphide, when testing for metals? Which metals are precipitated by hydrochloric acid? Which two groups of metals are precipitated by hydrogen sulphide in acid solution? How are the sulphides of the arsenic group separated from those of the lead group?

## 36. SEPARATION OF THE METALS OF EACH GROUP.

### TABLE III.—Treatment of the Precipitate Formed by Hydrochloric Acid.

The precipitate may contain **silver, mercurous,** and **lead chlorides.** Boil the washed precipitate with much water, and filter while hot.

| | | |
|---|---|---|
| Filtrate may contain **lead chloride.** Add dilute sulphuric acid; a white precipitate of lead sulphate is produced. | Residue may consist of **mercurous** and **silver chlorides.** Digest residue with ammonia water. | |
| | Solution may contain **silver.** Neutralize with nitric acid, when silver chloride is re-precipitated. | A dark gray residue indicates **mercury,** the white mercurous chloride having been converted into mercuric-ammonium chloride and mercury. |

**Treatment of the Precipitate Formed by Hydrogen Sulphide in Warm Acid Solution.**—The precipitate is collected upon a small filter, well washed with water, and then examined for its solubility in ammonium sulphide. This is done by placing a portion of the washed precipitate in a test-tube, adding ammonium sulphide, and warming gently. It is either wholly insoluble (metals of the lead group), and treated according to Table IV, or fully soluble (metals of the arsenic group), and treated according to Table V, or it is partly soluble and partly insoluble (metals of both groups). In the latter case, the total quantity of the washed precipitate is to be treated with warm ammonium sulphide; upon filtering, an insoluble residue is left, which is treated according to Table IV; to the filtrate, diluted sulphuric acid is added as long as a precipitate is formed, which precipitate contains the metals of the arsenic group as sulphides, generally with some sulphur from the ammonium sulphide.

Why is an acid solution neutralized or supersaturated by ammonium hydroxide before adding ammonium sulphide? Which two groups of metals are precipitated by ammonium sulphide, and in what forms of combination? Name the group-reagent for the alkaline earths. Which metals may be left in solution after hydrogen sulphide, ammonium sulphide, and ammonium carbonate have been added?

## TABLE IV.—Treatment of that portion of the hydrogen sulphide precipitate which is insoluble in ammonium sulphide.

The precipitate may contain the **sulphides of lead, copper, mercury, bismuth,** and **cadmium.** Heat the *well-washed* precipitate with nitric acid in a test-tube, and filter.

| Residue may consist of: | Filtrate may contain the **nitrates of lead, copper, bismuth,** and **cadmium.** Add to the solution a few drops of dilute sulphuric acid. | |
|---|---|---|
| **Mercuric sulphide,** which is black and easily dissolves in nitro-hydrochloric acid, which solution, after sufficient evaporation, is tested by potassium iodide, etc.<br>**Lead sulphate** is white, pulverulent, and soluble in ammonium tartrate.<br>**Sulphur** is yellow and combustible. | Precipitated is **lead,** as white lead sulphate which is soluble in ammonium tartrate with excess of ammonium hydroxide. | Solution may contain **copper, bismuth,** and **cadmium.** Supersaturate with ammonium hydroxide. |
| | | Precipitated is white **bismuth** hydroxide. Dissolve in hydrochloric acid and apply tests for bismuth. |
| | | Solution may contain **copper** and **cadmium.** Divide solution in two parts, and test for copper by potassium ferrocyanide in the acidified solution; a red precipitate indicates **copper.** To second part add potassium cyanide and hydrogen sulphide. A yellow precipitate indicates **cadmium.** |

## TABLE V.—Treatment of the hydrogen sulphide precipitate which is soluble in ammonium sulphide.

The precipitate may contain the **sulphides of arsenic, antimony, tin,** and a few of those metals which are but rarely met with in qualitative analysis, such as **gold, platinum, molybdenum,** and others, which latter metals, if suspected, may be detected by special tests.

Boil the washed precipitate with strong hydrochloric acid.

| An insoluble yellow residue consists of **arsenous sulphide.** The residue is dissolved by boiling with hydrochloric acid and a little potassium chlorate, and the solution examined by Fleitmann's test.<br>A dark-colored residue may indicate gold or platinum, for which use special tests. | The solution may contain the **chlorides of antimony** and **tin.** The solution is introduced into Marsh's apparatus when all antimony is gradually evolved as antimoniuretted hydrogen, while tin remains with the undissolved zinc as a black metallic powder, which may be collected, washed, dissolved in hydrochloric acid, and the solution tested by the special tests for tin. |
|---|---|

## TABLE VI.—Treatment of the precipitate formed by ammonium hydroxide and ammonium sulphide.

The precipitate may contain the **sulphides of iron, manganese, and zinc (cobalt and nickel),**[1] **the hydroxides of chromium and aluminum,** and possibly the **phosphates of barium, calcium, strontium, and magnesium.**[2]

Dissolve the washed precipitate in the smallest possible quantity of warm, dilute hydrochloric acid, and heat the solution with a few drops of nitric acid. To the clear solution add ammonium chloride, and supersaturate it with ammonium hydroxide

The precipitate may contain the **hydroxides of iron, aluminum and chromium,** and the **phosphates of the alkaline earths or of magnesium.** Dissolve the precipitate in a little hydrochloric acid, and supersaturate with potassium hydroxide.

The solution may contain **zinc, manganese, cobalt, and nickel.** Acidulate the ammonia solution with acetic acid, and add hydrogen sulphide.

Precipitated is **ferric hydroxide,** reddish-brown. Dissolve in dilute hydrochloric acid, and add *potassium ferrocyanide.* A blue precipitate indicates **iron.**

Precipitate may also contain the *phosphates of the alkaline earths or magnesium.* To the solution of the precipitate in hydrochloric acid add ammonium hydroxide until a precipitate is formed which does not redissolve on stirring. Add a few drops of acetic acid to dissolve the precipitate, and then ammonium oxalate. A white precipitate indicates *calcium.*

*Barium and strontium* are indicated by the addition of calcium sulphate, and distinguished by flame reaction.

Test for phosphoric acid by ammonium molybdate.

Solution may contain **aluminum,** and, if green, **chromium.**

Supersaturate the alkaline solution slightly with hydrochloric acid, and add ammonium carbonate A white gelatinous precipitate indicates **aluminum.**

If the precipitate is green it may contain *chromium,* or *aluminum* and *chromium.* Separate as follows: Dissolve the washed precipitate in the smallest possible quantity of nitric acid, evaporate solution in porcelain dish nearly to dryness, add about two volumes of strong nitric acid and fragments of potassium chlorate; heat until solution has assumed a bright orange color. Dilute with water and supersaturate with ammonia; a white precipitate indicates *aluminum.* To filtrate add barium chloride; a yellow precipitate indicates *chromium.*

Precipitate may contain the **sulphides of zinc, cobalt, and nickel.**

If the precipitate be white, it is zinc sulphide only; if black, it may contain cobalt and nickel If the latter be present, the precipitate is dissolved in hydrochloric acid with little nitric acid, and the solution supersaturated with potassium hydroxide. The filtrate then contains the **zinc,** the black precipitate **cobalt** and **nickel.**

Solution may contain **manganese,** which is verified by adding ammonium hydroxide and sulphide, which produce a flesh-colored precipitate.

[1] The sulphides of cobalt and nickel are but sparingly soluble in hydrochloric acid, but dissolve readily in nitro-hydrochloric acid.

[2] In the absence of a sufficient quantity of ammonium chloride some magnesium hydroxide may also be precipitated.

The precipitation of sulphur, in the absence of metals of the arsenic group, frequently leads beginners to the assumption that metals of this group are present. The precipitate consisting only of sulphur is white and milky, but flocculent, and more or less colored in the presence of the metals of the arsenic group.

### TABLE VII.—Treatment of the precipitate formed by ammonium carbonate.

The precipitate may contain the **carbonates of barium, calcium, and strontium.**[1] Dissolve the precipitate in acetic acid, and add potassium dichromate.

| | | |
|---|---|---|
| Precipitated is **barium**, as pale yellow **barium chromate.** | Solution may contain **calcium and strontium** Neutralize solution with ammonia water and add potassium chromate | |
| | Precipitated is **strontium**, as pale yellow **strontium chromate.** | Solution may contain **calcium** Add ammonium oxalate: a white precipitate indicates **calcium.** |

### TABLE VIII.—Detection of the alkalies and of magnesium.

The fluid which has been treated with hydrochloric acid, hydrogen sulphide, ammonium hydroxide, sulphide, and carbonate, may contain **magnesium and the alkalies.**

Divide solution into two portions.

To the first portion add sodium phosphate. A white crystalline precipitate indicates **magnesium.**[2]

The second portion is evaporated to dryness, further heated (or ignited) until all ammonium compounds are expelled, and white fumes are no longer given off. The residue is dissolved in water, and sodium cobaltic nitrite added. A yellow precipitate indicates **potassium.** The residue is also examined by flame test: a yellow color indicating **sodium,** a red color **lithium.**

**Ammonium compounds** have to be tested for in the original fluid by treating it with calcium hydroxide, when ammonia gas is liberated

[1] If an insufficient quantity of ammonium chloride should have been present, some magnesia may also be contained in this precipitate, and may be redissolved by treating it with ammonium chloride solution.

[2] If an insufficient quantity of ammonium chloride has been produced in the original solution by the addition of hydrochloric acid and ammonium hydroxide, a portion of the magnesia may have been precipitated by the ammonium hydroxide or carbonate.

QUESTIONS.—By what tests can mercurous chloride be distinguished from the chloride of silver or lead? How can it be proved that a precipitate produced by hydrogen sulphide in an acid solution contains a metal or metals of

## 37. DETECTION OF ACIDS.

**General Remarks.**—There are no general methods (similar to those for the separation of metals) by which all acids can be separated, first into different groups, and afterward into the individual acids. It is, moreover, impossible to render all acids soluble (when in combination with certain metals) without decomposition, as, for instance, in the case of carbonic acid when in combination with calcium; calcium carbonate is insoluble in water, and when the solution is attempted by means of acids, decomposition takes place with liberation of carbon dioxide. Many other acids suffer decomposition in a similar manner, when attempts are made to render soluble the substances in which they occur.

It is due to these facts that a complete separation of all acids is not so easily accomplished as the separation of metals. There is, however, for each acid a sufficient number of characteristic tests by which it may be recognized; moreover, the preliminary examination, as well as the solubility of the substance, and the nature of the metal or metals present, will aid in pointing out the acid or acids which are present.

If, for instance, a solid substance be completely soluble in water, and if the only metal found were iron, it would be unnecessary to test for carbonic and phosphoric acids and hydrogen sulphide, because the combinations of these with iron are insoluble in water; there might, however, be present sulphuric, hydrochloric, nitric, and many other acids, which form soluble salts with iron.

**Detection of Acids by Means of the Action of Strong Sulphuric Acid upon the Dry Substance.**—The action of sulphuric acid upon a dry powdered substance often furnishes such characteristic indications of the presence or absence of certain acids, that this treatment should never be omitted when a search for acids is made.

When the substance under examination is liquid, a portion should be evaporated to dryness, and, if a solid residue remains, it should be treated in the same manner as a solid.

Most non-volatile, organic substances (including most organic acids) color sulphuric acid dark when heated with it.

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either the arsenic or lead group? How can mercuric sulphide be separated from the sulphides of copper and bismuth? How does ammonium hydroxide act on a solution containing bismuth and copper? State the action of strong, hot hydrochloric acid on the sulphides of arsenic and antimony. Suppose a solution to contain salts of iron, aluminum, zinc, and manganese, by what process could these four metals be separated and recognized? How can barium, calcium, and strontium be recognized when dissolved together? By what tests is magnesium recognized? State a method of separating potassium when mixed with other metallic compounds. How are ammonium compounds recognized when in solution with other metals?

Dry inorganic salts when heated with sulphuric acid either are decomposed, with liberation of the acid (which may escape in the gaseous state), or with liberation of volatile products (produced by the decomposition of the acid itself), or no apparent action takes place. (See Table IX.)

**Detection of Acids by Means of Reagents Added to Their Neutral or Acid Solution.**—Whenever a substance is soluble in water, there is little difficulty of finding the acid by means of Table X; but if the substance is insoluble in water, and has to be rendered soluble by the action of acids, this table may, in some cases, be of no use, because the acid originally present in the substance may have been liberated, and escaped in a gaseous state (as, for instance, when dissolving insoluble carbonates in acids), or the tests mentioned in the table may refer to neutral solutions, while it is impossible to render the solution neutral without reprecipitating the dissolved acid. If calcium phosphate, for instance, be dissolved by hydrochloric acid, the magnesium test for phosphoric acid cannot be used, because this test can be applied to a neutral or an alkaline solution only; in attempting, however, to neutralize the hydrochloric acid solution, calcium phosphate itself is reprecipitated.

Table XI, showing the solubility or insolubility (in water) of over 300 of the most important inorganic salts, oxides, and hydroxides, will greatly aid the student in studying this important feature. It will also guide him in the analysis of inorganic substances, as it gives directions for over 300 (positive or negative) tests for metals, and an equal number for acids.

To understand this, it must be remembered that any salt (or oxide or hydroxide) which is insoluble in water may be produced and precipitated by mixing two solutions, one containing the metal, the other containing the acid of the insoluble salt to be formed. For instance: Table XI states that the carbonates of most metals are insoluble in water. To produce, therefore, the carbonate of any of these metals (zinc, for instance) it becomes necessary to add to any solution of zinc (sulphate, chloride, or nitrate of zinc) any soluble carbonate (sodium or potassium carbonate), when the insoluble zinc carbonate is produced.

Soluble carbonates consequently are reagents for soluble zinc salts, while at the same time soluble zinc salts are reagents for soluble carbonates.

For similar reasons soluble zinc salts are, according to Table XI, reagents for soluble phosphates, arsenates, arsenites, hydroxides, and sulphides, but not for iodides, chlorides, sulphates, nitrates, or chlorates.

The insolubility of a compound in water is not an absolute guide for preparing this compound according to the general rule given above for the precipitation of insoluble compounds, there being some exceptions.

For instance: Cupric hydroxide is insoluble in water; therefore by adding solution of cupric sulphate to any soluble hydroxide, the insoluble cupric hydroxide should be precipitated, and is precipitated by the soluble hydroxides of potassium and sodium, but not permanently by the soluble hydroxide of ammonium, on account of the formation of the soluble ammonium cupric sulphate.

There are not many such exceptions, and to mention them in the table would have greatly interfered with its simplicity, for which reason they have been omitted.

For the same reason some compounds, which are not known at all, have not been specially mentioned. For instance, according to Table XI, aluminum carbonate and chromium carbonate are insoluble salts: actually, however, these compounds can scarcely be formed, the affinity between the weak carbonic acid and the feeble bases not being sufficient to unite them. Also, bismuth nitrate and a few other salts are reported as soluble, while actually they suffer a decomposition by water.

Finally, it may be stated that no well-defined line can be drawn between soluble and insoluble substances. There is scarcely any substance which is not slightly soluble in water, and many of the so-called soluble substances are but very sparingly soluble, as, for instance, the hydroxide and sulphate of calcium.

Table XII shows the solubility of a large number of compounds more accurately than Table XI; it may be used for reference.

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QUESTIONS.—Why is sulphuric acid added to a solid substance when it is to be examined for acids? Mention some acids which cause the liberation of colorless, and some which cause the liberation of colored gases when the salts of these acids are heated with sulphuric acid. Mention an acid which is precipitated by barium chloride in acid solution, and some acids which are precipitated by the same reagent in neutral solution. Which acids may be precipitated by silver nitrate from neutral solutions, and which from either neutral or acid solutions? Mention some acids which form soluble salts only. Mention three soluble, and three insoluble carbonates, phosphates, arsenates, sulphates, and sulphides respectively. Which oxides or hydroxides are soluble, and which are insoluble in water? Mention some metals the solutions of which are precipitated by soluble chlorides, iodides, and sulphides. State a general rule according to which most insoluble salts may be formed from two other compounds. Why is it sometimes impossible to render a substance soluble in order to test for the acid in the solution obtained?

## TABLE IX.—Preliminary examination for inorganic acids.

A small quantity of the finely powdered substance is treated with about four times its weight of **concentrated sulphuric acid**, in a test-tube, care being taken not to heat to the boiling-point of sulphuric acid.

| No apparent change takes place. **No gas is evolved.** | **A colorless gas is evolved.** | **A colored gas is evolved.** |
|---|---|---|
| **Sulphuric acid** (hepar and barium test)<br>**Phosphoric acid** (molybdate of ammonium test).<br>**Boric acid** (green flame after moistening with sulphuric acid).<br>**Arsenic acid,**<br>**Silicic acid,**<br>**Molybdic acid,**<br>**Phosphorous acid,**<br>**Arsenous acid,** } Special tests. | **Hydrochloric acid** (silver test).<br>**Carbonic acid** (the gas is generated also by diluted acids in the cold, and renders lime-water turbid).<br>**Nitric acid** (the vapors turn red on the addition of ferrous sulphate).<br>**Sulphurous acid** (odor).<br>**Hydrogen sulphide** (odor).<br>**Hydrofluoric acid** (corrodes glass).<br>**Acetic acid** (odor of acetic ether on the addition of alcohol).<br>**Many organic acids** are decomposed with liberation of colorless gases. | **Hydriodic acid** (violet vapors of iodine).<br>**Hydrobromic acid** (brown vapors of bromine).<br>**Bromic acid** (brown vapors; deflagration on charcoal)<br>**Chloric acid** (the greenish-yellow gas explodes readily).<br>**Nitric acid** (vapors more red on adding ferrous sulphate).<br>**Nitrous acid** (red vapors). |

Whenever one or more acids are suspected or are indicated by the above tests, their presence is to be verified by the tests in Tables X and XI., or by the reactions given in connection with the consideration of the acids themselves For latter tests see Index.

## TABLE X.—Detection of the more important acids by means of reagents added to the solution.

| **Barium chloride** precipitates from *neutral* solution: | **Calcium chloride** precipitates from *neutral* or *alkaline* solution: | **Ferric chloride** precipitates from *neutral* solution: | **Magnesium sulphate** precipitates in the presence of **ammonium hydroxide and chloride:** | **Silver nitrate** precipitates | |
|---|---|---|---|---|---|
| | | | | from *neutral* solution; | from *neutral* or *acid* solution: |
| **Sulphuric acid,** white. | **Sulphuric acid,** white. | ..... ..... | .. ..... | ..... | **Hydrochloric acid,** white. |
| **Sulphurous acid,** white | **Sulphurous acid,** white. | ..... | ..... | **Sulphurous acid,** white. | **Hydrobromic acid,** white. |
| **Phosphoric acid,** white. | **Phosphoric acid,** white. | **Phosphoric acid,** yellowish-white. | **Phosphoric acid,** white. | **Phosphoric acid,** pale yellow. | **Hydriodic acid,** white. |
| **Phosphorous acid,** white. | **Phosphorous acid,** white. | ..... | ..... | **Phosphorous acid,** white, then black. | **Iodic acid,** white. |
| **Carbonic acid,** white. | **Carbonic acid,** white. | (Ferric hydroxide is precipitated and carbon dioxide escapes.) | ..... | **Carbonic acid,** white. | **Hydrocyanic acid,** white. |
| **Boric acid,** white. | **Boric acid,** white. | **Boric acid,** yellowish | ..... | **Boric acid,** white. | **Ferrocyanides,** white. |
| **Arsenic acid,** white. | **Arsenic acid,** white. | **Arsenic acid,** yellowish-white. | **Arsenic acid,** white. | **Arsenic acid,** brownish red. | **Ferricyanides,** reddish-brown. |
| **Arsenous acid,** white. | ..... | **Ferrocyanides,** blue. | ..... | **Arsenous acid,** yellow. | **Sulphocyanides,** white. |
| **Chromic acid,** pale yellow. | ..... ..... | **Sulphocyanides,** red coloration. | ..... .. | **Chromic acid,** red. | **Hydrosulphuric acid,** black |
| ..... | ..... | **Hydrogen sulphide,** black. | ..... | ..... ..... | |
| **Oxalic acid,** white. | **Oxalic acid,** white. | **Oxalic acid,** yellow. | ..... | **Oxalic acid,** white. | Not precipitated are: |
| **Tartaric acid,** white. | **Tartaric acid,** white. | **Tannic acid,** black. | **Tartaric acid,** white; precipitate forms slowly. | **Tartaric acid,** white. | **Nitric acid.** |
| **Citric acid,** white. | **Citric acid,** white. | **Acetic acid,** a reddish-brown coloration is produced, and, on boiling, a reddish-brown precipitate. | ..... ..... | **Citric acid,** white. | **Nitrous acid.** |
| | | | | | **Chloric acid.** |
| | | | | | **Hypochlorous acid.** |
| | | | | | **Acetic acid.** |

All the above precipitates are soluble in hydrochloric and most other acids, with the exception of barium sulphate.

Table XI.

**Systematically arranged table showing the solubility and insolubility of inorganic salts and oxides in water.**

*The dark squares represent insoluble, the white soluble compounds.*

| | | Carbonate. | Phosphate. | Arsenate. | Arsenite. | Oxide. | Hydroxide. | Sulphide. | Iodide. | Chloride. | Sulphate. | Nitrate. | Chlorate. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Potassium | Alkalies. | | | | | | | | | | | | |
| Sodium | | | | | | | | | | | | | |
| Ammonium | | | | | | | | | | | | | |
| Calcium | Alkaline Earths. | ■ | ■ | ■ | ■ | | | | | | | | |
| Barium | | ■ | ■ | ■ | ■ | | | | | | ■ | | |
| Strontium | | ■ | ■ | ■ | ■ | | | | | | ■ | | |
| Magnesium | | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | |
| Aluminum | | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | |
| Ferric | Iron Group. | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | |
| Ferrous | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | |
| Zinc | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | |
| Chromium | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | |
| Nickel | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | |
| Cobalt | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | |
| Manganese | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | |
| Stannic | Arsenic Group. | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | |
| Stannous | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | |
| Arsenic | | ■ | ■ | ■ | ■ | | | ■ | | | | | |
| Arsenous | | ■ | ■ | ■ | ■ | | | ■ | | | | | |
| Antimony | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | |
| Gold | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | |
| Platinum | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | |
| Copper | Lead Group. | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | |
| Bismuth | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | |
| Cadmium | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | |
| Mercuric | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | |
| Mercurous | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | |
| Silver | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | |
| Lead | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | |

## TABLE XII.—Table of solubility.

w = soluble in water. a = insoluble in water, soluble in acids (HCl, $HNO_3$). t = insoluble in water and acids. w a = sparingly soluble in water, but soluble in acids. w t = sparingly soluble in water and acids. a t = insoluble in water, sparingly soluble in acids.

| | Aluminum. | Ammonium. | Antimony. | Barium. | Bismuth. | Cadmium. | Calcium. | Chromium. | Cobalt. | Copper. | Ferrous. | Ferric. | Lead. | Magnesium. | Manganese. | Mercurous. | Mercuric. | Nickel. | Potassium. | Silver. | Sodium. | Strontium. | Zinc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acetate | w | w | ... | w | w | w | w | w | w | w | w | w | w | w | w | w a | w | w | w | w | w | w | w |
| Arsenate | a | w | a | a | a | a | a | a | a | a | a | a | a | a | a | a | a | w | a | w | a | w | a | ... |
| Arsenite | ... | w | a | a | ... | ... | a | ... | a | a | a | a | a | a | a | a | a | w | a | w | a | w | a | ... |
| Borate | a | w | ... | a | a | w a | a | a | a | a | a | a | a | w a | a | ... | ... | a | w | a | w | w | a | a |
| Bromide | w | w | w a | w | w a | w | w | w t | w | w | w | w | w t | w | w | a t | w | w | w | t | w | w | w |
| Carbonate | a | w | ... | a | a | a | a | ... | a | a | a | a | a | a | a | a | a | a | w | a | w | a | a |
| Chlorate | w | w | ... | w | w | w | w | w | w | w | w | w | w | w | w | w | w | w | w | w | w | w | w |
| Chloride | w | w | w a | w | w a | w | w | w | w | w | w | w | w t | w | w | a t | w | w | w | t | w | w | w |
| Chromate | ... | w | a | a | a | a | w a | a | a | w a | ... | w | a t | w | w | a | w a | a | w | a | w | w a | w |
| Citrate | w | w | ... | a | ... | a | w a | w | w | w | w | w | a | w | a | a | w a | w | w | a | w | a | w a |
| Cyanide | ... | w | ... | w a | ... | a | w | a | a t | a | a t | ... | a | w | a | ... | w | a t | w | t | w | w | a |
| Ferricyanide | ... | w | ... | ... | ... | ... | w | ... | t | ... | t | w | w a | w | t | ... | ... | t | w | t | w | ... | a |
| Ferrocyanide | ... | w | ... | w a | ... | ... | w | ... | t | t | t | t | a | w | a | ... | ... | t | w | t | w | w | a t |
| Fluoride | w | w | w | a t | w | w a | a | w | w a | a | w a | w | a | a t | a | ... | w a | w a | w | w | w | a t | w a |
| Hydroxide | a | w | a | w a | a | a | w a | a | a | a | a | a | a | a | a | ... | ... | a | w | ... | w | w a | a |
| Iodide | w | w | w a | w | a | w | w | w | w | w | w | w | w a | w | w | a | a | w | w | t | w | w | w |
| Nitrate | w | w | ... | w | w | w | w | w | w | w | w | w | w | w | w | w | w | w | w | w | w | w | w |
| Oxalate | a | w | a | a | a | a | a | w a | a | a | a | a | a | a | w a | a | a | a | w | a | w | a | a |
| Oxide | a *or* t | ... | a | w a | a | a | w a | a t | a | a | a | a | a | a | a | a | a | a | w | a | w | w a | a |
| Phosphate | a | w | w a | w *or* a | a | a | w a | a | a | a | a | a | a | a | a | a | a | a | w | a | w | a | a |
| Silicate | a t | ... | ... | a | . . | a | a | a | a | a | a | a | a | a | a | ... | ... | a | w | ... | w | a | a |
| Sulphate | w | w | a | t | w | w | t | w a | w | w | w | w | a t | w | w | w a | w | w | w | w a | w | t | w |
| Sulphide | a | w | a | w | a | a | w a | a t | a | a | a | a | a | a | a | a | a | a | w | a | w | w | a |
| Tartrate | w | w | a | a | a | w a | a | w | w | w | w a | w | a | w a | w a | w a | a | a | w | a | w | a | a |

**Special Remarks.**—Often a solution is presented for analysis instead of a solid substance, in which case some of it is evaporated to dryness. If a dry residue is left, this is tested for acids, as already described. But no residue may remain, and if the solution has a strongly acid reaction, the presence of the volatile acids is indicated, and the student, guided by the odor and change of color upon evaporation, should make tests for the following acids: hydrochloric, hydrobromic, hydriodic, nitric, sulphurous (hydrocyanic, acetic, formic).

If a strongly acid, fuming, oily residue is left, sulphuric acid is indicated.

A strongly acid, pasty, non-fuming residue indicates phosphoric acid.

If the solution is strongly acid and leaves a solid residue, the substance may be either an acid salt, or a salt held in solution by an acid, such as hydrochloric, nitric, sulphuric, etc., in which case several acids would have to be looked for. The presence of the volatile acids would be indicated by holding wet blue litmus-paper in the vapor as the liquid approached high concentration. If the residue upon evaporation is decidedly alkaline, this may be due to a salt having an alkaline reaction, or to a hydroxide, or both. The presence of a hydroxide is shown by adding some solution of silver nitrate to the diluted solution, when a dark precipitate of silver oxide is formed at once. In the absence of carbonate, the presence of hydroxide is also shown by adding some dry ammonium chloride to the solution and warming, when ammonia is liberated. A solution containing a hydroxide must, of course, be neutralized before applying the tests for acids. The acid usually employed for this is dilute nitric, but if tests are also to be made for the latter acid, another portion of the solution is neutralized with hydrochloric or acetic acid.

A solution may be colorless, odorless, practically neutral, leave no residue upon evaporation, and still not be plain water. In such a case, the student may suspect hydrogen dioxide. He would have reason to suspect this compound if he proceeded to search for metals before evaporating and found none, but got a precipitate of sulphur when using hydrogen sulphide, showing an oxidizing action.

The presence of some metals interferes with certain tests for acids, and these should be removed. After determining the kind of metal or metals in a substance or a mixture, and it is seen that there will be interference with the tests for acids, boil some of the substance with a slight excess of sodium or potassium carbonate for some time and filter. Non-alkali metals, except arsenic and antimony, remain behind, while the acids pass into the filtrate as alkali salts (with few exceptions). The filtrate is then exactly neutralized with nitric acid and boiled to expel all carbonic acid, and used for the various tests for acids. Arsenic and antimony may be removed by passing hydrogen sulphide into the warm acidified solution and filtering.

*Substances insoluble in water.* When a single substance, or that part of a mixture which is insoluble in water, is treated with hydrochloric acid in order to prepare a solution for the analysis of metals, something can be learned as to the nature of the acids in combination. Carbonates, sulphites, phosphates, arsenates, and arsenites behave the same as when treated with concentrated sulphuric acid in Table IX. Sulphides give the odor of hydrogen sulphide. If chlorine gas is given off, the presence of a higher oxide, like $MnO_2$, $PbO_2$, $BaO_2$, etc., or a chromate is indicated. If effervescence takes place and an inflamma-

ble gas is given off, the presence of a free metal is indicated. If the substance simply dissolves and no acids are subsequently found, the presence of an oxide or hydroxide is indicated, which can also be judged from a knowledge of the known compounds of the metals present.

The tests distinguishing between an arsenite and an arsenate (see Chapter on Arsenic) cannot be applied when the substance is insoluble in water (except the molybdate test, which can be used in an acid solution), but the treatment with hydrogen sulphide can be used to differentiate, because an arsenite gives a precipitate instantly even in cold solution, while an arsenate precipitates only after a long time.

If bismuth is present, remove it before testing for the acids by boiling with sodium carbonate, filtering, etc., as described above.

Substances insoluble in water and hydrochloric acid are next treated with nitric acid. Ordinarily very few such substances are presented. If brown vapors are evolved and sulphur separates, a sulphide is indicated, which the appearance of the substance will also suggest. If brown vapors alone are evolved, a free metal is indicated.

If the preliminary tests for metals show the presence of mercury, and the substance dissolves slowly on boiling with nitric acid, it is one of the halogen salts. The mercury should be removed by boiling the substance with an excess of caustic alkali, filtering, neutralizing the filtrate with nitric acid, and testing it for chloride, bromide, or iodide.

Before examining for metals, nitric acid solutions must be evaporated to dryness to expel excess of the acid. The residue is dissolved in water.

A few substances require nitro-hydrochloric acid for solution. The one most likely to occur ordinarily is mercuric sulphide, which is indicated by the presence of mercury, its black or vermilion color, and volatility on heating.

Of substances insoluble in all acids, the sulphates of barium, strontium, and lead are the most likely to be presented ordinarily. The treatment of these by fusion with sodium carbonate has already been mentioned. The presence of silver (as shown by the preliminary tests for metals) would indicate a chloride, bromide, iodide, or cyanide of this metal. The metal should be removed by boiling with caustic alkali and the filtrate tested. Silver iodide does not yield to this treatment, but its color and insolubility in strong ammonia is sufficient evidence of iodide. Silver cyanide with hydrochloric acid forms silver chloride and hydrocyanic acid, which is in solution and recognized by its odor.

The insoluble halogen salts of silver, lead, and mercury, also mercuric chloride and bromide, scarcely react when treated with concentrated sulphuric acid (Table IX).

Most of the points in the discussion above are shown in more convenient form in the following Tables, XIII and XIV, which are more detailed than Table IX, and will perhaps be of greater help to the student. Table XIV deals with difficultly soluble or insoluble substances, which may be subnitrate; subchloride; chloride (Pb, Hg(ous), Ag); bromide (Pb, Hg(ous), Ag); iodide; sulphate (Ca, Sr, Ba, Pb, Hg(ous); sulphite (except of alkalies); sulphide (except of alkalies and alkaline earths); carbonate, borate, phosphate, arsenate, arsenite (except of alkalies in each case); chromate (high color); fluoride; cyanide; oxide or hydroxide (except of alkali and alkaline earth metals); and a few others.

In the case of mixtures, the tables may be used to determine as far as

possible the nature of the acids, after which such other acids must be looked for as are not clearly indicated by the tables, but may be suggested as probably present by the preliminary examinations and the nature of the metals found.

TABLE XIII.—**Substances soluble in water.**

| *A. When the substance is already in solution, test with litmus paper and evaporate 20 c.c. to dryness:* | *B. When the substance is in the dry state, test its reaction to litmus paper and—* | |
|---|---|---|
| | *I. Warm a little with dilute sulphuric acid:* | *II. If I gives no indication, heat moderately a small quantity with concentrated sulphuric acid.* |
| *a.* If strongly acid and *no residue*, it may be free HCl, HBr, HI, $HNO_3$, HCN* or $H_2SO_3$. Note odor of vapors and test for the acid indicated by odor, etc. | *a.* Copious effervescence, *no color or odor*—test for carbonate (strongly alkaline) or bicarbonate (weakly alkaline). | *a.* White fumes—test for HCl, HF or $HNO_3$. Note odor. The salt is neutral or slightly acid. |
| *b.* A strongly acid, fuming residue—test for free $H_2SO_4$. | *b.* Moderate effervescence, *no color*, but with an<br>1. Odor of $SO_2$—test for sulphite (alkaline).<br>Odor of $SO_2$ + precipitate of sulphur—test for thiosulphate (neutral).<br>2. Odor of $H_2S$—test for a sulphide (alkaline).<br>3. Odor of HCN*—test for cyanide (alkaline)<br>4. Odor of HCN and a cryst. deposit, often bluish—test for ferro- or ferricyanide.<br>5. Odor of HCN + ppt of sulphur—test for a sulphocyanate. | *b.* Colored fumes:<br>1. Brownish—test for bromide.<br>2. Violet—test for iodide.<br>3. Greenish-yellow—test for chlorate.<br>(Bromates and iodates, like chlorates, also give colored fumes and deflagrate on charcoal.) |
| *c.* A strongly acid, soft, *non-fuming* mass—test for free $H_3PO_4$. | | |
| *d.* A *strongly acid*, combustible mass—test for free $H_4P_2O_6$: a *neutral* combustible mass, indicates a salt of $H_3PO_2$ (hypophosphorous acid). | *c.* Colored fumes.<br>1. Reddish—test for nitrite (alkaline).<br>2. Greenish, with odor of Cl—test for hypochlorite (alkaline). | *c.* Chromates and dichromates are recognized by their color and give green solutions in hot concentrated $H_2SO_4$. |
| *e.* Strongly acid, leaving a solid residue—it may be an acid salt or a salt held in solution by an acid, as HCl, $HNO_3$, $H_2SO_4$, etc. Refer to *B.* | | *d.* No change takes place. It may be sulphate (neutral or slightly acid), phosphate (alkaline), arsenate or arsenite (alkaline), borate (alkaline), boric acid, or a free base. All these acids would be indicated in the preliminary examinations and the analysis for the metals. If the substance is alkaline and gives a precipitate (dark) with solution of $AgNO_3$, a free base is present. Test also on $NH_4Cl$. |
| *f.* A slightly acid white residue which melts at high heat—test for free boric acid. | | |
| *g.* A weakly acid, neutral, or alkaline residue—it may be a salt or a free base, or both. Refer to *B.* | **Caution.*—Take care in smelling vapors of HCN, as they are poisonous. | |

## TABLE XIV.—Substances insoluble or very difficultly soluble in water.

| *A. When the substance is soluble in cold or hot, dilute or strong hydrochloric acid:* | *B. When the substance is insoluble or difficultly soluble in hydrochloric, but soluble in cold or hot, dilute or strong nitric acid:* | *C. When the substance is insoluble in either hydrochloric or nitric, but is soluble in a mixture of the acids:* |
|---|---|---|
| *Note.*—If Pb, Hg(ous), Ag, are indicated by the preliminary examination, omit treatment with HCl, but use $HNO_3$. | | |
| *a.* Note whether the effects are the same as in Table XIII, *B*, *I*, *a* and *b*. Make tests for the acids indicated there. | *a.* Brown vapors and a precipitate of sulphur indicate a sulphide. | It may be—<br>*a.* Mercuric sulphide, HgS, black or red, and volatile on foil by heat.<br>*b.* Gold.<br>*c.* Mercurous chloride, HgCl. (Slowly soluble in $HNO_3$. See *B*, *c*.)<br>*d* A few sulphides and oxides. |
| *b.* If chlorine is given off, a peroxide is present, as $MnO_2$, $PbO_2$, $BaO_2$, etc., or chromate (high color). | *b.* Brown vapors alone indicate free metal, as Ag, Pb, Hg, Bi, Cu, etc. | |
| *c.* If no change takes place except solution—<br>1. Subnitrate (or subchloride) is suspected if Bi or Sb is found as metal. Boil substance in slight excess $Na_2CO_3$, filter, neutralize filtrate and test for the acid.<br>2. Test for phosphate by molybdate solution.<br>3. Test for borate by alcohol flame.<br>4. Arsenate and arsenite are detected in analysis for metals: make further tests to distinguish the two.<br>5. If no acid is found and the substance is alkaline, it is CaO or $Ca(OH)_2$; if neutral, it is an oxide, as ZnO, MgO, PbO, etc., or their hydroxides. | *c.* If the substance is white, volatile on foil by heat, turns black with $NH_4OH$, and soluble in $HNO_3$ on long boiling, it is likely HgCl or HgBr. Test for the acid by boiling some with dilute NaOH, filter, acidify filtrate with $HNO_3$ and add $AgNO_3$.<br>(Likewise for HgI and $HgI_2$, which are yellow and red respectively.) | *D. When the substance is insoluble in all acids:* |
| *d.* Effervescence and inflammable gas—indicate a free metal, as Zn, Fe, Sn, etc. | *d.* If no change except solution, the substance is likely an oxide or hydroxide. This will also be indicated by the metal present and the appearance of the compound. | It may be—<br>*a.* Sulphate of Ba, Sr, Pb. These must be fused with $Na_2CO_3$.<br>*b.* Lead chloride, $PbCl_2$ ($PbBr_2$, $PbI_2$) (if not removed by much hot water.)<br>*c.* Chloride, bromide, iodide, or cyanide of silver, AgCl, AgBr, AgI, AgCN. Test solubility in $NH_4OH$ and $Na_2S_2O_3$.<br>(AgCN with HCl forms insoluble AgCl and leaves HCN in solution recognized by odor.)<br>*d.* Silicic acid and most silicates, native $Al_2O_3$, $Cr_2O_3$, $SnO_2$, $CaF_2$. |

## 38. METHODS FOR QUANTITATIVE DETERMINATIONS.

**General Remarks.**—Quantitative determination of the different elements or groups of elements may be accomplished by various methods, which differ generally with the nature of the substance to be examined. But even one and the same substance may often be analyzed quantitatively by entirely different methods, of which the two principal ones are the *gravimetric* and *volumetric* methods.

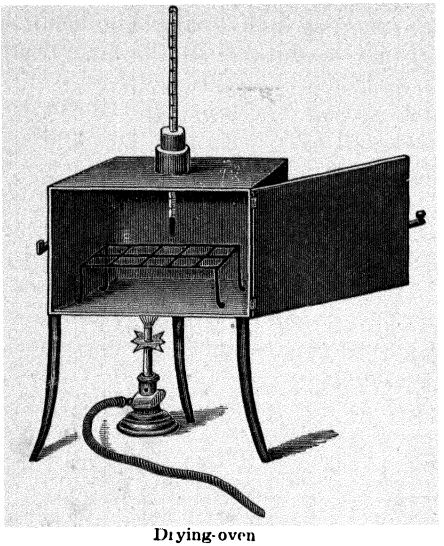
In the *gravimetric method,* the quantities of the constituents of a substance are determined by separating and weighing them either as such, or in the form of some compound the exact composition of which is known. For instance: From cupric sulphate, the copper may be precipitated as such by electrolysis and weighed as metallic copper, or it may be precipitated by sodium hydroxide as cupric oxide, CuO, and weighed as such. Knowing that every 79.6 parts by weight of cupric oxide contain of oxygen 16 parts and of copper 63.6 parts, the weight of copper contained in the cupric oxide found may be readily calculated.

In the *volumetric method,* the determination is accomplished by adding to a weighed quantity of the substance to be examined, a solution of a reagent of a known strength until the reaction is just completed, no excess being allowed. For instance: We know that every 80.12 parts by weight of sodium hydroxide precipitate 79.6 parts by weight of cupric oxide, containing 63.6 parts by weight of copper. Therefore, if we add a solution of sodium hydroxide of known strength to a weighed portion of cupric sulphate until all the copper is precipitated, we may calculate from the volume of soda solution used the weight of sodium hydroxide, and from this the weight of copper which has been precipitated. The operation of volumetric analysis is termed *titration.*

**Gravimetric Methods.**—While the quantitative determinations by these methods differ widely in some cases, there are a number of operations so often and so generally employed that a few remarks may be of advantage to the beginner. A small quantity (generally from 0.5 to 1 gram) of the substance to be analyzed is very exactly weighed on a delicate balance, transferred to a beaker, and dissolved in a suitable agent (water or acid). From this solution the constituent to be determined is precipitated completely, which is ascertained by allowing the precipitate to subside and adding to the clear liquid a few drops more of the agent used for precipitation. The precipitate is next collected upon a small filter of good filter paper containing as little of inorganic constituents (ash) as possible; the particles of precipitate which may adhere to the beaker are carefully washed off by means of a camel-hair brush. The precipitate is well washed (generally with pure water) until free from adhering solution, and dried by placing funnel and contents in a drying-oven, Fig. 33, in which a constant temperature of about 100° C. (212° F.) is maintained. The dried filter is then taken from the funnel and its con-

tents are transferred to a platinum (or porcelain) crucible, which has been previously weighed and stands on a piece of glazed, colored paper in order to collect any particle of the dried precipitate which

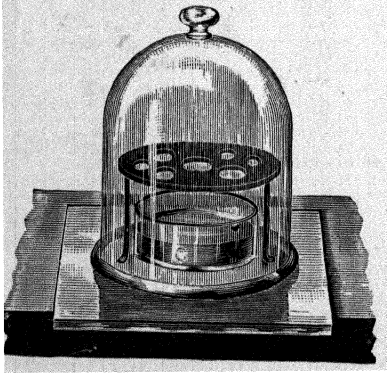
FIG. 33.



Drying-oven

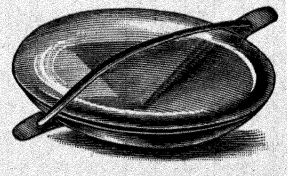
may happen to fall beside the crucible. The filter, from which the precipitate has been removed as completely as possible, by slightly rubbing it, is now folded, placed upon the lid of the crucible, which

FIG. 34.



Desiccator.

FIG. 35.



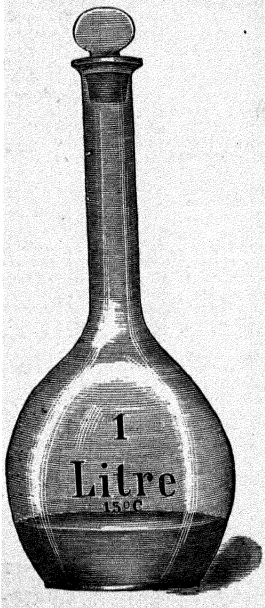
Watch-glasses for weighing filters.

rests on a triangle over a gas burner, and completely incinerated. The remaining filter-ash, with particles of the precipitate mixed with it, is transferred to the crucible, which is now placed over the burner and heated until all water (or possibly other substances) is completely

expelled. After cooling, the crucible is weighed, the weight of the empty crucible and that of the filter-ash (the latter having been previously determined by burning a few filters of the same kind) deducted, and thus the quantity of the precipitate determined.

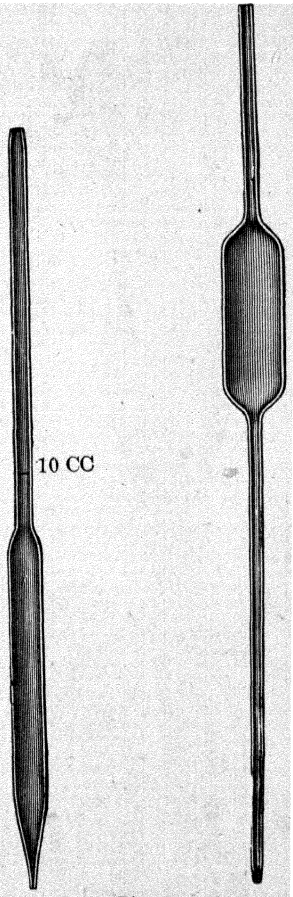
As platinum crucibles and many precipitates, after ignition, absorb moisture from the air, it is well to allow the heated crucible to cool in a *desiccator*. This is a closed vessel in which the contained air is

FIG. 36.




Liter flask.

FIG. 37.




Pipettes.

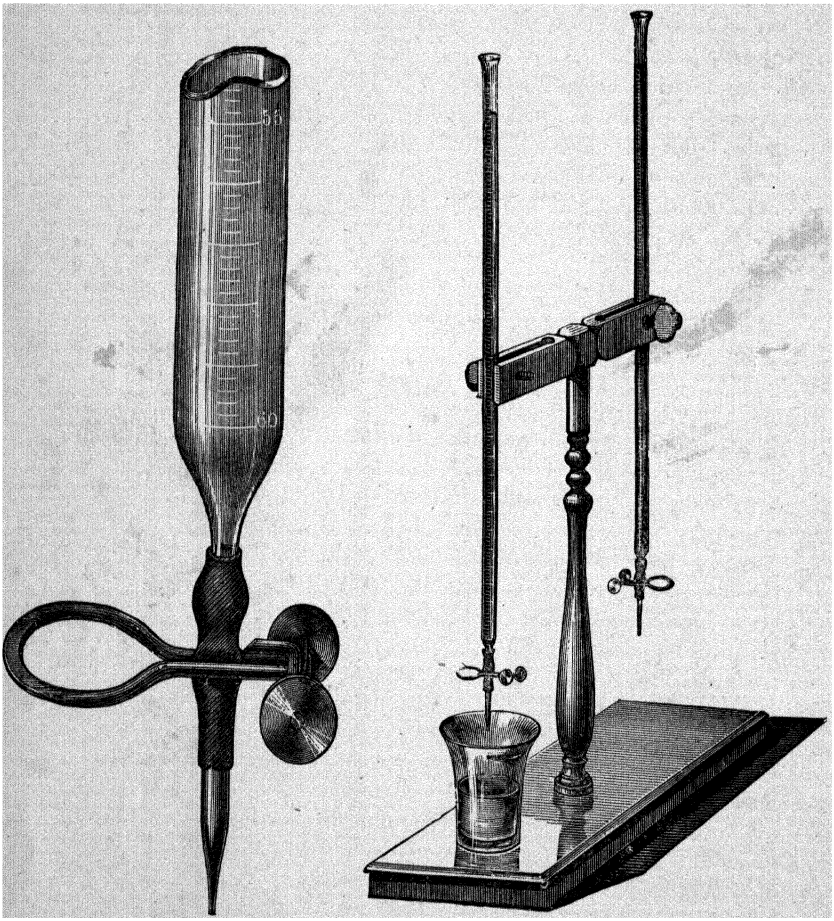
kept dry by means of concentrated sulphuric acid. Fig. 34 shows a convenient form of desiccator.

The empty crucibles should be weighed under the same conditions —*i. e.*, after having been heated and cooled in a desiccator.

Some precipitates (as, for instance, potassium platinic chloride), cannot be ignited without suffering partial or complete decomposition. It is for this reason that some precipitates are collected upon

filters which have been previously dried at 100° C. (212° F.) and weighed carefully. The precipitate is then collected upon the weighed filter, well washed, dried at 100° C. (212° F.) and weighed.

The weighing of dried filters is best accomplished by placing them between two watch-glasses held together by means of a brass or nickel clamp, as shown in Fig 35.



Mohr's Burette and clamp. Mohr's burette and holder.

The above-described methods may be employed for the determination of those substances which can be precipitated from their solutions in the form of some stable compound. Aluminum, zinc, iron, bismuth, copper, etc., may, for instance, be precipitated as hydroxides and weighed as oxides, into which the precipitated compound is converted by ignition. Sulphuric acid may be precipitated and weighed as barium sulphate, phosphoric acid may be precipitated by

magnesia mixture and weighed as magnesium pyrophosphate, etc. Some substances, like nitric acid, chloric acid, etc., cannot be precipitated from their solutions, for which reason other methods have to be employed for their determination.

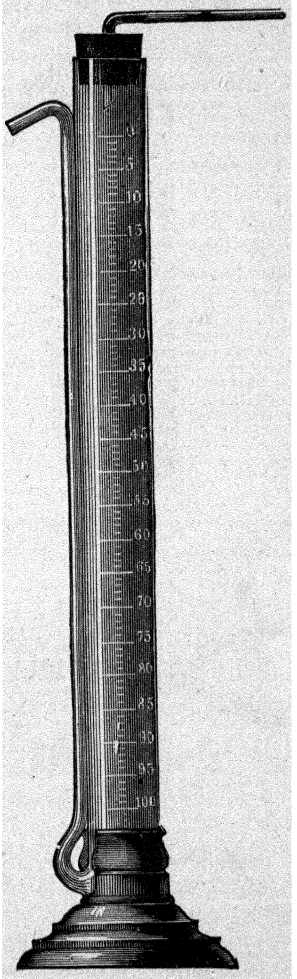
**Volumetric Methods.**—The great advantage of volumetric over gravimetric analysis consists chiefly in the rapidity with which these determinations are performed. Unfortunately, volumetric methods cannot be employed to advantage for the estimation of all substances.

The special apparatus required for volumetric analysis consists of a few flasks, some pipettes, burettes, and a burette-holder. The flasks should have a mark on the neck, indicating a capacity of 100, 250, 500, and 1000 c.c. respectively. (See Fig. 36.)

Of pipettes (Fig. 37), those having a capacity of 5, 10, 25, and 50 cubic centimeters are mostly used.

Of burettes many different forms are used; in most cases Mohr's burette (Figs. 38 and 39) answers all requirements, but its application is excluded whenever the test solution is chemically affected by rubber, as in the case of solutions of silver, permanganate, and a few other substances. For such solutions Mohr's burette with glass stopcock, or Gay Lussac's burette (Fig. 40) is generally used.

FIG. 40.



Gay Lussac's burette.

**Standard Solutions.**—Standard solutions are solutions containing a known and definite quantity of some reagent employed in volumetric analysis. A standard solution may be normal, or it may be an *empirical solution.* In the latter case it contains in a liter some arbitrarily chosen weight of reagent. As an instance may be mentioned Fehling's solution, used for the determination of sugar. This solution is so adjusted that 1 c.c. decomposes or indicates 0.005 gm. of grape-sugar.

**Normal Solutions.**—The solutions generally used in volumetric analysis are known as normal solutions, and are chemically equivalent to each other because of the standard adopted in their preparation. This standard is the weight of one atom of hydrogen expressed in grams, or the chemical equivalent of one atom of hydrogen, con-

tained in one liter of solution. For the sake of convenience the terms *gram-atom* and *gram-molecule* are often used in connection with volumetric work, and refer, of course, to the atomic or molecular weight of the substance considered, expressed in grams.

A consideration of the application of these principles to practical work in volumetric analysis may assist the student in understanding them fully.

Thus, a *normal acid solution* may be defined as one containing in a liter as much acid as contains one gram-atom of replaceable hydrogen. In such acids as HCl, HBr, $HNO_3$, a liter solution containing the gram-molecule would be normal, since each solution would contain one gram-atom of replaceable hydrogen. In order to make a normal solution of such acids as $H_2SO_4$, $H_2C_2O_4$, one-half the gram-molecule must be taken, since this quantity contains one atom of hydrogen, and so on.

A *normal alkali solution* may be defined as one containing that quantity of alkali in a liter which is chemically equivalent to—*i. e.*, neutralizes one gram-atom of acid hydrogen. For such compounds as KOH, NaOH, $NH_4OH$, the whole gram-molecule must be taken to make a liter of normal solution. In case of $Ba(OH)_2$ or $Ca(OH)_2$, one half the gram-molecule is taken.

It will easily be seen that all the acid solutions made as described are of equivalent strength and are exactly equivalent to the solutions of alkali—*i. e.*, one liter normal HCl will exactly neutralize one liter of normal KOH, or NaOH, or $Ba(OH)_2$. That this is so will appear at once on writing the equations which express the reactions between these alkalies and acids, thus:

$$\underset{36.47}{HCl} + \underset{56.11}{KOH} = KCl + H_2O.$$

$$2HCl + Ba(OH)_2 = BaCl_2 + 2H_2O.$$

or

$$\underset{36.47}{HCl} + \frac{Ba(OH)_2}{2} = \frac{BaCl_2}{2} + H_2O.$$

$$\underset{56.11}{KOH} + \frac{H_2SO_4}{2} = \frac{K_2SO_4}{2} + H_2O.$$

$$\frac{98.09}{2}$$

The above equations show that 36.47 grams of HCl are equivalent to 56.11 grams of KOH, but these are the quantities taken for a liter of normal solution repectively, hence these normal solutions must be equivalent. Similarly for HCl and $Ba(OH)_2$, for KOH and $H_2SO_4$, etc.

Conversely, if a solution of unknown strength be compared by titration with a second solution known to be normal, and then be properly diluted so that the two are equivalent, volume for volume, the first solution will also be normal, and from the definition of normal solutions the quantity of reagent in a liter of the solution becomes at once known. For example, if a solution of sulphuric acid be made equivalent to a normal solution of caustic alkali it will then contain 49.045 grams of absolute sulphuric acid per liter. It is thus an easy matter to prepare normal solutions, although it may be impossible to

weigh exactly the amount of reagent necessary for a liter of such solutions. All that is required is one normal solution as a starting-point.

Sodium carbonate, $Na_2CO_3$, may be used as an alkali, just as KOH or NaOH, because it neutralizes acids in precisely the same manner, for the carbonic acid has no effect, being volatile and escaping into the air. The decomposition taking place thus:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2,$$

shows that one molecule of sodium carbonate neutralizes two molecules of hydrochloric acid, consequently one-half gram-molecule of sodium carbonate must be taken to make a liter of normal solution. A similar consideration will show that of sodium bicarbonate the whole gram-molecule should be taken for a liter of normal solution, because this salt contains but one atom of sodium in the molecule.

A *normal salt solution* may be defined as one containing in a liter the quantity of salt resulting from the neutralization, or replacement of the hydrogen in a normal acid solution by metal. Thus, $\frac{Na_2SO_4}{2}$; NaCl, $AgNO_3$, $\frac{BaCl_2}{2}$, expressed in grams, would be contained in a liter of normal solution of the respective salts.

Often normal solutions are too strong, and are diluted ten or a hundred times. They are then called deci- or centi-normal solutions, respectively.

Normal solutions are generally designated by $\frac{N}{1}$, deci-normal solutions by $\frac{N}{10}$, centi-normal solutions by $\frac{N}{100}$; solutions containing twice the amount are designated as double normal, $\frac{2}{N}$; half the amount semi-normal, $\frac{N}{2}$.

**Different Methods of Volumetric Determination.**—Of these we have at least three, which may be called the direct, the indirect, and the method of rest or residue.

The *direct methods* are used in all cases in which the quantities of volumetric solutions can be added until the reaction is complete: for instance, until an alkaline substance has been neutralized by an acid, or a ferrous salt has been converted into a ferric salt by potassium permanganate, etc.

In the *indirect methods* one substance, which cannot well be determined volumetrically, is made to act upon a second substance, with the result that, by this action, an equivalent quantity of a substance is generated or liberated, which may be titrated. For instance: Peroxides, chromic and chloric acids when boiled with strong hydrochloric acid, liberate chlorine, which is not determined directly, but is caused to act upon potassium iodide, from which it liberates the iodine, which may be titrated with sodium thiosulphate.

The *methods of residue* are based upon the fact that while it is impossible or extremely difficult to obtain complete decomposition between certain substances and reagents, when equivalent quantities are added to one another, such a complete decomposition is accomplished by adding an excess of the reagent, which excess is afterward determined by a second volumetric solution. For instance: Car-

bonate of calcium, magnesium, zinc, etc., cannot well be determined directly, for which reason an excess of normal acid is used for their decomposition, this excess being titrated afterward by means of an alkali.

**Indicators.**—In all cases of volumetric determination it is of the greatest importance to observe accurately the completion of the reaction. In some cases the final point is indicated by a change in color, as, for instance, in the case of potassium permanganate, which changes from a red to a colorless solution, or chromic acid, which changes from orange to green under the influence of deoxidizing agents. In other cases the determination is indicated by the formation or cessation of a precipitate, and in yet others the final point could not be noticed with precision unless rendered visible by a third substance added for that purpose.

Such substances are termed *indicators*. Litmus, phenolphthalein, methyl-orange, etc., are used as indicators in acidimetry and alkalimetry. Starch paste is an indicator for iodine, potassium chromate for silver, etc. A few drops of indicators are in most cases sufficient for the purpose.

*Litmus Solution.*—This is made by exhausting coarsely powdered litmus repeatedly with boiling alcohol, which removes a red coloring matter, erythrolitmin. Each extraction should last about one hour. The residue is treated with about an equal weight of cold water, so as to dissolve the excess of alkali present in litmus. The remaining mass is extracted with about five times its weight of boiling water, and after thoroughly cooling is filtered. The solution should be kept in wide-mouthed bottles, stoppered with loose plugs of cotton to exclude dust but to admit air. *Blue* and *red litmus paper* is made by impregnating strips of unsized white paper with the blue solution obtained by the above process, or with this solution after just enough hydrochloric acid has been added to impart to it a distinct red tint.

*Phenolphthalein Solution.*—1 gram of phenolphthalein is dissolved in 100 c.c. of alcohol. The colorless solution is colored deep purplish-red by alkali hydroxides or carbonates, but not by bicarbonates; acids render the red solution colorless. The solution is not suitable as an indicator for ammonia, nor in the presence of ammonium salts. Carbonates must be titrated in boiling solution to drive off carbon dioxide.

*Methyl-orange Solution.*—1 gram of methyl-orange (also known as helianthin, tropæolin D, or Poirier's orange 3 P), the sodium or ammonium salt of dimethylamino-azobenzenesulphonic acid $(CH_3)_2N.C_6H_4.N.NC_6H_4.SO_3H$, is dissolved in 1000 c.c. of water. To the solution is carefully added, with constant stirring, $\frac{N}{10}$ sulphuric acid, in drops, until the liquid turns red and just ceases to be transparent; it is then filtered. The solution is yellow when in contact with alkaline hydroxides, carbonates, or bicarbonates. Carbonic acid does not affect it, but mineral acids change its color to crimson. It should be used in cold solutions, but not in alcohol, nor for titrating organic acids.

*Methyl-red Solution.*—0.2 gram are dissolved in 100 c.c. of alcohol. Methyl-red is similar in composition to methyl-orange, being dimethylamino-azobenzene-carboxylic acid. It occurs in violet crystals, very slightly soluble in cold water but readily soluble in alcohol. It is used in the same instances in which methyl-

orange is employed. The indicator is yellow in alkaline solutions, rose-red in faintly acid, and violet-red in strongly acid solutions. Its end-points are sharper than those of methyl-orange and it is far more sensitive in the titration of very dilute solutions of weak bases.

*Hæmatoxylin Solution.*—0.2 gram of hæmatoxylin (a vegetable coloring-matter derived from hæmatoxylon) is dissolved in 100 c.c. of alcohol. The alkaline solution has a purple color which is changed to yellow or orange by acids.

*Rosolic Acid Solution.*—1 gram of commercial rosolic acid (chiefly $C_{20}H_{16}O_3$) is dissolved in 10 c.c. of alcohol, and water added to make 100 c c. The solution turns violet red with alkalies, yellow with acids. Ammoniacal solutions must be highly diluted. It is useless for organic acids.

Other indicators used at times in acidimetry are solutions of brazil-wood, cochineal, methyl-violet, alizarin, iodeosin, Congo red, turmeric, etc.

*Ionic explanation of the action of indicators.* The substances used to indicate the neutralization point are themselves very weak acids or bases, capable of forming salts with the bases or acids that are brought together in solution for the purpose of neutralization. The undissociated molecules of the indicator have a different color from its ions, and it must have feeble dissociating power in the uncombined state. The latter is a characteristic of feeble acids in general. The salts of the indicators are easily dissociated into ions. Substances that are strong acids or bases cannot be used as indicators, because they dissociate in the free state, and thus give no different color when they are neutralized. The indicators that dissociate least in the free state are the most sensitive in color changes when combined with traces of acids or bases. The neutral point in neutralization experiments is really overstepped by the amount of acid or alkali required to produce change of color with the indicator, but in the case of sensitive indicators this amount is a mere trace and is negligible.

Litmus is an acid with slight dissociating power, which in pure water gives a violet color. Addition of acids represses the slight dissociation and the color changes to red, which is the color of the undissociated molecules of litmus. Alkalies form salts with litmus, which dissociate easily, the negative ions showing a blue color.

Phenolphthalein is an acid of less dissociating power than litmus. In pure water or acids it is colorless, in alkaline solutions it is red, which is the color of the negative ions of the dissociated molecules of the salt of the indicator.

Methyl-orange is an acid of greater dissociating power than litmus. It dissociates slightly when greatly diluted in water, giving a yellow color, which is the color of the negative ions. With less water the color is orange, which is the resultant of the yellow color of the ions and the red color of the undissociated molecules. In acid solutions the dissociation of the indicator is repressed, and the color is pure red. In alkaline solutions, salts of the indicator are formed which dissociate freely and give an intense yellow color.

Because different indicators, as well as different acids and bases, show great differences in their degrees of dissociation, marked variations in the sensitiveness of indicators to acids and bases are observed. Hence, indicators must be chosen to suit the particular case of neutralization in hand for accurate work.

For example, if an active acid is titrated with ammonia and phenolphthalein as indicator, color is not produced sharply at the neutral point, because ammonium hydroxide is so little dissociated that it requires an appreciable excess beyond the neutral point to produce the dissociated salt with the indicator. In this case litmus or methyl-orange is suitable to use.

**Titration.**—This term is used for the process of adding the volumetric solution from the burette to the solution of the weighed substance until the reaction is completed. We also speak of the *standard* or *titer* of a volumetric test-solution, when we refer to its strength per volume (per liter or per cubic centimeter).

Of the principal processes of titration, or of volumetric methods used, those may be mentioned which are based upon *neutralization* (acidimetry and alkalimetry), *oxidation and reduction* (permanganates and chromates as oxidizing, oxalic acid and ferrous salts as reducing agents) *precipitation* (silver nitrate by sodium chloride), and finally those which depend on the *action of iodine* and *thiosulphate* (iodimetry).

The substance to be titrated should be diluted with pure water to a volume of about 75 c.c. The relationship between any two volumetric solutions, for example, acid and alkali, should also be determined in the same volume. Any convenient quantity, as 10 or 20 c.c., of one solution is drawn from a burette into a beaker and diluted to about 75 c.c. before titrating with the other solution. If the comparison is made in a much smaller or much greater volume, a somewhat different relationship will be found. In general, the titer of a volumetric solution should be determined in a volume corresponding approximately to that in which the titration of a substance is to be carried out. This is usually the volume stated above, but sometimes, for certain reasons, it may be much greater.

**Acidimetry and Alkalimetry.**—Preparing the volumetric test-solutions is often more difficult than to make a volumetric determination. Whenever the reagents employed can be obtained in a chemically pure condition it is an easy task to prepare the solution, because a definite weight of the reagent is dissolved to a definite volume in water. In many instances, however, the reagent cannot be obtained absolutely pure, and in such cases a solution is made and its standard adjusted afterward by methods which will be spoken of later.

Neither the common mineral acids, such as sulphuric, hydrochloric, and nitric acids, nor the alkaline substances, such as sodium hydroxide or ammonium hydroxide, are sufficiently pure to permit of being used directly for volumetric solutions, because these substances contain water, and an absolutely correct determination of the amount of this water is an operation which involves a knowledge of gravimetric methods.

The most important thing in preparing volumetric solutions is to have an accurate solution as a beginning, from which any number of other solutions may be prepared by comparison. In the case of

acid solution, the method generally adopted by those who are capable of carrying out gravimetric determinations and have the conveniences at hand, is to standardize a solution of sulphuric acid, by precipitating barium sulphate from an accurately measured portion of the acid and calculating the weight of absolute acid contained therein, and from this the amount contained in a liter. The solution may be used as an empirical one, or it may be diluted, if more than normal, so that a liter of the diluted solution contains exactly 49.045 grams of absolute sulphuric acid, that is, becomes normal. A solution of hydrochloric acid is standardized similarly by precipitating silver chloride and from the weight of the precipitate making the calculations as just indicated.

Ten c.c. of normal sulphuric acid, containing 0.49045 gram of absolute acid, gives 1.1672 grams of barium sulphate, and 10 c.c. of normal hydrochloric acid, containing 0.3646 gram of absolute acid, give 1.4334 grams of silver chloride.

For the pharmacist and physician, a simpler procedure is to get a start by using some acid substance which can be obtained pure and is stable in the air, and either weigh directly the amount theoretically required to make a liter of normal solution, or weigh an amount that would make about 50 c.c. of a normal solution and titrate this with an alkali solution, and by proper calculation establish the strength or titer of the alkali. Or, conversely, a pure alkaline substance like anhydrous sodium carbonate, prepared according to the directions in the U. S. P., may be used to establish the strength of an acid solution by titration and subsequent calculation.

Pure oxalic acid and acid potassium tartrate are two acid substances which can be bought in the market and serve very well for getting a start in preparing volumetric solutions. Likewise pure anhydrous sodium carbonate can readily be made by heating pure bicarbonate at red-heat.

**Normal Acid Solution.**—Crystallized oxalic acid has the composition $H_2C_2O_4.2H_2O$ and a molecular weight of 126.05. Being dibasic, only half of its weight is taken for the normal solution, which is made by placing 63.025 grams of pure crystallized oxalic acid in a liter flask, dissolving it in pure water, filling up to the mark at the temperature of 25° C. (77° F.) and mixing thoroughly.

*Normal solutions of sulphuric or hydrochloric acid* are, for various reasons, often preferred to oxalic acid. These solutions are best made by diluting approximately the acids named, titrating the solution with normal sodium hydroxide, using methyl-orange as an indicator, and adding water until equal volumes saturate one another. For instance, if it should be found that 10 c.c. normal alkali solution neutralize 7.6 c.c. of the acid, then 24 c.c. of water have to be added to every 76 c.c. of the acid in order to obtain a normal solution. Normal sulphuric acid contains 49.045 grams of $H_2SO_4$, and normal hydrochloric acid 36.46 grams of HCl per liter.

These normal solutions can be made conveniently by diluting either 30 c.c. of pure, concentrated sulphuric acid of sp. gr. 1.84, or 130 c.c. of hydrochloric acid of sp. gr. 1.16 to 1000 c.c. The solutions thus obtained are yet too concentrated and are adjusted as described above.

An alternative method for standardizing approximately normal sulphuric or hydrochloric acid given in the U. S. P., is to weigh accurately about 2 grams of pure anhydrous sodium carbonate, dissolve it in 100 c.c. of water and titrate it with the acid, using methyl-orange indicator. One gram of anhydrous carbonate requires 18.868 c.c. of normal acid for neutralization. Assuming that exactly 2.25 grams of carbonate were weighed for titration, this would require $18.868 \times 2\,25 = 42.453$ c.c. of normal acid for titration. If 38 c.c. of the approximate acid be actually used, we can say that this volume is equivalent to 42.453 c.c. of normal acid. The following proportion gives the volume of the acid solution that must be diluted to 1 liter to make a normal solution:

$$42.453 \text{ c.c.} : 38 \text{ c.c.} :: 1000 \text{ c.c.} : x \text{ c.c.}$$
$$x = 895.11 \text{ c.c.}$$

If this volume be diluted with water to 1 liter a normal acid will result. Instead of measuring this volume of acid solution, a simpler way is to measure 104.89 c.c. of water into a dry liter flask and fill up to the mark on the neck of the flask with the acid solution.

**Normal Alkali Solution.**—A normal solution of sodium carbonate may be made by dissolving 53 grams (one-half the molecular weight) of pure sodium carbonate (obtainable by heating pure sodium bicarbonate to a low red-heat) in water, and diluting to one liter. This solution, however, is not often used, but may serve for standardizing acid solutions, as it has the advantage of being prepared from a substance that can be easily obtained in a pure condition, which is not the case in preparing the otherwise more useful *normal solutions of potassium or sodium hydroxide,* both of which substances contain and absorb water.

The solutions are made by dissolving about 70 grams of potassium hydroxide or 60 grams of sodium hydroxide in about 1000 c.c. of water, titrating this solution with normal acid, and diluting it with water, until equal volumes of both solutions neutralize each other exactly.

The indicators used in alkalimetry are chiefly solutions of litmus, phenolphthalein, or methyl-orange, only a few drops of either solution being needed for a determination.

The method adopted by the U. S. P. for standardizing the caustic alkali solution, prepared as above mentioned, depends on the use of chemically pure potassium bitartrate which acts on the alkali thus:

$$KHC_4H_4O_6 + KOH = K_2C_4H_4O_6 + H_2O.$$

As the molecular weight of potassium bitartrate is 188.14, it follows that this weight in grams will neutralize one liter of normal alkali solution. The Pharmacopœia directs to dissolve 4.7035 grams of potassium bitartrate in boiling water and titrating with a portion of the caustic alkali solution, the remainder of which is then diluted

as described above under Sulphuric Acid. 4.7035 grams of bitartrate requires exactly 25 c.c. of normal alkali for neutralization. Phenolphthalein is used as indicator.

Whenever carbonates are titrated with acids, or *vice versa*, the solution has to be boiled toward the end of the reaction in order to drive off the carbon dioxide, as neither litmus nor phenolphthalein gives reliable results in the presence of carbonic acid or an acid carbonate. This boiling is unnecessary when methyl orange is used, because it is not influenced by carbonic acid.

When salts of organic acids with alkali metals are to be titrated with normal acids, these salts are first converted into carbonates. This is accomplished by igniting the weighed quantity of the salt in a crucible of porcelain or platinum. The chemical action which takes place during the ignition of potassium acetate may be shown thus:

$$2KC_2H_3O_2 + 8O = K_2CO_3 + 3H_2O + 3CO_2.$$

In a similar manner the alkali salts of all organic acids are converted into carbonates. Frequently some carbon is left unburned; this, however, does not interfere with the result of the titration. The titration is made with the liquid obtained by dissolving in water the residue left after ignition.

In some of the titrations of the U. S. P., solutions other than normal are employed, for example $2n$, $\frac{n}{2}$, $\frac{n}{10}$, $\frac{n}{50}$ and $\frac{n}{100}$ alkali and $\frac{n}{2}$, $\frac{n}{10}$ and $\frac{n}{50}$ acid. Such solutions are prepared in the same manner as described above, or by diluting an accurate normal solution to the proper degree.

**Method for Calculating Results.**—Before one can calculate how much, say, of an acid is in a solution which he is titrating with a normal alkali, it is necessary to know how much of the acid in question is equivalent to—*i. e.*, is required to neutralize—one c.c. of the alkali. Knowing this, it is easy to find how much acid is equivalent to a certain number of c.c. of normal alkali used in titration. These alkali equivalents of normal acid, or acid equivalents of a normal alkali, are easily found by the student from the equation of reaction.

Thus, to find how much HCl is equivalent to one c.c. of normal alkali, we use the equation:

$$\underset{36.47}{HCl} + \underset{56.11}{KOH} = KCl + H_2O,$$

from which we see that

36.47 gm. HCl = 56.11 gm. KOH = 1000 c.c. normal KOH,
or, 0.03647 gm. HCl = 1 " " "

Again,

$$\underset{2 \times 56.11}{2KOH} + \underset{98.09}{H_2SO_4} = K_2SO_4 + 2H_2O.$$

98.09 gm. $H_2SO_4$ = $2 \times 56.11$ gm. KOH = 2000 c.c. normal KOH.
49.045 " " = 56.11 " " = 1000 " " "
0.049045 " " = 1 " " "
25

Phosphoric acid presents a peculiar case. When tropæolin is used as an indicator the change in color takes place when this reaction is completed:

$$H_3PO_4 + KOH = KH_2PO_4 + H_2O.$$
$$98.06 \quad 56.11$$

Hence,

98.06 gm. $H_3PO_4$ = 56.11 gm. KOH = 1000 c.c. normal KOH.
0.09806 " " = 1 " " "

With phenolphthalein, the indicator changes color when the subjoined reaction is completed:

$$H_3PO_4 + 2KOH = K_2HPO_4 + 2H_2O.$$

Hence,

98.06 gm. $H_3PO_4$ = 2 × 56.11 gr. KOH = 2000 c.c. normal KOH.
or 0.04903 " " = 1 " " "

The calculation for the amount of acid or alkali is made in this way. Suppose we weigh off 10 grams of dilute sulphuric acid. On titrating with normal KOH it is found that 20 c.c. are required to cause the change in the indicator (litmus)—*i. e.*, to completely neutralize the acid. We know from the above that 1 c.c. normal KOH requires 0.049045 gram $H_2SO_4$ for neutralization, hence 20 c.c. normal KOH require 0.049045 × 20 = 0.9809 gram $H_2SO_4$. That is, in the 10 grams dilute acid weighed off there are 0.9809 gram $H_2SO_4$, or in 100 grams there are 9.809 grams, or 9.81 per cent. This instance will serve as a type for all calculations of percentages.

**Use of Empirical Solutions.**—The primary advantage in using normal, deci-normal, etc., solutions is the fact that the calculations of results is very much simplified in a system which involves molecular and atomic weights, or simple fractions thereof. But any solution of definite strength can be employed. All normal, deci-normal, etc., solutions deteriorate in time, some very slowly, others rapidly, especially when not properly preserved. To restore the titer of such solutions each time they are to be used involves an unnecessary outlay of time. All that is necessary to know is the exact ratio between the solutions and a normal or deci-normal solution, to determine which an accurately standardized solution should be always available.

To illustrate, suppose 12.5 c.c. of a hydrochloric acid solution, exactly neutralize 10 c.c. of normal potassium hydroxide solution, then 1 c.c. of the hydrochloric acid is equivalent to 0.8 c.c. of normal acid, and the volume of acid used in any titration is readily converted into the equivalent volume of normal acid by multiplying by the factor 0.8.

**Neutralization Equivalents.**—The normal solutions of acid and alkali may be used for the determination of a large number of substances, either directly (as in the case of free acids, alkalies and alkali carbonates and bicarbonates) or indirectly (as in the case of salts of most of the organic acids with alkalies, which are first converted into carbonates by ignition).

One c.c. of normal acid is the equivalent of:

| | Gram. |
|---|---|
| Ammonia, $NH_3$ | 0.01703 |
| Ammonium carbonate, $(NH_4)_2CO_3$ | 0.04804 |
| Ammonium carbonate (U. S. P.), $NH_4HCO_3.NH_4NH_2CO_2$ | 0.05237 |
| Barium hydroxide, $Ba(OH)_2.8H_2O$ | 0.15775 |
| Calcium carbonate, $CaCO_3$ | 0.05003 |
| Calcium hydroxide, $Ca(OH)_2$ | 0.03704 |
| Lead acetate, crystallized $Pb(C_2H_3O_2)_2.3H_2O$[1] | 0.18960 |
| Lead subacetate, $Pb_2O(C_2H_3O_2)_2$[1] | 0.13706 |
| Lithium carbonate, $Li_2CO_3$ | 0.03694 |
| Lithium salicylate, $LiC_7H_5O_3$[2] | 0.14398 |
| Potassium acetate, $KC_2H_3O_2$ | 0.09812 |
| Potassium bicarbonate, $KHCO_3$ | 0.10011 |
| Potassium bitartrate, $KHC_4H_4O_6$[2] | 0 18814 |
| Potassium carbonate, $K_2CO_3$ | 0.06910 |
| Potassium citrate, crystallized, $K_3C_6H_5O_7.H_2O$[2] | 0.10812 |
| Potassium hydroxide, KOH | 0.05611 |
| Potassium permanganate, $KMnO_4$ | 0.03161 |
| Potassium sodium tartrate, $KNaC_4H_4O_6.4H_2O$[2] | 0.14110 |
| Sodium acetate, $NaC_2H_3O_2.3H_2O$[2] | 0.13607 |
| Sodium benzoate, $NaC_7H_5O_2$[2] | 0.14404 |
| Sodium bicarbonate, $NaHCO_3$ | 0.08401 |
| Sodium borate, crystallized, $Na_2B_4O_7.10H_2O$ | 0.19108 |
| Sodium carbonate, monohydrate, $Na_2CO_3.H_2O$ | 0.06201 |
| Sodium carbonate, $Na_2CO_3$ | 0.05300 |
| Sodium citrate, crystallized, $Na_3C_6H_5O_7.2H_2O$[2] | 0.09802 |
| Sodium hydroxide, NaOH | 0.04001 |
| Sodium salicylate, $Na(C_7H_5O_3)$[2] | 0.16004 |
| Sodium tartrate, $Na_2C_4H_4O_6.2H_2O$[2] | 0.11515 |

One c.c. of normal sodium carbonate, potassium hydroxide, or sodium hydroxide, is the equivalent of:

| | Gram. |
|---|---|
| Acetic acid, $HC_2H_3O_2$ | 0.06003 |
| Boric acid, $H_3BO_3$ | 0.06202 |
| Citric acid, crystallized, $H_3C_6H_5O_7.H_2O$ | 0.07003 |
| Formaldehyde, $CH_2O$ | 0.03002 |
| Hydrobromic acid, HBr | 0.08093 |
| Hydrochloric acid, HCl | 0.03647 |
| Hydriodic acid, HI | 0.12793 |
| Hypophosphorous acid, $HPH_2O_2$ | 0.06606 |
| Lactic acid, $HC_3H_5O_3$ | 0.09005 |
| Nitric acid, $HNO_3$ | 0.06302 |
| Oxalic acid, crystallized, $H_2C_2O_4.2H_2O$ | 0.06302 |
| Paraformaldehyde, $(CH_2O)_3$ | 0.03002 |
| Phosphoric acid, $H_3PO_4$ (to form $K_2HPO_4$; with phenolphthalein) | 0.04903 |
| Phosphoric acid, $H_3PO_4$ (to form $KH_2PO_4$; with methyl-orange) | 0.09806 |

[1] With sulphuric acid and methyl-orange. [2] After ignition [3] With oxalic acid only.

| | Gram. |
|---|---|
| Potassium bitartrate, $KHC_4H_4O_6$ | 0.18814 |
| Sodium bitartrate, $NaHC_4H_4O_6$ | 0.19015 |
| Sulphuric acid, $H_2SO_4$ | 0.04904 |
| Tartaric acid, $H_2C_4H_4O_6$ | 0.07503 |
| Trichloracetic acid, $CCl_3COOH$ | 0.16339 |

**Oxidimetry.**—A normal oxidizing solution is one which will liberate from a liter as much oxygen as is chemically equivalent to one gram-atom of hydrogen. This is one-half gram-atom, or 8 grams of oxygen, for

$$H_2 + O = H_2O, \text{ or } H + \frac{O}{2} = HO\tfrac{1}{2}.$$

The substances generally used in oxidimetry are potassium permanganate and potassium dichromate.

**Potassium Permanganate, $KMnO_4$, 158.03.**—Potassium permanganate is chiefly used for normal or deci-normal oxidizing solution, and the titration is always carried out in solution acidified with sulphuric acid. When the salt breaks up to give off oxygen, it does so in this manner:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O + 3H_2O.$$

The oxygen is used in oxidizing the substance which is titrated. The object of adding the acid is to facilitate the decomposition of the $KMnO_4$ and to take up the potassium and manganese to form salts, which being colorless form a colorless solution.

As 2 molecules of permanganate give up 5 atoms of oxygen, the quantity to be taken to liberate $\frac{1}{2}$ atom or 8 gm. is $\frac{2KMnO_4}{10} = \frac{5}{10}$, or $\frac{1}{2}$ O—*i. e.*, $\frac{1}{5}$ the molecular weight in grams, or 31.606 gms. It is this quantity which is contained in one liter of normal solution.

When oxalic acid is oxidized with permanganate solution this reaction takes place:

$$H_2C_2O_4.2H_2O + O = 2CO_2 + 3H_2O,$$

or more fully,

$$5H_2C_2O_4.2H_2O + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + 18H_2O + K_2SO_4 + 2MnSO_4.$$

This shows that one molecule of oxalic acid requires one atom of oxygen for oxidation, or one-half molecule of acid requires one-half atom of oxygen. As one-half gram-molecule of oxalic acid is the quantity in one liter of normal solution, it follows that the liter of normal oxalic acid is exactly oxidized by a liter of normal permanganate solution—*i. e.*, the two solutions are equivalent, since a liter of normal permanganate solution gives off one-half gram-atom of oxygen. Hence, it is convenient to use normal or deci-normal oxalic acid for standardizing the permanganate solution.

Permanganate solution, when recently made, without observing certain precautions, will deteriorate for a certain length of time—*i. e.*, until all traces of

organic and other deoxidizing matters have become oxidized by the permanganate.

To prepare a permanent $\frac{N}{10}$ solution of potassium permanganate, dissolve about 3.3 grams of the pure crystals (Potassii Permanganas, U. S. P.) in 1000 c.c. of distilled water in a flask, and boil for 5 minutes. Close the flask with absorbent cotton, and set aside for at least two days, so that suspended matters may deposit. Then decant the clear liquid without stirring up the sediment, or for greater precaution filter it through a layer of purified shredded asbestos (paper or cotton should not be used). The water to be employed for diluting this solution should be distilled from about 1 gram of potassium permanganate.

To determine the strength of the solution draw off 10 c.c. of deci-normal oxalic acid solution into a beaker, dilute to 100 c.c. with pure water and add 3 c.c. of pure concentrated sulphuric acid, heat the mixture to about 80° C. (176° F.), then add gradually from a glass-cock burette the permangante, while stirring constantly, until a faint pink color is produced, which remains permanent for one-half minute. Note the number of cubic centimeters consumed and dilute the solution so that it is exactly equivalent to the deci-normal oxalic acid. Verify the accuracy of the dilution by a new titration. When properly prepared and preserved in glass-stoppered bottles, permanganate solution will keep for at least six months without changing its strength.

A second method for preparing a deci-normal solution of permanganate through the medium of a deci-normal thiosulphate solution is described in the U. S. P. as follows.

To a solution of about 1 gram of potassium iodide in 10 c.c. of dilute sulphuric acid, 25 c.c. of the permanganate solution to be standardized are added. This reaction takes place:

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

The mixture is at once diluted with about 200 c.c. of pure water, and deci-normal thiosulphate solution slowly added from a burette with constant stirring until the color of the iodine is just discharged. The number of c c. of the thiosulphate solution is noted, and the permanganate solution is diluted so that equal volumes of the two solutions correspond to each other.

Instead of using oxalic acid for standardizing permanganate as described above, the U. S. P. employs sodium oxalate which can be obtained very pure in the market. The salt is dried to constant weight at 110° C., and about 0.3 gram, accurately weighed, are added to 250 c.c. pure water containing 5 c.c. of concentrated sulphuric acid. The mixture is heated to 85° C. and kept at this temperature while being titrated with the permanganate solution. The reaction is represented by the following equation:

$$Na_2C_2O_4 + H_2SO_4 + O = Na_2SO_4 + H_2O + 2CO_2,$$

from which it follows that $\frac{1}{20}$ of the molecular weight of sodium oxalate, 6.7 grams, is equivalent to 1 liter of decinormal permanganate solution, or 0.0067 gram of the oxalate is equivalent to 1 c.c. of deci-normal permanganate.

Assuming that 0.268 gram of sodium oxalate had been weighed, this would have required $0.268 \div 0.0067 = 40$ c.c. of deci-normal permanganate, and if 36 c.c. of the approximate permanganate solution were used in the titration, the following proportion gives the volume of the solution that must be diluted to a liter to make a deci-normal solution:

$$40 \text{ c.c. } \tfrac{n}{10} : 36 \text{ c.c. } :: 1000 \text{ c.c. } \tfrac{n}{10} : x \text{ c.c.}$$

**Equivalents.**—The equivalent of 1 c.c. normal $KMnO_4$ for the various substances which can be oxidized by it must be deduced from the equations of reaction, just as in the case of acids and alkalies.

All nitrites react thus:

$$MNO_2 + O = MNO_3, \text{ where M = metal.}$$

$MNO_2$ = 1 atom O = quantity liberated by 2 liters $\frac{N}{1}$ $KMnO_4$,

$\frac{MNO_2}{2}$ = ½ " = 1 liter $\frac{N}{1}$ $KMnO_4$,

$\frac{MNO_2}{2 \times 10}$ = 1 liter $\frac{N}{10}$ "

$\frac{MNO_2}{2 \times 10 \times 1000}$ = 1 c.c. $\frac{N}{10}$ "

In this manner all other equivalents are found. The reactions between permanganate and ferrous salts, and hydrogen dioxide respectively, are expressed in these equations:

$$\left.\begin{array}{l} 2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O. \\ H_2O_2 + O = H_2O + 2O. \end{array}\right|$$

One c.c. of deci-normal potassium permanganate, containing of this salt 0.0031606 gram, is the equivalent of:

| | Gram |
|---|---|
| Calcium oxide, CaO (as oxalate) | 0.002803 |
| Ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_26H_2O$ | 0 039216 |
| Ferrous carbonate, $FeCO_3$ | 0.011584 |
| Ferrous oxide, FeO | 0.007184 |
| Ferrous sulphate, $FeSO_4$ | 0 015191 |
| Ferrous sulphate, crystallized, $FeSO_4.7H_2O$ | 0.027802 |
| Hydrogen dioxide, $H_2O_2$ | 0.001701 |
| Iron, in ferrous compounds, Fe | 0.005584 |
| Oxalic acid, crystallized, $H_2C_2O_4.2H_2O$ | 0.006302 |
| Oxygen, O | 0.000800 |
| Potassium nitrite, $KNO_2$ | 0.004255 |
| Sodium nitrite, $NaNO_2$ | 0.003450 |
| Sodium oxalate, $Na_2C_2O_4$ | 0.006700 |

Deci-normal oxalic acid solution is the companion to permanganate. It is used either to titrate excess of permanganate, as in the assay of nitrite, or to act directly with certain substances, the excess of acid being back-titrated with permanganate solution. Examples of the latter use are the titration of lead acetate and subacetate in which the lead is converted into oxalate, and excess of oxalic acid in the filtrate is titrated with permanganate; and of manganese dioxide which in the presence of sulphuric acid and heat oxidizes oxalic acid

into carbon dioxide and water, the excess of oxalic acid being titrated with permanganate solution.

One c.c. of deci-normal oxalic acid, containing 0.006302 gram of the acid, is the equivalent of:

| | Gram. |
|---|---|
| Calcium carbonate, $CaCO_3$ | 0.005003 |
| Calcium hydroxide, $Ca(OH)_2$ | 0.003704 |
| Lead, Pb | 0.010355 |
| Lead acetate, $Pb(C_2H_3O_2)_2$ | 0.016257 |
| Lead subacetate, $Pb_2O(C_2H_3O_2)_2$ | 0.013706 |
| Manganese dioxide, $MnO_2$ | 0.004346 |
| Potassium permanganate, $KMnO_4$ | 0.003161 |

**Potassium Dichromate, $K_2Cr_2O_7$ = 294.20.**—Whenever this salt oxidizes other substances in acid solution it breaks up according to this equation:

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3O + 4H_2O.$$

That is, one molecule of $K_2Cr_2O_7$ gives up three atoms of oxygen. Hence to make a normal solution one-sixth the molecular weight of $K_2Cr_2O_7$ (49.033 grams) is taken in the liter, and one-tenth this quantity, equal to 4.9033 grams of the pure salt, for deci-normal solution.

The disadvantage of this solution is that the final point of titration cannot be well seen, for which reason in the determination of iron, for which it is chiefly used, the end of the reaction is determined by the method of spotting, —*i. e.*, by taking out a drop of the solution and testing it on a white porcelain plate with a drop of freshly prepared potassium ferricyanide solution; when this no longer gives a blue color the reaction is at an end.

In all determinations by this solution dilute sulphuric acid has to be added, because both the potassium and the chromium require an acid to combine with, as shown in the above equation.

The titration equivalents of this solution for ferrous salts are the same as those of deci-normal potassium permanganate solution.

**Iodimetry.**—Solutions of iodine and of sodium thiosulphate (hyposulphite) act upon each other with the formation of sodium iodide and sodium tetrathionate:

$$2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

A normal solution of one can be standardized by a normal solution of the other. As indicator starch solution is used, which is colored blue by minute portions of free iodine.

**Starch solution** is made by mixing 1 gram of starch with 10 c.c. of cold water, and then adding enough boiling water, with constant stirring, to make about 200 c.c. of a transparent jelly. If the solution is to be preserved for any length of time, 10 grams of zinc chloride should be added.

Many other substances, such as sulphurous acid, hydrogen sulphide, arsenous oxide, act upon iodine with the formation of colorless compounds, and may therefore be estimated by a volumetric solution of iodine, while the iodine may be standardized by the thiosulphate solution. In many cases the latter solution is also used for the determination of chlorine, bromine and other oxidizing substances, which liberate iodine from potassium iodide, the liberated iodine being titrated.

**Deci-normal Iodine Solution.**—Iodine being a univalent element, the weight of its atom, 126.92, in grams, is used to make one liter of normal solution. Deci-normal solution is generally employed, and is made by dissolving 12.692 grams of pure iodine in a solution of 18 grams of potassium iodide in about 200 c.c. of water, and diluting the solution to 1000 c.c.

To the article to be estimated by this solution is added a little starch solution, and then the iodine solution until, on stirring, the blue color ceases to be discharged.

Iodine of sufficient purity to permit of weighing an exact amount for a standard solution does not occur in the market. It can be purified, but as this is somewhat tedious, a simpler plan of making a solution, which is given in the U. S. P., is generally followed. It consists in making a liter of solution, somewhat stronger than deci-normal, by dissolving about 14 grams of iodine instead of 12.692 grams as described above. 10 c.c. of this solution are titrated, while stirring constantly, with deci-normal thiosulphate solution until the yellow color of iodine just vanishes. The iodine solution is then properly diluted so that it is exactly equivalent to the thiosulphate solution.

Many substances, such as sulphurous acid and its salts, hydrogen sulphide, arsenous oxide, etc., are acted upon by iodine in such a manner that this element enters into combination with constituents of the compounds named, or iodine acts as an oxidizing agent through the medium of water. The quantity of iodine thus taken up forms the basis for calculating the quantity of the substance acted upon.

In the case of *arsenous oxide* the titration is made in alkaline solution, because in neutral or acid medium, iodine does not act on arsenous compounds. In fact arsenic acid and its salts, in acid medium, liberate iodine from potassium iodide, the arsenic being reduced to the arsenous state. The same is true of antimony compounds. This behavior of pentavalent arsenic is made the basis of titration of sodium arsenate in the U. S. P. A definite weight of arsenous oxide is dissolved in the least amount of caustic alkali, the solution is diluted to about 75 c.c., made slightly acid with dilute hydrochloric acid to remove any free alkali which would unite with iodine, then made alkaline with excess of sodium bicarbonate and titrated with iodine solution, which oxidizes the sodium metarsenite to sodium metarsenate.

$$NaAsO_2 + 2I + 2NaHCO_3 = NaAsO_3 + 2NaI + H_2O + 2CO_2.$$

The essential change in the above reaction may be shown thus:

$$As_2O_3 + 4I + 2H_2O = As_2O_5 + 4HI.$$

That is, the arsenous oxide which may be considered present in the metarsenite

is oxidized to arsenic oxide in the metarsenates. Hence it is seen that 1 liter of one-tenth normal solution is equivalent to $\frac{As_2O_3}{4 \times 10}$ in grams.

When *hydrogen sulphide, sulphurous acid, sulphites,* or *acid sulphites* are titrated with iodine the addition of an alkali is unnecessary; but in titrating these substances they must be added to a measured excess of iodine solution, and the excess after the reaction is complete determined by back-titration with thiosulphate solution; the action is this:

$$H_2S + 2I = 2HI + S.$$
$$H_2SO_3 + 2I + H_2O = H_2SO_4 + 2HI.$$
$$Na_2SO_3 + 2I + H_2O = Na_2SO_4 + 2HI.$$

In the titration of *antimony and potassium tartrate* by iodine an alkaline solution is required, and for this reason sodium bicarbonate is added to the solution. The reaction which takes place is somewhat doubtful, but the following equation, even if not absolutely correct, corresponds to the quantities of the substances acting upon one another:

$$2KSbOC_4H_4O_6 + H_2O + 4I + 4NaHCO_3 =$$
$$2HSbO_3 + 2KHC_4H_4O_6 + 4NaI + 4CO_2 + H_2O.$$

One c.c. of deci-normal iodine solution, containing of iodine 0.012692 gram, is the equivalent of:

| | Gram. |
|---|---|
| Antimony and potassium tartrate, $2KSbOC_4H_4O_6.H_2O$ | 0.016617 |
| Arsenic iodide, $AsI_3$ | 0.022786 |
| Arsenous oxide, $As_2O_3$ | 0.004948 |
| Calcium sulphide, CaS | 0.003607 |
| Iron, Fe | 0.002792 |
| Mercurous chloride, HgCl | 0.023606 |
| Mercurous iodide, HgI | 0.032752 |
| Mercury (in mercurous compounds), Hg | 0.020060 |
| Potassium sulphite, crystallized, $K_2SO_3.2H_2O$ | 0.009715 |
| Sodium bisulphite, $NaHSO_3$ | 0.005204 |
| Sodium hyposulphite (thiosulphate), $Na_2S_2O_3.5H_2O$ | 0.024822 |
| Sodium sulphite, anhydrous, $Na_2SO_3$ | 0.006304 |
| Sulphur dioxide, $SO_2$ | 0.003203 |

**Sodium Thiosulphate (Hyposulphite).**—From the equation:

$$\underset{2 \times 248.22}{2Na_2S_2O_3.5H_2O} + \underset{2 \times 126.92}{2I} = Na_2S_4O_6 + 10H_2O + 2NaI.$$

we see that 248.22 grams of crystallized sodium thiosulphate are equivalent to—*i. e.*, will exactly decolorize—126.92 grams of iodine; hence, to make a $\frac{N}{1}$ solution of this compound, 248.22 grams must be taken in a liter, and for a $\frac{N}{10}$ solution 24.822 grams are used. If the salt should not be absolutely pure, a somewhat larger quantity (30 grams) should be dissolved in 1000 c.c. of water, and this solution titrated with deci-normal solution of iodine and diluted with a sufficient quantity of water to obtain the deci-normal solution.

If a deci-normal iodine solution is not at hand, and perfectly pure sodium thiosulphate cannot be obtained, the method adopted by the U. S. P. may be followed. 30 grams of good sodium thiosulphate are dissolved in sufficient sterilized water to make 1 liter. To 25 c.c. of deci-normal potassium dichromate solution in a glass-stoppered flask of about 500 c.c. volume, about 2 grams of potassium iodide (free from iodate) and 10 c.c. of diluted sulphuric acid are added, followed by 200 c.c. of distilled water in such a way that the two liquids do not mix in order to prevent loss of iodine as much as possible. The securely stoppered flask is set aside for half an hour in a dark place, after which the stopper and neck of the flask are rinsed with distilled water, and the thiosulphate solution dropped in from a burette slowly, with constant shaking, until most of the iodine is decolorized. Finally, a little starch solution is added and, cautiously, more thiosulphate until the blue color changes to a light green. After noting the volume used, the thiosulphate is diluted so that it is exactly equivalent to the deci-normal dichromate solution.

Potassium dichromate can be otained pure, and the deci-normal solution easily made by weighing the exact quantity needed. The solution, moreover, is perfectly stable. Deci-normal permanganate solution may also be used to standardize thiosulphate solution.

The article to be tested, containing free iodine, either in itself or after the addition of potassium iodide, is treated with this solution until the color of iodine is nearly discharged, when a little starch liquor is added, and the addition of the solution continued until the blue color has just disappeared.

The titration of iron in ferric salts by thiosulphate is based on the liberation of iodine from potassium iodide by all ferric salts:

$$2FeCl_3 + 2KI = 2FeCl_2 + 2KCl + 2I.$$

The reaction shown in the above equation requires a temperature of 40° to 50° C. (104° to 122° F.), and at least half an hour's time to make sure of its completion. The digestion should be performed in a closed flask. If iron be present in combination with organic acids, the addition of some hydrochloric acid becomes necessary. Before titration the solution is allowed to cool, and the titration should be promptly finished, as otherwise errors by re-oxidation of the ferrous salt may be made.

Other substances which are assayed by causing them to liberate iodine from potassium iodide, either in neutral solution or in the presence of an acid, and titrating the liberated iodine with thiosulphate solution, are bromine, chlorine, chromium trioxide, copper sulphate, potassium bromate, potassium dichromate and sodium arsenate. The reactions that take place, from which equivalents may be deduced, are:

$$Cl + KI = KCl + I.$$

$$2CrO_3 + 6KI + 6H_2SO_4 = Cr_2(SO_4)_3 + 3K_2SO_4 + 6H_2O + 6I.$$

$$CuSO_4 + 2KI = K_2SO_4 + CuI + I.$$

$$KBrO_3 + 6KI + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + KBr + 6I.$$

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 6I.$$

$$Na_2HAsO_4 + 2KI + 2H_2SO_4 = H_3AsO_3 + Na_2SO_4 + K_2SO_4 + H_2O + 2I.$$

One c.c. of deci-normal solution of sodium thiosulphate, containing 0.024822 gram of the crystallized salt, is the equivalent of:

| | Gram. |
|---|---|
| Bromine, Br | 0.007992 |
| Chlorine, Cl | 0.003546 |
| Chromium trioxide, $CrO_3$ | 0.003333 |
| Copper sulphate, $CuSO_4.5H_2O$ | 0.024972 |
| Iodine, I | 0.012692 |
| Iron, Fe, in ferric salts | 0.005584 |
| Potassium bromate, $KBrO_3$ | 0.002784 |
| Potassium dichromate, $K_2Cr_2O_7$ | 0.004903 |
| Sodium arsenate, anhydrous, $Na_2HAsO_4$ | 0.009298 |
| Sodium arsenate, crystallized, $Na_2HAsO_4.7H_2O$ | 0.015604 |

**Deci-normal Bromine Solution** (*Koppeschaar's Solution*).—The great volatility of bromine, even from aqueous solutions, interferes very much with the stability of volumetric solutions. For this reason a solution is prepared which does not contain free bromine, but an alkali bromide and bromate, from which, by addition of an acid, a definite quantity of bromine (7.992 grams per liter) may be liberated when required. The chemical change is this:

$$5NaBr + NaBrO_3 + 6HCl = 6NaCl + 3H_2O + 6Br.$$

As the bromine salts are rarely chemically pure, a solution is made which is stronger than necessary and is then adjusted to the titer of thiosulphate solution.

The solution is prepared as follows: Dissolve 3 grams of potassium bromate and 50 grams of potassium bromide in 950 c c. of water. Of this solution, which is too concentrated, transfer 20 c.c. into a bottle of about 250 c.c. provided with a glass stopper. Next add 75 c.c. of water and 5 c.c. of pure hydrochloric acid, and immediately insert the stopper. Shake the bottle a few times to cause liberation of the bromine, then quickly introduce 1 gram of potassium iodide, taking care that no bromine vapor escapes. Gradually an equivalent quantity of iodine is liberated from the potassium iodide by the bromine. When this has taken place add, from a burette, a deci-normal thiosulphate solution until the iodine tint is discharged, using toward the end a few drops of starch solution as indicator. Note the number of c.c. of sodium thiosulphate solution thus consumed, and then dilute the bromine solution so that equal volumes of it and of $\frac{N}{10}$ sodium thiosulphate solution will exactly correspond to each other.

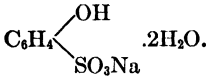
The use of bromine solution is directed by the U. S. P. in the titration of phenol, resorcinol and sodium phenolsulphonate, of which the most important is phenol (carbolic acid). This substance forms with bromine tribromphenol and hydrobromic acid:

$$C_6H_5OH + 6Br = C_6H_2Br_3OH + 3HBr.$$

The molecular weight of phenol is 94.05, and as it reacts with 6 atoms of bromine, one-sixth of 94.05, or 15.68 grams of phenol correspond to 1 liter of normal, and 1.568 grams to deci-normal bromine solution—*i. e.*, 1 c.c. of deci-normal bromine solution corresponds to 0.001568 gram of phenol. The U. S. P.

directs the assay to be made as follows: Dissolve 1.568 grams of the specimen in water to make 1 liter. Transfer 25 c.c. of this solution (0.0392 phenol) to a glass-stoppered bottle of about 200 c.c. capacity, and add 30 c.c. of deci-normal bromine solution and 5 c.c. of hydrochloric acid. Shake the contents of the bottle repeatedly, during half an hour, then quickly introduce 1 gram of potassium iodide, allow the reaction to take place and titrate the solution with deci-normal thiosulphate, as described above. Deduct the number of c.c. of thiosulphate used from the 30 c.c. of bromine solution. The remainder multiplied by 4 indicates the percentage of phenol in the carbolic acid examined.

Resorcinol and sodium phenolsulphonate are assayed like phenol, the former giving a tribrom derivative, the latter a dibrom derivative. Accordingly, 1 c.c. of deci-normal bromine solution is equivalent to 0.001834 gram of resorcinol $C_6H_4(OH)_2$, and to 0.005804 gram of sodium phenolsulphonate:




**Deci-normal Solution of Silver.**—The pure, dry crystallized silver nitrate, $AgNO_3 = 169.89$, is used for this solution, which is made by dissolving 16.989 grams of the salt in water to make 1000 c.c. The standard of this solution may be found by means of a deci-normal solution of sodium chloride containing of this salt 5.846 grams in one liter.

Volumetric silver solution is used directly for the estimation of most chlorides, iodides, bromides, and cyanides, including the free acids of these salts. Insoluble chlorides must first be converted into a soluble form by fusing them with sodium hydroxide, dissolving the fused mass (containing sodium chloride) in water, filtering and neutralizing with nitric acid.

The hydroxides and carbonates of alkali metals and of alkaline earths may be converted into chlorides by evaporation to dryness with pure hydrochloric acid, and heating to about 120° C. (248° F.). The chlorides thus obtained may be titrated with silver solution.

In the case of chlorides, iodides, and bromides, normal potassium chromate is used as an indicator. This salt forms with silver nitrate a red precipitate of silver chromate, but not before the silver chloride (bromide or iodide) has been precipitated entirely. In case free acids are determined by silver, these are neutralized with sodium hydroxide free from chloride before titration.

The operation is conducted as follows: The weighed quantity of the chloride is dissolved in 50–100 c.c. of water, neutralized if necessary, mixed with a little potassium chromate, and silver solution added from the burette until a red coloration is just produced, which does not disappear on shaking.

In estimating cyanides, the operation can be conducted as above described, or it can be modified, use being made of the formation of soluble double cyanides of silver and an alkali metal. The reaction takes place thus:

$$2KCN + AgNO_3 = AgK(CN)_2 + KNO_3.$$

In the process adopted by the U. S. P., a suitable quantity of hydrocyanic acid, or of a cyanide, is diluted with water, and 5 c.c. of ammonia water and a few drops of potassium iodide solution are added. Silver solution is then added until a slight permanent cloudiness is produced, at which point half of the cyanide is converted into silver cyanide, which is held in solution by the other half of the cyanide as a double salt. The least excess of silver solution after this stage is indicated by the insoluble silver iodide formed. As but one-half of the silver solution has been added which is needed for the complete conversion of the cyanogen present into silver cyanide, each c.c. of the standard silver solution employed will indicate twice as much cyanide as it does when used with chromate indicator, or in other words the silver solution functions as a fifth normal solution.

One c.c. of deci-normal silver nitrate solution, containing 0.016989 gram of $AgNO_3$, is the equivalent of:

| | Gram. |
|---|---|
| Ammonium bromide, $NH_4Br$ | 0.009796 |
| Ammonium chloride, $NH_4Cl$ | 0.005350 |
| Ammonium iodide, $NH_4I$ | 0 014496 |
| Calcium bromide, $CaBr_2$ | 0.009995 |
| Calcium chloride, $CaCl_2$ | 0.005550 |
| Calcium hypophosphite, $Ca(PH_2O_2)_2$ | 0.002836 |
| Ferrous bromide, $FeBr_2$ | 0.010784 |
| Ferrous iodide, $FeI_2$ | 0.015484 |
| Hydriodic acid, HI | 0.012793 |
| Hydrobromic acid, HBr | 0.008093 |
| Hydrochloric acid, HCl | 0.003647 |
| Hydrocyanic acid, HCN, to first formation of precipitate | 0.005404 |
| Hydrocyanic acid, HCN, with indicator | 0.002702 |
| Lithium bromide, LiBr | 0.008686 |
| Lithium chloride, LiCl | 0.004240 |
| Phosphoric acid, $H_3PO_4$ | 0.003269 |
| Potassium bromide, KBr | 0.011902 |
| Potassium chloride, KCl | 0.007456 |
| Potassium cyanide, KCN, to first formation of precipitate | 0.013022 |
| Potassium cyanide, KCN, with indicator | 0.006511 |
| Potassium hypophosphite, $KPH_2O_2$ | 0.003472 |
| Potassium iodide, KI | 0.016602 |
| Potassium nitrate, $KNO_3$ | 0.010111 |
| Potassium sulphocyanate, KCNS | 0.009713 |
| Sodium bromide, NaBr | 0.010292 |
| Sodium chloride, NaCl | 0.005846 |
| Sodium cyanide, NaCN, to first formation of precipitate | 0.009802 |
| Sodium hypophosphite, $NaPH_2O_2.H_2O$ | 0.003536 |
| Sodium iodide, NaI | 0.014992 |
| Sodium nitrate, $NaNO_3$ | 0.008501 |
| Sodium phosphate, anhydrous, $Na_2HPO_4$ | 0.004735 |
| Strontium bromide, $SrBr_26H_2O$ | 0.017779 |
| Strontium iodide, $SrI_2.6H_2O$ | 0.022479 |
| Strontium salicylate, $Sr(C_7H_5O_3)_2.2H_2O$ | 0.099435 |
| Zinc chloride, ZnCl | 0.006814 |

The U. S. P. has adopted the silver nitrate method of titrating phosphoric acid in place of the neutralization method with phenolphthalein indicator. The phosphoric acid is first neutralized to disodium phosphate, then excess of silver nitrate solution is added, followed by some zinc oxide to neutralize nitric acid set free in the reaction.

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$
$$2HNO_3 + ZnO = Zn(NO_3)_2 + H_2O.$$

The precipitate of silver phosphate is filtered off, and the excess of silver nitrate in the filtrate is titrated. The difference between the total silver solution added and the excess found, gives the amount used in forming silver phosphate, from which the calculation is made. Sodium phosphate is titrated in the same way, except that it need not be first neutralized.

Hypophosphites are first oxidized to phosphates, which are then titrated with silver solution as above described.

**Deci-normal Solution of Sodium Chloride.**—This solution is made by dissolving 5.846 grams of pure sodium chloride in enough water to make 1000 c.c. The titration is made in neutral solution, normal potassium chromate being used as an indicator. (See explanation in previous paragraph on silver solution.)

One c.c. of deci-normal sodium chloride solution, containing 0.005846 gram of NaCl, is the equivalent of:

| | Gram |
|---|---|
| Silver, Ag | 0.010788 |
| Silver nitrate, $AgNO_3$ | 0.016989 |
| Silver oxide, $Ag_2O$ | 0.011588 |

**Deci-normal Solution of Potassium Sulphocyanate** (*Volhard's Solution*).—This solution, like the sodium chloride solution, is used as a companion to silver nitrate; it has the advantage that it can be used in acid solutions, with ferric ammonium sulphate (ferric alum) as indicator. Silver nitrate forms in the potassium sulphocyanate a white precipitate of silver sulphocyanate:

$$KCNS + AgNO_3 = AgCNS + KNO_3.$$

Ferric alum is used as indicator, which produces with sulphocyanate a deep brownish-red color, which, however, does not appear permanently until all silver has been precipitated.

As potassium sulphocyanate is rarely pure, 11 grams are dissolved in 1000 c.c. of water. This solution has to be adjusted by standardizing with deci-normal silver solution until equal volumes decompose one another exactly. One liter of the solution then contains 9.718 grams of the salt.

The sulphocyanate solution is used in the determination of the amount of ferrous iodide in the saccharated salt and in the syrup.

The operation is performed thus: To the solution of the ferrous iodide are added nitric acid, ferric alum, and of deci-normal silver nitrate solution a quantity more than sufficient to convert all iodine

into silver iodide. The excess of silver nitrate present in the mixture is determined by sulphocyanate solution. The ferric alum and nitric acid must not be added until the silver nitrate has precipitated all iodine, otherwise iodine will be liberated. This holds in all cases where iodides are titrated.

**Alkaline Cupric Tartrate Solution** (*Fehling's Solution*).—This is used either for quantitative estimation of sugars, or for their qualitative test. The solution is deep blue, but when heated with certain sugars, the copper is reduced from the cupric to the cuprous state, reddish cuprous oxide, $Cu_2O$, more or less hydrated, is precipitated, and the solution changes from blue to colorless. Other things besides sugars, however, reduce Fehling's solution.

A. *Copper Solution.*—34.66 grams of small, uneffloresced and dry crystals of pure copper sulphate are dissolved in enough distilled water to make 500 c.c. at 25° C., and the solution is preserved in small, well-stoppered bottles.

B. *Alkaline Tartrate Solution.*—173 grams of crystallized potassium and sodium tartrate and 50 grams of solid sodium hydroxide are dissolved in enough distilled water to make 500 c.c. at 25° C., and the solution is kept in small, rubber-stoppered bottles. For use, exactly equal volumes of these two solutions are mixed at the time when required.

One c.c. of Fehling's solution is the equivalent of:

| | Gram. |
|---|---|
| Cane sugar, $C_{12}H_{22}O_{11}$ (after inversion) . . . . . | 0.00475 |
| Glucose, anhydrous, $C_6H_{12}O_6$ . . . . . | 0.00500 |
| Milk sugar, anhydrous, $C_{12}H_{22}O_{11}$ . . . . . | 0.00678 |

The accuracy of Fehling's solution when used in titrations may be verified thus:

A solution of 0.95 gram of pure cane sugar in 50 c.c. of distilled water, to which 2 c.c. of hydrochloric acid are added, is heated at 70° C. for ten minutes. After neutralization with sodium carbonate, it is diluted to 1 liter. 50 c.c. of this dilution should reduce the copper in exactly 10 c.c. of Fehling's solution.

**Gas Analysis.**—The analysis of gases is generally accomplished by measuring gas volumes in graduated glass tubes (eudiometers) over mercury (in some cases over water), noting carefully the pressure and temperature at which the volume is determined.

From gas mixtures, the various constituents present may often be eliminated by causing them to be absorbed one after another by suitable agents. For instance: From a measured volume of a mixture of nitrogen, oxygen, and carbon dioxide, the latter compound may be removed by allowing the gas to remain in contact for a few hours with potassium hydroxide, which will absorb all carbon dioxide, the diminution in volume indicating the quantity of carbon dioxide originally present. The volume of oxygen may next be determined by introducing a piece of phosphorus, which will gradually absorb the oxygen, the remaining volume being pure nitrogen.

In some cases gaseous constituents of liquids or solids are eliminated and measured as gases. Thus, the carbon dioxide of carbonates, the nitrogen dioxide evolved from nitrates, the nitrogen of urea and other nitrogenous bodies, are instances of substances which are eliminated from solids in the gaseous state and determined by direct measurement.

The gas volume thus found is, in most cases, converted into parts by weight. The basis of this calculation is the weight of 1 c.c. of hydrogen, which, at the temperature of 0° C. (32° F.) and a pressure of 760 mm. of mercury is 0.0000898 gram. 1 c.c. of any other gas weighs as many times the weight of 1 c.c. hydrogen as the molecule of this substance is heavier than that of hydrogen. Thus the molecular weight of carbon dioxide is 21.835 times greater than that of hydrogen, consequently 1 c.c. of carbon dioxide weighs 21.835 times heavier than 1 c.c. of hydrogen, or 0.0019608 gram.

It has been shown on pages 23 and 40 that heat and pressure cause a regular increase or decrease in volume. The data there given are used in calculating the volume of the measured gas at the temperature of 0° C. (32° F.) and a pressure of 760 m.m.

The reason for reducing volumes of gases to 0° C. and 760 m.m. pressure, known as normal temperature and pressure, is that the densities of gases are given for these conditions. Therefore, to find the weight of any volume of gas it must be reduced to normal temperature and pressure.

A simple rule for reducing volumes of gases to 0° C. is this: The volume of a gas is proportional to its absolute temperature. The absolute temperature is obtained by adding 273° to the reading of the centigrade scale. Thus, if a gas measures 66 c.c. at 54.6° C., its volume at 0° C. is found from the proportion:

$$66 \text{ c.c.} : [54.6° + 273°] :: x : [0° + 273°],$$

or,

$$66 : 327.6 :: x : 273,$$

and

$$x = \frac{66 \times 273}{327.6} = 55 \text{ c.c.}$$

In this reduction the pressure is supposed to remain constant. That is, the volume of 55 c.c. at 0° C. is still at the same pressure as the volume 66 c.c. was.

To reduce a gas volume under any pressure to the volume it would occupy if the pressure were changed to the normal—*i. e.*, to 760 m.m.—use is made of Boyle's law, viz., the product of the pressure times the corresponding volume of a gas is always constant when the temperature is the same. This law is expressed in the equation, $PV = pv$, where $PV$ and $pv$ are corresponding pressures and volumes.

If we assume that in the above case the volume of 55 c.c. is under a pressure of 750 m.m., its volume at normal, or 760 m.m. pressure, is found by using the equation:

$$55 \times 750 = x \times 760,$$

$$x = \frac{55 \times 750}{760} = 54.28.$$

This shows that the gas-volume of 66 c.c. at 54.6° C. and 750 m.m. pressure becomes 54.28 c.c. at 0° C. and 760 m.m. pressure. Knowing the volume at 0° C. and 760 m.m. pressure, and the weight of 1 c.c. of the gas under these conditions, the weight of the total volume is easily found.

The reduction for temperature and pressure can be made in one operation by using the formula:

$$V = \frac{v \times p \times 273}{760 \times (273 + t)},$$

$V$ = volume at 0° C. and 760 m.m. pressure, which is to be found.
$v$ = volume read at some pressure, $p$, other than the normal.
$t$ = temperature in centigrade degrees at which volume $v$ is read.

Thus, in above case:

$$V = \frac{66 \times 750 \times 273}{760 \times (273° + 54.6)} = 54.28.$$

Methods of gas-analysis have been adopted by the U. S. P. in the quantitative determination of amyl nitrite and ethyl nitrite. The operation is performed in an apparatus known as a nitrometer, consisting of two glass tubes held in upright position and connected at the lower ends by a piece of rubber tubing. One of the tubes is open, the other one is graduated and provided with a glass stopcock near the upper end. In using the nitrometer for the analysis of ethyl nitrite the graduated tube is filled with saturated solution of sodium chloride, in which nitrogen dioxide is almost insoluble. Next are introduced through the stopcock the measured (or weighed) quantity of ethyl nitrite with a sufficient amount of solution of potassium iodide and sulphuric acid. By the action of these agents nitrogen dioxide is liberated, and from the volume obtained the quantity of nitrite present is calculated. The decomposition is shown by the equation:

$$C_2H_5NO_2 + KI + H_2SO_4 = C_2H_5OH + I + KHSO_4 + NO$$

**Water analysis.** The objects of water analysis are various. Thus, the analysis may serve to decide the fitness of a water for manufacturing, medicinal, or household purposes. Accordingly, more or less stress is laid on the exact determination of certain constituents. While the student is referred to special books treating on the different methods of water analysis, a brief outline of the chemical examination of *drinking-water* is here given.

It should be remembered that the results obtained by chemical examination only are sometimes insufficient to furnish positive proof of the fitness of a water for drinking-purposes. The reason is that micro-organisms may be present which cannot be detected by chemical means. It is the microscope, aided by appropriate bacteriological methods, which has to be used in such cases, and these methods cannot, of course, be considered in this book.

**Standard of purity.** A fixed standard has not as yet been generally adopted for judging the purity of wholesome drinking-water, but most authorities agree that the following maxima of admixtures should not be exceeded. They are expressed in milligrams per liter—*i. e.*, parts by weight in one million. The following data refer to one liter of water used:

*Total residue* left on evaporation: 500 mg.

*Potassium permanganate* decomposed by organic matter: 10 mg. (= 31.71 c.c. $\frac{N}{100}$ $KMnO_4$).

*Ammonia*, present as such or as an ammonium salt: 0.05 mg.

*Albuminoid ammonia—i. e.*, ammonia formed from nitrogenous organic matter by distillation with $KMnO_4$: 0.1 mg.
*Nitrates:* 10 mg. of $N_2O_5$.
*Nitrites:* a mere trace, not to exceed 0.05 mg. of $N_2O_3$.
*Sulphates:* 60 to 100 mg. of $H_2SO_4$.
*Chlorine:* 15 mg.
*Phosphates:* a mere trace.

The water should be clear, colorless, odorless and practically tasteless.

**Total solids.** If the water be turbid, a liter of it is passed through a small filter, previously dried and weighed. After drying at 110° C., filter and contents are weighed together and the difference is quantity of *suspended solids.* The evaporation to dryness of one liter of the clear water in a platinum or nickel dish at a moderate temperature, with subsequent heating to 110° C., gives the total inorganic and organic solids in solution.

The subsequent heating of the dried residue to redness causes the expulsion of all organic matter; but as also inorganic matters, such as carbon dioxide from acid carbonate, oxygen from nitrates, etc., may escape, the determination is of relatively little value.

**Organic matters.** While we have no good method by which the quantity of organic matter in water can be readily determined, the oxidizing power of permanganate for organic matters is used for an approximate determination. This is made by acidifying 100 c.c. of water with 5 c.c. of sulphuric acid, and adding 10 c.c. of $\frac{N}{100}$ potassium permanganate, or enough to impart a distinct red color. The liquid is boiled for ten minutes. Should the red color disappear, more permanganate must be added. When color remains permanent, 10 c.c. of $\frac{N}{100}$ oxalic acid are added and the mixture is again heated. To this solution permanganate is added until it shows a red tint. From the total number of c.c. of permanganate used, 10 c.c. are deducted for the oxalic acid added.

As the organic constituents in water at different times and places have no uniform composition, the quantity of organic matter present cannot be calculated from the quantity of permanganate used. It is therefore customary to speak simply of the *oxygen-consuming power* of water. It should, however, be remembered that water may contain deoxidizing agents, other than organic matters, such as hydrogen sulphide, nitrites, ferrous salts, etc.

**Ammonia.** Nitrogenous organic matters, when undergoing decomposition by the agency of bacteria, generate ammonia, which is gradually converted into nitrites and nitrates. It is for this reason that the presence of these three compounds is looked upon as indicative of nitrogenous matters, though small quantities of ammonia and nitrites may also be present in the water by absorption from the air.

It is customary to speak in water analysis of free ammonia and albuminoid ammonia. By free ammonia is meant the ammonia present as ammonium hydroxide, or more generally as an ammonium salt, chiefly carbonate. Albuminoid ammonia refers to the ammonia obtainable from nitrogenous matter by oxidation with alkaline permanganate solution.

The process for the determination of both kinds of ammonia is carried out as follows: 500 c.c. of the water are placed in a flask of about one liter capacity and 5 c.c. of a saturated solution of sodium carbonate are added. The flask is connected with a suitable condenser whose outlet is so connected with a receiver that no loss of ammonia can occur. Heat is then applied to the flask until 300 c.c. have distilled over. To this distillate, containing all the "free ammonia," is added enough pure water to restore the original volume of 500 c.c., and the distillate is set aside for Nesslerizing.

To the liquid remaining in the distilling flask are now added 50 c.c. of an alkaline permanganate solution (made by dissolving 8 gm. of $KMnO_4$ and 200 gm. KOH in water to make 1 liter), and distillation is resumed until 200 c.c. have passed over, which distillate is also diluted to the original volume of water used—*i. e.*, to 500 c.c.

Both distillates, containing the free and the albuminoid ammonia respectively, are now ready to be tested for ammonia by a method depending on the intensity of color imparted to them by Nessler's reagent. This reagent gives with highly diluted ammonia a color varying from pale straw-yellow to brown. In order to have a standard for comparison of the colors, an empirical solution of ammonium chloride is made, containing of this salt 3.137 gm. in 1 liter, corresponding to 1 mg. of $NH_3$ in each c.c. Just before use, 5 c.c. of this solution are diluted with pure water to 100 c.c., of which 1 c.c. now contains 0.05 mg. $NH_3$.

To make the test there are required five small cylinders of colorless glass, of about 30 m.m. diameter and about 100 m.m high, each having a mark at 50 c.c., and being numbered from 1 to 5. Into four of these cylinders are measured 0.5, 1, 1.5, and 2 c.c., respectively, of the standard ammonium chloride solution, and all are then filled with water up to the 50 c.c. mark. This makes the contents of the four cylinders correspond to water containing 0.5, 1, 1.5, and 2 mg. of $NH_3$ per liter.

Cylinder No. 5 is next filled with 50 c.c. of the water specimen prepared for the ammonia determination, and to each of the five cylinders, standing on white paper, is added 1 c.c. of Nessler's reagent (see index), which is well mixed with the water. A comparison of the yellow color produced in the sample with that of the cylinders 1 to 4, containing known quantities, will afford an estimate of the quantity of ammonia in the water examined.

Should the color of the specimen be deeper than that of cylinder No. 4, or lighter than that of No. 1, then the experiment has to be repeated, the water or the standard solution being diluted in definite proportions until similarity of color is reached. The calculation is based on the dilution made.

Of course, both distillates have to be treated in this manner. Great care must be taken to make sure that the water, reagents, and apparatus used in the operation are absolutely free from ammonia. When only free ammonia is to be determined the distillation can be dispensed with. If the water should contain any considerable quantity of calcium salts, these must be precipitated by digesting the water with a little sodium carbonate and sodium hydroxide before Nesslerizing.

**Nitric acid.** While there are methods by which nitric acid can be determined more accurately, it often suffices to make the tests with brucine, diphenylamine, and pyrogallic acid, as described under the analytical reactions of nitric acid on page 108.

**Nitrous Acid.** A solution made by dissolving 1 gm. of metaphenylene-diamine in 200 c.c. water, containing 5 gm. $H_2SO_4$, is used for the determination of nitrites in the same manner as Nessler's solution is used for ammonia. The required standard nitrite solution is prepared by dissolving 0.406 gm. silver nitrite and 0.225 gm. potassium chloride in hot water, mixing and, after cooling, filling up to 1 liter. After filtering off the precipitated silver chloride, 100 c.c. of the filtrate are diluted to 1000 c.c. This solution contains nitrous acid equivalent to 10 mg. of $N_2O_3$ per liter.

Metaphenylene-diamine solution, prepared as above, gives with nitrites a yellow color, the intensity of which serves for the quantitative estimation of the nitrites present. The test is made by using definite dilutions of the above standard nitrite solution in the four test-cylinders, adding 1 c.c. of the metaphenylene-diamine to each 50 c.c., and comparing the colors produced with that obtained in the water specimen, treated in like manner. Immersion of the cylinders in warm water accelerates the reaction.

**Sulphates.** While there are volumetric methods for the determination of sulphates, this can be conveniently made by the gravimetric method—*i. e.*, by precipitating the sulphate with barium chloride and weighing the precipitated $BaSO_4$. From 100 to 250 c.c. of water should be used.

**Chlorine.** If the water under examination has had an opportunity to become charged with sodium chloride from its proximity to the sea coast, to salt lakes, or by flowing through strata containing salt deposits, then a considerable quantity of chlorides may be present and yet the water may be used without detriment to health. But in other cases the chlorides are derived from cesspools, sewage, etc., and their presence is then indicative of dangerous pollution.

The determination of chlorine is made by titrating 100 c.c. of water with $\frac{N}{10}$ $AgNO_3$, using potassium chromate as an indicator. For water containing much organic matter the gravimetric method should be used.

**Phosphates.** The ammonium molybdate test (see analytical reactions of phosphoric acid, page 181) should give no indication of phosphoric acid, as the presence of soluble phosphates in water is almost positive proof that pollution with urine has taken place.

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QUESTIONS.—Explain the principles which are made use of in gravimetric and volumetric determinations. Give an outline of the operations to be performed in the gravimetric determination of copper in cupric sulphate. What are normal and deci-normal solutions, and how are they made? What is the use of indicators in volumetric analysis? Mention some indicators and explain their action. Why is oxalic acid preferred in preparing normal acid solution? What quantity of oxalic acid is contained in a liter, and why is this quantity used? Suppose 2 grams of crystallized sodium carbonate require 13.9 c.c. of normal acid for neutralization: What are the percentages of crystallized sodium carbonate and of pure sodium carbonate contained in the specimens examined. Ten grams of dilute hydrochloric acid require 35.5 c.c. of normal sodium hydroxide solution for neutralization; what is the strength of this acid? Explain the action of potassium permanganate and of potassium dichromate when used for volumetric purposes. Which substances may be determined

## 39. DETECTION OF IMPURITIES IN OFFICIAL INORGANIC CHEMICAL PREPARATIONS.

**General Remarks.**—Very little has been said, heretofore, about impurities which may be present in the various chemical preparations, and this omission has been intentional, because it would have increased the bulk of this book beyond the limits considered necessary for the beginner.

Impurities present in chemical preparations are either derived from the materials used in their manufacture, or they have been intentionally added as adulterations. In regard to the last, no general rule for detecting them can be given, the nature of the adulterating article varying with the nature of the substance adulterated; the general properties of the substance to be examined for purity will, in most cases, suggest the nature of those substances which possibly may have been added, and for them a search has to be made, or, if necessary, a complete analysis, by which is proved the absence of everything else but the constituents of the pure substance.

Impurities derived from the materials used in the manufacture of a substance (generally through an imperfect or incorrect process of manufacture), or from the vessels used in the manufacture, are usually but few in number (in any one substance), and their nature can, in most cases, be anticipated by one familiar with the process of manufacture. For one not acquainted with the mode of preparation it would be a rather difficult task to study the nature of the impurities which might possibly be present.

The same remarks apply to the methods by which the impurities can be detected. One familiar with analytical chemistry can easily find, in most cases, a good method by which the presence or absence of an impurity can be demonstrated; but to one unacquainted with chemistry it might be an impossibility to detect impurities, even if a method were given.

For these reasons little stress has been laid upon the occurrence of impurities in the various chemical preparations heretofore considered. Moreover, the U. S. P. gives, in most cases, directions for the detection of impurities, so explicit that anyone acquainted with analytical operations will find no difficulty in performing these tests satisfactorily.

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volumetrically by solutions of iodine and sodium thiosulphate? Explain the mode in which the determinations by these agents are accomplished. Suppose 1 gram of potassium iodide requires for titration 60 c.c. of deci-normal solution of silver nitrate: What quantity of pure potassium iodide is indicated by this determination? Describe in detail the volumetric determination of carbolic acid. For what purposes is potassium sulphocyanate used volumetrically, and what is its action? Explain the method used for the analysis of ethyl nitrite.

However, while the Pharmacopœia gives exact instructions how to manipulate, it furnishes no explanations why certain methods have been adopted, or why certain operations are to be performed. It is for this reason, and for the special benefit of the beginner, that a few paragraphs are devoted to the consideration of official methods for testing the chemical preparations of the U. S. P.

**Official Chemicals and Their Purity.**—Absolute purity of chemicals is essential in some cases, as, for instance, when they are intended as reagents; such chemicals are commercially designated as C. P. (chemically pure). For the majority of medicinal chemicals, however, such absolute purity is unnecessary, as the small proportion of harmless impurities present in nowise interferes with the therapeutic action of the substance, and a demand for absolute purity, which greatly enhances the cost of chemicals, is therefore unreasonable and not required by the Pharmacopœia.

The presence of a small fraction of 1 per cent. of sodium chloride in many official chemicals cannot be looked upon as objectionable, while the same amount of arsenic would render the preparation unfit for medicinal use.

The methods used by the Pharmacopœia to determine the quality of a chemical preparation may be divided into four classes, as follows: 1. Tests as to identity; 2. Qualitative tests for impurities; 3. Quantitative tests for the limit of impurities; 4. Quantitative determination of the chief constituent.

**Tests as to Identity.**—These tests are partly of a physical, partly of a chemical character. They include, in the physical part, the examination of the appearance, color, crystalline structure, specific gravity, fusing-point, boiling-point, etc.

The chemical tests given are sufficiently characteristic to leave no doubt as to the true nature or identity of the substance. In order to accomplish this object it is not necessary to apply *all* the analytical reagents characteristic of the substance or its component parts, but the U. S. P. selects from the often large number of known tests one, or possibly a few, which answer best in the special case.

For instance, while we have a number of tests, both for potassium and iodine, the U. S. P., in the article on potassium iodide, gives but one reaction for each of these elements. Yet these tests have been selected with sufficient judgment to admit of no doubt regarding the nature of the substance.

**Qualitative Tests for Impurities.**—These tests are in many cases described minutely, *i. e.*, the quantity to be taken of both the substance to be examined and the reagent to be added is stated. Moreover the amount of solvent (water, acid, etc.) to be used is mentioned. and other details are given. The object of this exactness in describing the tests is not only to render the work easy for one not fully familiar with analytical methods, but also, in some cases, to fix a limit for the admissible quantity of an impurity. A certain reagent

may, in a concentrated solution, indicate the presence of a trace of an impurity, while in a more dilute solution this reagent will fail to detect it. The selection of the reagents used in certain tests is also made with the view of establishing a sufficient purity for pharmacopœial purposes of the article examined without demanding an absolute purity.

A few instances may help to illustrate these remarks: Potassium can be precipitated from a solution of its salts by a number of reagents, which, however, differ widely in sensitiveness. Thus, tartaric acid will cause the formation of a precipitate of potassium bitartrate in a solution containing at least 0.1 per cent. of potassium; in solutions containing a less amount no precipitate is formed. Platinic chloride is somewhat more sensitive than tartaric acid, and sodium cobaltic nitrite, which is still more delicate, causes a precipitate in solutions containing even as little as 0.04 per cent. of potassium. It is evident that by using either one or the other of the three reagents mentioned for the detection of potassium, this metal may or may not be found, according to the quantity present in a solution. The Pharmacopœia, in directing the use of one of these reagents, limits the amount of a permissible quantity of potassium according to the sensitiveness of the reagent.

Again, in testing for arsenic, the chemist has his choice between a number of more or less delicate tests. Gutzeit's test is so sensitive that by means of it arsenic can be detected in a solution containing only 0.000001 gram of arsenous oxide in a cubic centimeter. This test would be, therefore, by far too severe when applied to a number of pharmaceutical preparations, for which reason the Pharmacopœia directs in many cases the less sensitive hydrogen sulphide test.

**Quantitative Tests for the Limit of Impurities.**—While, as above stated, even the qualitative tests are often so made as to be to some extent of a quantitative character, the U. S. P. recommends in many cases methods by which a stated limit of an impurity can be detected without the necessity of determining by quantitative analysis the actual amount of the impurity present.

Formerly it was, and to some extent it is now, customary to limit the amount of a permissible quantity of an impurity by referring to the intensity of the reaction. In case the impurity was to be detected by precipitation (as, for instance, sulphates or chlorides in potassium nitrate) it was stated that the respective reagents used for the detection (in the case named, barium chloride or silver nitrate) should not produce more than a very slight precipitate, or turbidity, or cloudiness, etc. These descriptions are, of course, very indefinite, and the conclusion arrived at depends largely upon the individuality of the observer.

In order to obviate this uncertainty the U. S. P. has introduced a number of more exact methods. These depend upon the addition of a definite quantity of a reagent capable of eliminating a certain quan-

tity of the impurity from a given quantity of the substance to be examined. In thus examining a preparation the impurity may or may not be present; if present, the permissible quantity will be removed by the operation, and if originally not present in larger quantity, the substance will now be found free from the impurity, while if present in larger proportions than can be removed by the quantity of reagent added, the excess can be detected by appropriate tests.

If an excess of impurity is thus discovered, regardless of the fact whether the excess be large or small, the substance examined does not come up to the pharmacopœial requirements.

Thus, in potassium bromide, the pharmacopœial limit of potassium carbonate is 0.069 per cent. In order to determine whether or not this limit is exceeded, the Pharmacopœia directs the addition of 0.1 c.c. of $\frac{N}{10}$ sulphuric acid to a solution of 1 gram of the salt in 10 c.c. of water. Since 0.1 c.c. of $\frac{N}{10}$ sulphuric acid is capable of neutralizing 0.000691 gram of potassium carbonate, the whole quantity allowed would be neutralized by the addition of the prescribed quantity of acid, and no red tint should be imparted to the heated liquid by adding a few drops of phenolphthalein solution; a red color would indicate that more alkali carbonate was present in the weighed sample than could be neutralized by the quantity of acid added.

**Quantitative Determination of the Principal Constituent.**—These determinations are made in the majority of cases volumetrically, and require no special explanation here, as the methods have been fully considered in the previous chapter. Gravimetric methods are used in the determination of several alkaloids and also in a few other cases.

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QUESTIONS.—What are the sources of the impurities found in chemical preparations? Why is it not obligatory to use chemically pure chemicals for medicinal purposes? Which are the leading features adopted by the U. S. P. in the identification of chemical preparations? State the reasons why the U. S. P. describes the tests for impurities so minutely. Why can we not use indiscriminately either one of a number of reagents or tests by which the presence of the same impurity may be indicated? What is the principle applied in the methods of the Pharmacopœia for the determination of a permitted quantity of an impurity? How can we decide the question whether a sample of potassium acetate contains more than 1 per cent. of potassium chloride without making a quantitative estimation of chlorine?

# IV.

# CONSIDERATION OF CARBON COMPOUNDS, OR ORGANIC CHEMISTRY.

## 40. INTRODUCTORY REMARKS. ELEMENTARY ANALYSIS.

**Definition of Organic Chemistry.**—The term *organic chemistry* was originally applied to the consideration of compounds formed in plants and in the bodies of animals, and these compounds were believed to be created by a mysterious power, called "vital force," supposed to reside in the living organism.

This assumption was partly justified by the failure of the earlier attempts to produce these compounds by artificial means, and also by the fact that the peculiar character of the compounds, and the numerous changes which they constantly undergo in nature, could not be sufficiently explained by the experimental methods then known, and the laws then established.

It was in accordance with these views that a strict distinction was made between inorganic and organic compounds, and accordingly between inorganic and organic chemistry, the latter branch of the science considering the substances formed in the living organism and those compounds which were produced by their decomposition.

Since that time it has been shown that many substances which formerly were believed to be produced exclusively in the living organism, under the influence of the so-called vital force, can be formed artificially from inorganic matter, or by direct combination of the elements. It was in consequence of this fact that the theory of the supposed "vital force," by which organic substances could be formed exclusively, had to be abandoned.

The first instance of the preparation of an organic compound from inorganic material occurred in 1828, when Wohler discovered that an aqueous solution of ammonium cyante, on evaporation, yields crystals of urea. The latter up to that time had been believed to be formed in the animal system exclusively. As potassium cyanate may be obtained by oxidation of the cyanide, and as the latter can be made by passing nitrogen over a heated mixture of potassium carbonate and carbon, it follows that urea can be made from the elements.

The conversion of ammonium cyanate into urea is due to a rearrangement of the atoms within the molecule, thus:

$$\begin{matrix}NH_4\\CN\end{matrix}\!>\!O \text{ or } CN_2H_4O = \begin{matrix}NH_2\\NH_2\end{matrix}\!>\!CO \text{ or } CN_2H_4O.$$

Ammonium cyanate. Urea.

An organic compound, according to modern views, is simply a compound of carbon generally containing hydrogen, frequently also oxygen and nitrogen, and sometimes other elements. As this definition would include carbonic acid and its salts, such as marble, $CaCO_3$, spathic iron ore, $FeCO_3$, and others—*i. e.*, substances which we are accustomed to look upon as belonging to the mineral kingdom—it is better to omit carbon dioxide, carbonic acid, and carbonates, and define organic compounds as compounds containing carbon in a combustible form.

The definition usually given is: *Organic chemistry is the chemistry of the hydrocarbons and their derivatives.* Hydrocarbons, as the name implies, are compounds of carbon and hydrogen, which are to organic chemistry what the elements are to inorganic chemistry.

In a strictly systematically arranged text-book of chemistry organic compounds should be considered in connection with the element carbon itself, but as these carbon compounds are so numerous, their composition often so complicated, and the decompositions which they suffer under the influence of heat or other agents so varied, it has been found best for purposes of instruction to defer the consideration of these compounds until the other elements and their combinations have been studied.

**Elements Entering into Organic Compounds.**—Organic compounds contain generally but a small number of elements. These are, besides carbon, chiefly hydrogen, oxygen, and nitrogen, and sometimes sulphur and phosphorus. Other elements, however, enter occasionally into organic compounds, and by artificial means all metallic and non-metallic elements may be made to enter into organic combinations.

Here the question presents itself: Why is it that the four elements carbon, hydrogen, oxygen, and nitrogen are capable of producing such an immense number (in fact, thousands) of different combinations? To this question but one answer can be given, which is that these four elements differ more widely from each other, in their chemical and physical properties, than perhaps any other four elements.

Carbon is a black, solid substance, which can scarcely be fused or volatilized, while hydrogen, oxygen, and nitrogen are colorless gases which can only be converted into liquids with difficulty. Moreover, hydrogen is very combustible, oxygen is a supporter of combustion, while nitrogen is perfectly indifferent. Finally, hydrogen is univalent, oxygen bivalent, nitrogen trivalent, and carbon quadrivalent. These elements are therefore capable of forming a greater

number and a greater variety of compounds than would be the case if they were elements of equal valence and of similar properties.

It will be shown later that carbon atoms have, to a higher degree than the atoms of any other element, the power of combining with one another by means of a portion of the affinities possessed by each atom, thus increasing the possibilities of the formation of complex compounds.

The number of thoroughly investigated organic compounds is estimated at 180,000, and each year is increased by 8000 to 9000.

**General Properties of Organic Compounds.**—The substances formed by the union of the four elements just mentioned have properties in some respects intermediate to those of their components. Thus, no organic substance is as permanently solid[1] as carbon, nor as permanently gaseous as hydrogen, oxygen, and nitrogen.

Some organic substances are solids, others liquids, others gases; generally they are solids when the carbon atoms predominate; they are liquids or gases when the gaseous elements, and especially hydrogen, predominate; likewise, it may be also said that compounds containing a small number of atoms in the molecule are gases or liquids which are easily volatilized; they are liquids of high boiling-points, or solids, when the number of atoms forming the molecules is large.

The combustible property of carbon and hydrogen is transferred to all organic substances, every one of which will burn when sufficiently heated in atmospheric air. (If carbon dioxide, carbonic acid and its salts be considered organic compounds, we have an exception to the rule, as they are not combustible.)

The properties possessed by organic compounds are many and widely different. There are organic acids, organic bases, and organic neutral substances; there are some organic compounds which are perfectly colorless, tasteless, and odorless, while others show every possible variety of color, taste, and odor; many serve as food, while others are most poisonous; in short, organic substances show a greater variety of properties than the combinations formed by any other four elements.

And yet, the cause of all the boundless variety of organic matter is that peculiar attraction called chemical affinity, acting between the atoms of a comparatively small number of elements and uniting them in many thousand different proportions.

It would, of course, be entirely inconsistent with the object of this book, if all the many organic substances already known (the number of which is continually being increased by new discoveries) were to be considered, or even mentioned. It must be sufficient to state the general properties of the various groups of organic sub-

[1] Non-volatile organic substances are decomposed by heat with generation of volatile products.

stances, to show by what processes they are produced artificially or how they are found in nature, how they may be recognized and separated, and, finally, to point out those members of each group which claim a special attention for one reason or another.

**Difference in the Analysis of Organic and Inorganic Substances.**—The analysis of organic substances differs from that of inorganic substances, in so far as the qualitative examination of an organic substance furnishes in many cases but little proof of the true nature of the substance (except that it is organic), while the qualitative analysis of an inorganic substance discloses in most cases the true nature of the substance at once.

For instance: If a white, solid substance, upon examination, be found to contain potassium and iodine, and nothing else, the conclusion may at once be drawn that the compound is potassium iodide, containing 39.1 parts by weight of potassium, and 126.92 parts by weight of iodine. Or, if another substance be examined, and found to be composed of mercury and chlorine, the conclusion may be drawn that the compound is either mercurous or mercuric chloride, as no other compounds containing these two elements are known, and whether the examined substance be the lower or higher chloride of mercury, or a mixture of both, can easily be determined by a few simple tests.

While thus the qualitative examination discloses the nature of the substance, it is different with organic compounds. Many thousand times the analysis might show carbon, hydrogen, and oxygen to be present, and yet every one of the compounds examined might be entirely different; it is consequently not only the *quality* of the elements, but chiefly the *quantity* present which determines the nature of an organic substance, and in order to identify an organic substance with certainty, it frequently becomes necessary to make a quantitative determination of the various elements present, and this quantitative analysis is generally called *ultimate or elementary analysis.*

There are, however, for many organic substances such characteristics tests that these substances may be recognized by them; these reactions will be mentioned in the proper places.

An analysis by which different organic substances, when mixed together, are separated from each other is frequently termed *proximate analysis.* Such an analysis includes the separation and determination of essential oils, fats, alcohols, sugars, resins, organic acids, albuminous substances, etc., and is one of the most difficult branches of analytical chemistry.

**Qualitative Analysis of Organic Substances.**—The presence of *carbon* in a combustible form is decisive in regard to the organic nature of a compound. If, consequently, a substance burns with generation of carbon dioxide (which may be identified by passing the gas through lime-water), the organic nature of this substance is established. (See chapter on Carbon.)

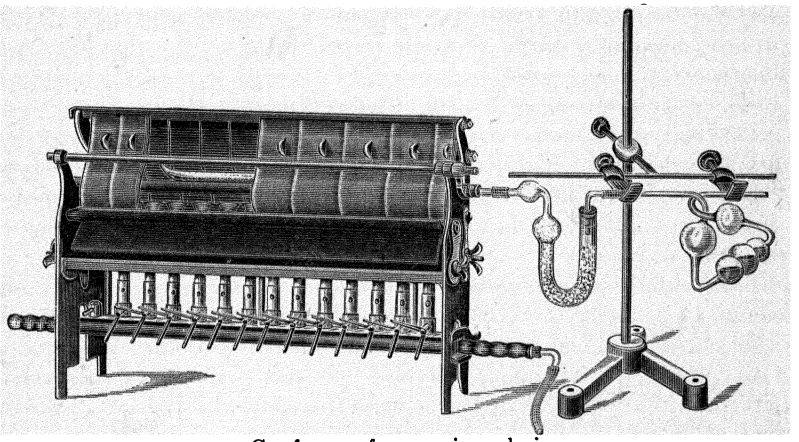
The presence of *hydrogen* can be proven by allowing the gaseous products of the combustion to pass through a cool glass tube, when drops of water will be deposited.

It is difficult to show by qualitative analysis the presence or absence of *oxygen* in an organic compound, and its determination is therefore generally omitted.

The presence of *nitrogen* is determined by heating the substance with dry *soda-lime* (a mixture of two parts of calcium hydroxide and one part of sodium hydroxide), when the nitrogen is converted into ammonia gas, which may be recognized by its odor or by its action on paper moistened with solution of cupric sulphate, a dark blue color indicating ammonia.

**Ultimate or Elementary Analysis.**—While the student must be referred to books on analytical chemistry for a detailed description of the apparatus required and the methods employed for elementary

FIG. 41.



Gas-furnace for organic analysis.

analysis, it may here be stated that the quantitative determination of carbon and hydrogen is generally accomplished by the following process: A weighed quantity of the pure and dry substance is mixed with a large excess of dry cupric oxide, and this mixture is introduced into a glass tube, the open end of which is connected by means of a perforated cork and tubing with two glass vessels, the first one of which (generally a U-shaped tube) is filled with pieces of calcium chloride, the other (usually a tube provided with several bulbs) with solution of potassium hydroxide. The two glass vessels, containing the absorbents named, are weighed separately after having been filled. Upon heating the combustion-tube in a suitable furnace, the organic matter is burned by the oxygen of the cupric oxide, the hydrogen is converted into water (steam), which is absorbed by the

calcium chloride, and the carbon is converted into carbon dioxide, which is absorbed by the potassium hydroxide. The apparatus represented in Fig. 41 shows the gas-furnace in which rests the combustion-tube with calcium chloride tube and potash bulb attached. Upon re-weighing the two absorbing vessels at the end of the opertion, the increase in weight will indicate the quantity of water and carbon dioxide formed during the combustion, and from these figures the amount of carbon and hydrogen present in the organic matter may easily be calculated.

For instance: 0.81 gram of a substance having been analyzed, furnishes, of carbon dioxide 1.32 grams, and of water 0.45 gram. As every 44 parts by weight of carbon dioxide contain 12 parts by weight of carbon, the above 1.32 grams contains, of carbon 0.36 gram, or 44.444 per cent. As every 18.02 parts of water contain 2.02 parts of hydrogen, the above 0.45 gram consequently contains 0.0503 gram, or 6.213 per cent.

Oxygen is scarcely ever determined directly, but generally indirectly, by determining the quantity of all other elements and deducting their weight, calculated to percentages from 100. The difference is oxygen.

If, in the above instance, 44.444 per cent. of carbon and 6.213 per cent. of hydrogen were found to be present, and all other elements except oxygen, to be absent, the quantity of oxygen is, then, equal to 49.384 per cent. and the composition of the substance is as follows:

| | |
|---|---|
| Carbon . . . . . | 44.444 per cent. |
| Hydrogen . . . . . | 6.213 " |
| Oxygen . . . . . | 49.343 " |
| | 100.000 |

**Determination of Nitrogen.**—Nitrogen is generally determined by the *Kjeldahl method*, which consists in boiling in a suitable flask a weighed quantity of the organic compound with 30 to 40 times its weight of sulphuric acid and a little potassium permanganate or mercuric oxide. By this treatment all nitrogen present is converted into ammonium sulphate, from which by the addition of an excess of sodium hydroxide ammonia is liberated. This ammonia is distilled over into a known volume of normal acid. By titration with normal alkali the unsaturated portion of acid is determined and from the result the percentage of nitrogen is calculated.

Nitrogen may also be determined by the *Will-Varrentrap method*, which is based on the formation of ammonia whenever nitrogenous matter is heated with soda-lime (a mixture of sodium hydroxide and calcium oxide). The method is not applicable to all compounds, because the nitrogen of some is not all converted into ammonia by the process.

A third method, known as the *Dumas* or *absolute method*, consists in oxidizing, at a red heat, the nitrogenous substance by means of cupric oxide and

then decomposing, by means of highly heated metallic copper, any oxide of nitrogen which may have been formed. By this operation all nitrogen is obtained in the elementary state; it is collected, measured, and from the volume the weight is calculated.

For the details of manipulation in the above method, which are simply outlined, large works on quantitative analysis must be consulted.

**Determination of Sulphur and Phosphorus.**—These elements are determined by mixing the organic substance with sodium carbonate and nitrate, and heating the mixture in a crucible. The oxidizing action of the nitrate converts all carbon into carbon dioxide, hydrogen into water, sulphur into sulphuric acid, phosphorus into phosphoric acid. The latter two acids combine with the sodium of the sodium carbonate, forming sulphate and phosphate of sodium. The fused mass is dissolved in water, and sulphuric acid precipitated by barium chloride in the acidified solution, phosphoric acid by magnesium sulphate and ammonium hydroxide and chloride. From the weight of barium sulphate and magnesium pyrophosphate (obtained by heating the magnesium ammonium phosphate) the weight of sulphur and phosphorus is calculated.

**Determination of Atomic Composition from Results Obtained by Elementary Analysis.**—The elementary analysis gives the quantity of the various elements present in percentages, and from these figures the relative number of atoms may be found by dividing the figures by the respective atomic weights. For instance: The analysis above mentioned gave the composition of a compound, as carbon 44.444 per cent., hydrogen 6.213 per cent., and oxygen 49.343 per cent. By dividing each quantity by the atomic weight of the respective element, the following results are obtained:

$$\frac{44.444}{12} = 3.703$$

$$\frac{6.213}{1.01} = 6.151$$

$$\frac{49.343}{16} = 3.084$$

The figures 3.703, 6.151, and 3.084 represent the relative number of atoms present in a molecule of the compound examined. In order to obtain the most simple proportion expressing this relation, the greatest divisor common to the whole has to be found, a task which is sometimes rather difficult on account of slight errors made in the quantitative determination itself. In the above case, 0.6151 is the greatest divisor, which gives the following results:

$$\frac{3.703}{0.6151} = 6.021; \quad \frac{6.151}{0.6151} = 10; \quad \frac{3.084}{0.6151} = 5.013.$$

The simplest numbers of atoms are, accordingly, carbon 6, hydrogen 10, oxygen 5, or the composition is $C_6H_{10}O_5$.

**Empirical and Molecular Formulas.**—A chemical formula is termed *empirical* when it merely gives the simplest possible expression of the composition of a substance. In the above case, the formula $C_6H_{10}O_5$ would be the empirical formula. It might, however, be possible that this formula did not represent the actual number of atoms in the molecule, which might contain, for instance, twice or three times the number of atoms given, in which case the true composition would be expressed by the formula $C_{12}H_{20}O_{10}$ or $C_{18}H_{30}O_{15}$.

If it could be proven that one of the latter formulas is the correct one, it would be termed the *molecular formula*, because it expresses not only the numerical relations existing between the atoms, but also the absolute number of atoms of each element contained in the molecule.

The best method for determining the actual number of atoms contained in the molecule is the determination of the density of the gaseous compound. For instance: Assume the analysis of a liquid substance gave the following result:

| | |
|---|---|
| Carbon | 92.308 per cent. |
| Hydrogen | 7.692 " |
| | 100.000 |

From this result the empirical formula, CH, is deduced by applying the method stated above. If this formula were the molecular formula, the density of the vapors of the substance would, according to the law of Avogadro (see chapter 19), be 0.5809 gram per liter when reduced to standard temperature and pressure, 0° C., and 760 mm. of mercury pressure.

If, however, the density of the vapor of the substance, as actually determined experimentally and reduced to standard temperature and pressure, is 3.485 grams per liter, the molecular weight then must be 78.04 as shown by the proportion:

| Density of oxygen. | | Density of substance. | | Mol wt. of oxygen. | | Mol. wt. of substance. |
|---|---|---|---|---|---|---|
| 1.429 | : | 3.485 | : : | 32 | : | $x$. |

$$x = \frac{3.485 \times 32}{1.429} = 78.04.$$

This molecular weight is six times that of a substance having the formula CH (13.008). Hence the formula of the compound in question must be $C_6H_6$.

Not all organic compounds can be converted into gases or vapors without undergoing decomposition, and the determination of the molecular formulas of such compounds has to be accomplished by other methods. If the substance, for instance, is an acid or a base, the molecular formula may be determined by the analysis of a salt formed by these substances. For instance: The empirical formula of

acetic acid is $CH_2O$; the analysis of the potassium acetate, however, shows the composition $KC_2H_3O_2$, from which the molecular formula $HC_2H_3O_2$ is deduced for acetic acid.

In many cases, however, it is as yet absolutely impossible to give with certainty the molecular formula of some compounds.

**Rational, Constitutional, Structural, or Graphic Formulas.**—These formulas are intended to represent the theories which have been formed in regard to the arrangement of the atoms within the molecule, or to represent the modes of the formation and decomposition of a compound, or the relation which allied compounds bear to one another.

The molecular formula of acetic acid, for instance, is $C_2H_4O_2$, but different constitutional formulas have been used to represent the structure of the acetic acid molecule.

Thus, $H.C_2H_3O_2$ is a formula analogous to $H.NO_3$, indicating that acetic acid (analogous to nitric acid), is a monobasic acid, containing one atom of hydrogen, which can be replaced by metallic atoms.

$C_2H_3O^{i}.OH^{i}$ is a formula indicating that acetic acid is composed of two univalent radicals which may be taken out of the molecule and replaced by other atoms or groups of atoms. This formula indicates also that acetic acid is analogous to hydroxides, the radical $C_2H_3O$ having replaced one atom of hydrogen in $H_2O$.

$CH_3.CO_2H^{i}$ is a formula indicating that acetic acid is composed of the two compound radicals, methyl and carboxyl.

It may be said finally, that quite a number of other rational formulas have been applied, or, at least, have been proposed by different chemists and at different times, to represent the structure of acetic acid, but it should be remembered that these formulas are not intended to represent the actual arrangement of the atoms in space, but only, as it were, their relative mode of combination, showing which atoms are combined directly and which only indirectly, that is, through the medium of others.

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QUESTIONS.—What is organic chemistry, according to modern views? Mention the four chief elements entering into organic compounds, and name the elements which may be made to enter into organic compounds by artificial processes. State the reason why the four elements, carbon, hydrogen, oxygen, and nitrogen, are better adapted to form a larger number of compounds than most other elements. State the general properties of organic compounds. Why does a qualitative analysis of an organic compound, in most cases, not disclose its true nature? By what test may the organic nature of a compound be established? By what tests may the presence of carbon, hydrogen, and nitrogen be demonstrated in organic compounds? State the methods by which the elements carbon, hydrogen, oxygen, sulphur, and phosphorus are determined quantitatively. By what general method may a formula be deduced from the results of a quantitative analysis? What is meant by an empirical, molecular, and constitutional formula; how are they determined, and what is the difference between them?

## 41. CONSTITUTION, DECOMPOSITION, AND CLASSIFICATION OF ORGANIC COMPOUNDS.

**Radicals or Residues.**—The nature of a radical or residue has been stated already in chapter 10, but the important part played by radicals in organic compounds renders it necessary to consider them more fully.

In most compounds there is one or several groups of atoms which remain unchanged in the various reactions to which the compounds may be submitted. The group behaves like a unit or an element, although it cannot exist in the free state. Such groups are called *radicals*.

Radicals exist in organic and inorganic compounds; an inorganic radical spoken of heretofore is the water residue or hydroxyl, OH, obtained by removal of one atom of hydrogen from one molecule of water. Hydroxyl does not exist in the separate state, but it exists in hydrogen dioxide, $H_2O_2$, or HO—OH, and is also a constituent of the various hydroxides, as, for instance, of KOH, $Ca(OH)_2$, $Fe(OH)_3$, etc.

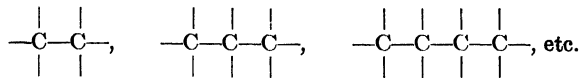
If one atom of hydrogen be removed from the saturated hydrocarbon methane, $CH_4$, the univalent residue methyl, $CH_3$, is left, which is capable of combining with univalent elements, as in methyl chloride, $CH_3Cl$, or, with univalent residues, as in methyl hydroxide, $CH_3OH$.

If two atoms of hydrogen be removed from $CH_4$, the bivalent residue methylene, $CH_2$, is left, capable of forming the compounds $CH_2Cl_2$, $CH_2(OH)_2$, etc.

If three atoms of hydrogen be removed from $CH_4$, the trivalent residue CH is left, capable of combining with three atoms of univalent elements, as in $CHCl_3$, or with another trivalent radical, etc.

**Chains.**—The expression, chain, designates a series of multivalent atoms (generally, but not necessarily, of the same element), held together by one or more affinities. While such linkage of atoms into chains occurs with a number of elements, it appears that silicon and carbon have a greater tendency to form chains than other elements.

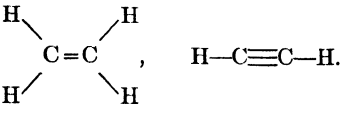
The linkage of carbon atoms may be represented thus:



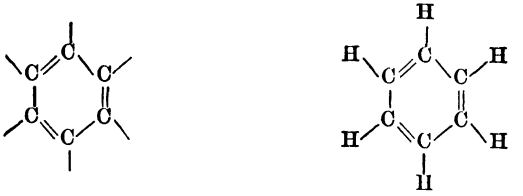
The above carbon chains have 6, 8, and 10 available affinities, respectively, which may be saturated by the greatest variety of atoms or radicals. The chain combination of carbon, above indicated by the first three members of a series, may, as far as is known, be continued indefinitely. This fact, in connection with the possibility of saturating the other affinities with various atoms or radicals, indicates the almost unlimited number of possible combinations to be formed in this way. In fact, the existence of such an enormous number of carbon compounds is greatly due to the property of carbon to form these chains.

It is not always the case that the atoms when forming a chain are

united by one affinity only, as above, but they may be united by two or three affinities, as indicated by the compounds $C_2H_4$ and $C_2H_2$, the graphic formulas of which may be represented by



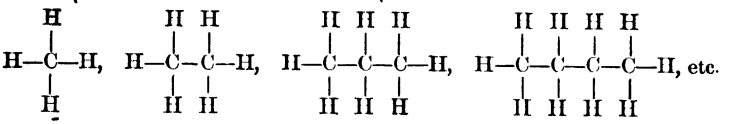
Finally, it is assumed that the carbon atoms are united partially by double and partially by single union, as, for instance, in the so-called *closed chain* of $C_6$, capable of forming the hydrocarbon benzene, $C_6H_6$:



A chain has also been termed a skeleton, because it is that part of an organic compound around which the other elements or radicals arrange themselves, filling up, as it were, the unsaturated affinities.

**Homologous Series.**—This term is applied to any series of organic compounds the terms or members of which, preceding or following each other, differ by $CH_2$. Moreover, the general character, the constitution, and the general properties of the members of an homologous series are similar.

The explanation regarding the formation of an homologous series is to be found in the above-described property of carbon to form chains. By saturating, for instance, the affinities in the open carbon chains mentioned above, we obtain the compounds $CH_4$, $C_2H_6$, $C_3H_8$, $C_4H_{10}$, etc.



Many homologous series of various organic compounds are known, as, for instance:

| | | |
|---|---|---|
| $CH_3Cl$, | $CH_4O$, | $CH_2O_2$. |
| $C_2H_5Cl$, | $C_2H_6O$, | $C_2H_4O_2$. |
| $C_3H_7Cl$, | $C_3H_8O$, | $C_3H_6O_2$. |
| $C_4H_9Cl$, | $C_4H_{10}O$, | $C_4H_8O_2$. |
| $C_5H_{11}Cl$, | $C_5H_{12}O$, | $C_5H_{10}O_2$. |
| etc. | etc. | etc. |

**Substitution.**—Substitution is a term used for those reactions or chemical changes which depend on the replacement of an atom or a group of atoms by other atoms or groups of atoms. Substitution takes place in organic or inorganic substances, and its nature may be illustrated by the following instances:

$$\underset{\text{Potassium.}}{K} + \underset{\text{Water.}}{H_2O} = \underset{\text{Potassium hydroxide.}}{KOH} + \underset{\text{Hydrogen.}}{H}.$$

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Chlorine.}}{2Cl} = \underset{\text{Monochloracetic acid.}}{C_2H_3ClO_2} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Nitro-benzene.}}{C_6H_5NO_2} + \underset{\text{Water.}}{H_2O}.$$

**Derivatives.**—This term is applied to bodies derived from others by some kind of decomposition, generally by substitution. Thus, nitro-benzene is a derivative of benzene; chloroform, $CHCl_3$, is a derivative of methane, $CH_4$, obtained from the latter by replacement of three atoms of hydrogen by the same number of atoms of chlorine.

**Isomerism.**—Two or more substances may have the same elements in the same proportion by weight (or the same centesimal composition), and yet be different bodies, showing different properties. Such substances are called isomeric bodies. Three kinds of isomerism are distinguished, viz., metamerism, polymerism, and stereo-isomerism.

**Metamerism.**—Substances are metameric when their molecules contain equal numbers of atoms of the same elements. Thus, cane-sugar and milk-sugar have both the composition $C_{12}H_{22}O_{11}$, and yet they have different physical properties, and may be distinguished by their solubility and by a number of characteristic tests.

The explanation given regarding this difference of properties is, that the atoms are arranged differently within the molecule. In some cases this arrangement is as yet unknown, in other cases structural or graphic formulas showing this atomic arrangement may be given.

For instance: acetic acid and methyl formate both have the composition $C_2H_4O_2$, but the arrangement of the atoms (or the structure) is very different, as shown by the formulas:

Acetic acid. $C_2H_3O\diagdown O.$ $H\diagup$

Methyl formate. $CHO\diagdown O.$ $CH_3\diagup$

As another instance may be mentioned the compound $CN_2H_4O$, which represents either ammonium cyanate or urea:

Ammonium cyanate. $NH_4\diagdown O.$ $CN\diagup$

Urea. $NH_2\diagdown CO.$ $NH_2\diagup$

**Polymerism.**—Substances are said to be polymeric when they have the same centesimal composition, but a different molecular weight, or, in other words, when one substance contains some multiple of the number of each of the atoms contained in the molecule of the other.

For instance, some volatile oils have the composition $C_{20}H_{32}$, which is double the number of atoms contained in oil of turpentine, $C_{10}H_{16}$; acetylene, $C_2H_2$, is polymeric with benzene, $C_6H_6$, and styrene, $C_8H_8$; formaldehyde, $CH_2O$, acetic acid, $C_2H_4O_2$, lactic acid, $C_3H_6O_3$, and glucose, $C_6H_{12}O_6$, are polymeric compounds.

**Stereo-isomerism.**—There has long been known a number of bodies having the same molecular and constitutional formulas (*i. e.*, behaving alike chemically), but which exhibit differences in properties, as, for instance, in their behavior toward polarized light and in the form of their crystals. The explanation at present given of these differences is based on this assumption: that the different atoms or radicals in combination with a carbon atom may occupy toward it different relative positions, and that actually they do.

In order to understand what is meant by this statement we should bear in mind that we represent the grouping of our atoms on the flat surface of paper, while actually the formation of molecules takes place in space—*i. e.*, in three directions. If we assume, for instance, that four different radicals are in combination with a carbon atom, we can well imagine that the relative positions in which these radicals are grouped around the carbon atom have an influence on the nature of the compound. There are bodies which contain the same elements in the same quantities but in which the molecular structures seem to be reversed, precisely as they would be if seen directly and then observed after reflection from a mirror. In fact, there are known isomeric bodies the crystals of which seem to exhibit exactly that relation to each other.

The term *stereo-isomerism* is therefore used for that kind of isomerism found in substances which contain apparently the same radicals, show practically the same chemical behavior toward other agents, but differ in certain physical properties. Of stereo-isomeric substances may be mentioned 2 malic acids, 3 lactic acids, 4 tartaric acids, etc. (For details of stereo-isomerism the student is referred to works treating more fully on this subject.)

**Various Modes of Decomposition.**—The principal changes which a molecule may suffer are as follows:

*a.* The atoms may arrange themselves differently within the molecule. Ammonium cyanate, $NH_4CNO$, is easily converted into urea, $CO(NH_2)_2$. This is called molecular rearrangement.

*b.* A molecule may split up into two or more molecules. For instance:

$$\underset{\text{Grape-sugar.}}{C_6H_{12}O_6} = \underset{\text{Alcohol.}}{2C_2H_6O} + \underset{\text{Carbon dioxide.}}{2CO_2}.$$

This decomposition is spoken of as *cleavage*. When cleavage is accompanied by the taking up of the constituents of water the change is called *hydrolytic cleavage* or *hydrolysis*. The following reaction belongs to this class:

$$\underset{\text{Hippuric acid.}}{C_9H_9NO_3} + H_2O = \underset{\text{Benzoic acid.}}{C_7H_6O_2} + \underset{\text{Glycocoll.}}{C_2H_3NH_2O_2}.$$

*c.* Two molecules, either of the same kind, or of different substances, may unite directly:

$$\underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Bromine.}}{2Br} = \underset{\text{Ethylene bromide.}}{C_2H_4Br_2}.$$

*d.* Atoms may be removed from a compound without replacing them by other atoms:

$$\underset{\text{Alcohol.}}{C_2H_6O} + \underset{\text{Oxygen.}}{O} = \underset{\text{Aldehyde.}}{C_2H_4O} + \underset{\text{Water.}}{H_2O}.$$

*e.* Atoms may be removed and replaced by others at the same time (substitution):

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Chlorine.}}{2Cl} = \underset{\text{Monochloracetic acid.}}{C_2H_3ClO_2} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

**Action of Heat upon Organic Substances.**—As a general rule, organic bodies are distinguished by the facility with which they decompose under the influence of heat or chemical agents; the more complex the body is, the more easily does it undergo decomposition or transformation.

Heat acts differently upon organic substances, some of which may be volatilized without decomposition, while others are decomposed by heat with generation of volatile products. This process of heating non-volatile organic substances in such a manner that the oxygen of the atmospheric air has no access, and to such an extent that decomposition takes place, is called *dry or destructive distillation.*

The nature of the products formed during this process varies not only with the nature of the substance heated, but also with the temperature applied during the operation. The products formed by destructive distillation are invariably less complex in composition, that is, have a smaller number of atoms in the molecule, than the substance which suffered decomposition; in other words a complex, molecule is split up into two or more molecules less complex in composition.

Otherwise, the products formed show a great variety of properties; some are gases, others volatile liquids or solids, some are neutral, others basic or acid substances. In most cases of destructive distillation a non-volatile residue is left, which is nearly pure carbon.

**Action of Oxygen upon Organic Substances.—Combustion. Decay.**—All organic substances are capable of oxidation, which takes place either rapidly with the evolution of heat and light and is called

*combustion*, or it takes place slowly without the emission of light, and is called *slow combustion* or *decay*. The heat generated during the decay of a substance is the same as that generated by burning the substance; but as this heat is liberated in the first instance during weeks, months, or perhaps years, its generation is so slow that it can scarcely be noticed.

No organic substance found or formed in nature contains a sufficient quantity of oxygen to cause the complete combustion of the combustible elements (carbon and hydrogen) present; by artificial processes such substances may, however, be produced, and are then either highly combustible or even explosive.

During common combustion, provided an excess of atmospheric oxygen be present, the total quantity of carbon is converted into carbon dioxide, hydrogen into water, sulphur and phosphorus into sulphuric and phosphoric acids, while nitrogen is generally liberated in the elementary state.

During the process of decay the compounds mentioned above are produced finally, although many intermediate products are generated. For instance: If a piece of wood be burnt, complete oxidation takes place; intermediate products also are formed chiefly in consequence of the destructive distillation of a portion of the wood, but they are consumed almost as fast as they are produced, as was mentioned in connection with the consideration of flame. Again, when a piece of wood is exposed to the action of the atmosphere, it slowly burns or decays. The intermediate products formed in this case are entirely different from those produced during common combustion.

Common alcohol has the composition $C_2H_6O$; in burning, it requires six atoms of oxygen, when it is converted into carbon dioxide and water:

$$C_2H_6O + 6O = 2CO_2 + 3H_2O.$$

But alcohol may also undergo slow oxidation, in which case oxygen first removes hydrogen, with which it combines to form water, while at the same time a compound known as acetic aldehyde, $C_2H_4O$, is formed:

$$C_2H_6O + O = C_2H_4O + H_2O.$$

This aldehyde, when further acted upon by oxygen, takes up an atom of this element, thereby forming acetic acid:

$$C_2H_4O + O = C_2H_4O_2.$$

The three instances given above illustrate the action of oxygen upon organic substances, which action may consist in a mere removal of hydrogen, in a replacement of hydrogen by oxygen, or in an oxidation of both the carbon and hydrogen, and also of sulphur and phosphorus, if they be present.

An organic substance, when perfectly dry and exposed to dry air only, may not suffer decay for a long time (not even for centuries), but in the presence of moisture and air this oxidizing action takes place in many instances.

Besides the slow oxidation or decay which all dead organic matter undergoes in the presence of moisture, there is another kind of slow oxidation, which takes place in the living animal. In respiration, oxygen of the air enters into combination with the hæmoglobin of red blood corpuscles, by which it is carried to all the tissues of the body. The oxygen is given up to these tissues, and carbon dioxide formed by oxidation is absorbed by the blood where it exists partly in simple solution and partly in a loose combination with hæmoglobin. During respiration, the carbon dioxide escapes from the blood stream in the capillaries of the lung into the air.

**Fermentation and Putrefaction.**—These terms are applied to peculiar kinds of decomposition, by which the molecules of certain organic substances are split up into two or more molecules of a less complicated composition. These decompositions take place when three factors are simultaneously acting upon the organic substance. These factors are: presence of moisture, favorable temperature, and presence of a substance generally termed ferment.

The most favorable temperature for these decompositions lies between 25° and 40° C. (77° and 104° F.), but they may take place at lower or higher temperatures. No substance, however, will either ferment or putrefy at or below the freezing-point, or at or above the boiling-point of water.

The nature of the various ferments differs widely, and their true action cannot, in many cases, be explained; what we do know is, that the presence of comparatively small (often minute) quantities of one substance (the ferment) is sufficient to cause the decomposition of large quantities of certain organic substances, the ferment itself suffering often no apparent change during this decomposition.

Ferments have been divided into two classes: (1) *Organized ferments* (sometimes called true ferments), being unicellular living microorganisms chiefly of vegetable origin. (2) *Soluble ferments, unorganized ferments*, or *enzymes* (false ferments) which are in most cases nitrogenous substances closely related to the proteins.

This classification was based on the belief that the living cell itself was the acting agent. It has, however, been shown that this view is incorrect and that the decomposing influence exerted by these ferments is due to some substance produced by the living cell, from which it may be separated or extracted in a more or less pure condition. It is consequently more in conformity with our present views to apply the term enzyme to that agent which causes the decomposition. Enzymes are always products of the cell action of a living organism, but this organism may be a microörganism, such as the yeast cell; or it may be a highly developed plant, such as the almond tree which produces emulsine, an enzyme which decomposes amygdalin; or it may be an animal or man, generating such enzymes as ptyalin, pepsin, etc. (Enzymes will be more fully considered later on.)

The nature of the ferment generally determines the nature of the decomposition which a substance suffers, or, in other words, one and the same substance will under the influence of one ferment decompose with liberation of certain products, while a second ferment causes other products to be evolved. Sugar, for instance, under the influence of yeast, is converted into alcohol and carbon dioxide, while under the influence of certain other ferments it is converted into lactic acid.

The difference between fermentation and putrefaction is that the first term is used in those cases where the decomposing substance belongs to the group of carbohydrates, all of which contain the elements carbon, hydrogen, and oxygen only, while substances belonging to the proteins, which contain, in addition to these three elements, also nitrogen and sulphur, undergo putrefaction. The two last-named elements are generally evolved as ammonia or derivatives of ammonia and hydrogen sulphide, which gases give rise to an offensive odor, the putrefying mass being generally designated as fetid matter.

As a general rule the oxygen of the air takes no part in either fermentation or putrefaction, but the presence or absence of atmospheric air may cause or prevent decomposition, inasmuch as the atmosphere is filled with millions of bacteria, which may act as ferments when in contact with organic matter under favorable conditions.

One of the fermentations in which oxygen takes part is acetic acid fermentation, resulting in the conversion of alcohol into acetic acid by oxidation. This conversion may be brought about by suitable oxidizing agents, or even by atmospheric oxygen, and is then practically a slow combustion or decay. But the transfer of oxygen may be brought about by microorganisms and the process is then defined as fermentation.

Whenever organic bodies (a dead animal, for instance) undergo decomposition in nature, the processes of fermentation and putrefaction are generally accompanied by oxidation or decay.

The conditions under which a substance will ferment or putrefy have been stated above, and the non-fulfillment of these conditions enables us to prevent decomposition artificially.

Thus, we make use of a low temperature in our refrigerators or by cold storage. We expel water by drying or by dehydrating agents such as absolute alcohol. We prevent the action of the ferments either by antiseptic agents (salt, carbolic or salicylic acid, etc.) which are incompatible with organic life, or by excluding the air, and with it the ferments, by enclosing the substances in air-tight vessels (glass jars, tin cans, etc.), which, when filled, are heated sufficiently to destroy any bacteria which may have been present.

**Antiseptics and Disinfectants.**—While the term *antiseptics* is applied to those substances which retard or prevent fermentation and putrefaction, the term *disinfectants* refers to those agents actually

destroying the organisms which are the causes of these decompositions. If we assume that all infectious diseases are due to micro-organisms, or germs of various kinds, disinfectants may be considered as equivalent to *germicides*. Disinfectants are generally antiseptics also, but the latter are not in all cases disinfectants. The solution of a substance of certain strength may act as a disinfectant and antiseptic, while the same solution diluted further may act as an antiseptic only, but not as a disinfectant.

**Deodorizers.**—Deodorizes are those substances which convert the strongly smelling products of decomposition into inodorous compounds. Strong oxidizing agents are generally good deodorizers, as, for instance, chlorine, potassium permanganate, hydrogen dioxide, etc. Among the best antiseptics and disinfectants are mercuric chloride (a solution of 1 : 500 or 1 : 1000); carbolic acid (5 per cent. solution); potassium permanganate (5 per cent. solution); chlorine (generally used in the form of a 4 per cent. solution of calcium hypochlorite); formaldehyde, used in solution or as a gas; hydrogen peroxide, salicylic acid, boric acid, sulphur dioxide, ferrous or cupric sulphate, alcohol, chloroform, thymol, etc.

The selection of a disinfectant depends on the respective conditions. While the relatively harmless salicylic acid is often used as a preservative for articles of food it is the powerful but strongly poisonous mercuric chloride which is used externally in the operating room. The surgeon disinfects his hands by first scrubbing with soap and water, immersing in a saturated solution of potassium permanganate and washing finally in solution of oxalic acid. The latter removes through its deoxidizing and dissolving power that portion of the permanganate which adheres to the hands. For the disinfection of rooms gases, such as formaldehyde, sulphur dioxide or chlorine, are indicated. Instruments may be disinfected by heat or by immersion in suitable solutions.

The term *asepsis* refers to the absence of living germs of fermentation, putrefaction or disease, while the term *sterilization* is used for the process of destroying all living micro-organisms in the object or material operated on. Aseptic conditions by means of sterilizing may be brought about either by the use of antiseptic agents or by application of heat.

**Action of Chlorine and Bromine.**—These two elements act upon organic substances (similarly to oxygen) in three different ways, viz., they either (rarely, however) combine directly with the organic substance, or remove hydrogen, or replace hydrogen. The following equations illustrate this action:

$$\underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Bromine.}}{2Br} = \underset{\text{Ethylene bromide.}}{C_2H_4Br_2}.$$

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} + \underset{\text{Chlorine.}}{2Cl} = \underset{\text{Aldehyde.}}{C_2H_4O} + \underset{\text{Hydrochloric acid.}}{2HCl}.$$

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Chlorine.}}{2Cl} = \underset{\text{Monochloracetic acid.}}{C_2H_3ClO_2} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

In the presence of water, chlorine and bromine often act as oxidizing agents by combining with the hydrogen of the water and liberating oxygen; iodine may act in a similar manner as an oxidizing agent, but it rarely acts directly by substitution.

**Action of Nitric Acid.**—This substance acts either by direct combination with organic bases forming salts, or as an oxidizing agent, or by substitution of nitryl, $NO_2$, for hydrogen. As instances of the latter action may be mentioned the formation of nitro-benzene and cellulose nitrate:

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Nitro-benzene.}}{C_6H_5NO_2} + \underset{\text{Water.}}{H_2O}.$$

$$\underset{\text{Cellulose.}}{C_6H_{10}O_5} + \underset{\text{Nitric acid.}}{3HNO_3} = \underset{\text{Cellulose trinitrate}}{C_6H_7(NO_2)_3O_5} + \underset{\text{Water.}}{3H_2O}.$$

The additional quantity of oxygen thus introduced into the molecules renders them highly combustible, or even explosive.

**Action of Dehydrating Agents.**—Substances having a great affinity for water, such as strong sulphuric acid, phosphoric oxide, and others, act upon many organic substances by removing from them the elements of hydrogen and oxygen, and combining with the water formed, while, at the same time, frequently dark or even black compounds are formed, which consist largely of carbon. The black color imparted to sulphuric acid by organic matter depends on this action.

**Action of Alkalies.**—The hydroxides of potassium and sodium act in various ways on organic substances.

In some cases substitution products are decomposed:

$$\underset{\text{Ethyl chloride.}}{C_2H_5Cl} + \underset{\substack{\text{Potassium}\\\text{hydroxide.}}}{KOH} = \underset{\substack{\text{Potassium}\\\text{chloride.}}}{KCl} + \underset{\text{Ethyl alcohol.}}{C_2H_5OH}.$$

Salts are formed:

$$\underset{\substack{\text{Acetic}\\\text{acid.}}}{C_2H_4O_2} + \underset{\substack{\text{Sodium}\\\text{hydroxide.}}}{NaOH} = \underset{\substack{\text{Sodium}\\\text{acetate.}}}{NaC_2H_3O_2} + \underset{\text{Water.}}{H_2O}.$$

Fats are decomposed with the formation of soap:

$$\underset{\text{Oleate of glyceryl.}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\text{Sodium hydroxide.}}{3NaOH} = \underset{\text{Glycerin.}}{C_3H_5(OH)_3} + \underset{\text{Sodium oleate.}}{3NaC_{18}H_{33}O_2}.$$

Oxidation takes place, while hydrogen is liberated:

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_6O} + \underset{\substack{\text{Potassium}\\\text{hydroxide.}}}{KOH} = \underset{\substack{\text{Potassium}\\\text{acetate.}}}{KC_2H_3O_2} + \underset{\text{Hydrogen.}}{4H}.$$

From compounds containing nitrogen, ammonia is evolved:

$$\underset{\text{Acetamide.}}{NH_2C_2H_3O} + \underset{\substack{\text{Potassium}\\\text{hydroxide.}}}{KOH} = \underset{\substack{\text{Potassium}\\\text{acetate.}}}{KC_2H_3O_2} + \underset{\text{Ammonia.}}{NH_3}.$$

**Action of Reducing Agents.**—Deoxidizing or reducing agents, especially hydrogen in the nascent state, act upon organic substances either by direct combination:

$$\underset{\text{Acetic aldehyde.}}{C_2H_4O} + 2H = \underset{\text{Ethyl alcohol.}}{C_2H_6O.}$$

or by removing oxygen (and also chlorine or bromine):

$$\underset{\text{Benzoic acid.}}{C_7H_6O_2} + 2H = \underset{\text{Benzoic aldehyde.}}{C_7H_6O} + H_2O.$$

$$\underset{\text{Benzoic aldehyde.}}{C_7H_6O} + 2H = \underset{\text{Benzylic alcohol.}}{C_7H_8O.}$$

In some cases hydrogen replaces oxygen :

$$\underset{\text{Nitro-benzene.}}{C_6H_5NO_2} + 6H = \underset{\text{Aniline.}}{C_6H_5NH_2} + 2H_2O.$$

**Classification of Organic Compounds.**—There are great difficulties in arranging the immense number of organic substances properly, and in such a manner that natural groups are formed the members of which are similar in composition and possess like properties.

Various modes of classification have been proposed, some of which, however, are so complicated that the beginner will find it difficult to make use of them. The grouping of organic substances here adopted, while far from being perfect, has the advantages of being simple, easily understood, and remembered.

1. *Hydrocarbons.* All compounds containing the two elements carbon and hydrogen only. For instance, $CH_4$, $C_6H_6$, $C_{10}H_{16}$, etc.

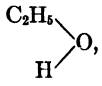
2. *Alcohols.* These are hydrocarbon radicals in combination with hydroxyl, OH. For instance, ethyl alcohol, $C_2H^{i}_5OH$, glycerin, $C_3H^{iii}_5(OH)_3$, etc.

3. *Aldehydes.* Hydrocarbon radicals in combination with the radical COH; they are compounds intermediate between alcohols and acids, or alcohols from which hydrogen has been removed. For instance:

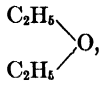
| $C_2H_6O$, | $CH_3.COH$, | $C_2H_4O_2$. |
|---|---|---|
| Ethyl alcohol. | Aldehyde. | Acetic acid. |

4. *Organic Acids.* Hydrocarbon radicals in combination with carboxyl, a radical having the composition $CO_2H$, or compounds formed by replacement of hydrogen in hydrocarbons by carboxyl. Instances: Acetic acid, $CH_3CO_2H$; pyrotartaric acid, $C_3H_6(CO_2H)_2$.

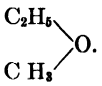
5. *Ethers.* Compounds formed from alcohols by replacement of the hydrogen of the hydroxyl by other hydrocarbon radicals, or, what is the same, by other alcohol radicals. For instance:



Ethyl alcohol.

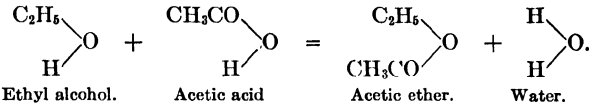


Ethyl ether.



Ethyl-methyl ether.

6. *Compound Ethers or Esters.* Formed from alcohols by replacement of the hydrogen of the hydroxyl by acid radicals, or from acids by replacement of the hydrogen of carboxyl by alcoholic radicals. For instance:




Ethyl alcohol. Acetic acid Acetic ether. Water.

The various fats belong to this group of compound ethers.

7. *Carbohydrates.* (Sugars, starch, cellulose, etc.) These are compounds of carbon, hydrogen, and oxygen, in which the number of carbon and oxygen atoms is the same, while the number of hydrogen atoms is double that of the oxygen atoms. As the hydrogen and oxygen are present in the proportion to form water, they are hence called carbohydrates. There are only a few exceptions to the above statement. Most carbohydrates are capable of fermentation, or of being easily converted into fermentable bodies. Instances: $C_6H_{12}O_6$, $C_6H_{10}O_5$, etc.

Glucosides are substances the molecules of which may be split up in such a manner that several new bodies are formed, one of which is sugar.

8. *Amines and Amides.* Substances formed by replacement of hydrogen in ammonia by alcohol or acid radicals. For instance: ethyl amine, $NH_2.C_2H_5$, urea, $N_2H_4.CO$, etc. The alkaloids belong to this group.

9. *Cyanogen and its Compounds.* Substances containing the radical cyanogen, CN. For instance: potassium cyanide, KCN.

10. *Proteins or Albuminous Substances.* These, besides carbon, hydrogen, and oxygen, always contain nitrogen and sulphur, sometimes also other elements. Instances: albumin, casein, fibrin, etc.

In connection with each of these groups have to be considered the derivatives obtained from them directly or indirectly.

As all those organic compounds, the constitution of which has been explained, may be looked upon as derivatives of either methane, $CH_4$, or benzene, $C_6H_6$, a separation of organic compounds is made into two large classes, each one embodying all the derivatives of one of the two hydrocarbons named. The derivatives of methane are

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QUESTIONS.—Explain the term residue or radical. What is understood by the expression chain, when used in chemistry? What are the characteristics of an homologous series? Give an explanation of the terms isomerism, metamerism, and polymerism. How does heat act upon organic compounds? What is destructive distillation? State the difference between combustion, decay, fermentation, and putrefaction; what is the nature of these processes, and under what conditions do they take place? How do chlorine, nitric acid, and alkalies act upon organic substances? What is the action of hydrogen and of dehydrating agents upon organic substances? Mention the chief groups of organic compounds.

often termed *fatty compounds*, those of benzene *aromatic compounds*. Methane derivatives have representatives in each one of the above ten groups: benzene derivatives are missing in a few. As far as practicable, the two classes will be considered separately, because the properties of fatty and aromatic compounds differ so widely, in some respects, that this method of studying the nature of carbon compounds is to be preferred.

## 42. HYDROCARBONS AND THEIR HALOGEN DERIVATIVES.

**Occurrence in Nature.**—Hydrocarbons are seldom derived from animal sources, being more frequently products of vegetable life; thus, the various essential oils (oil of turpentine and others) of the composition $C_{10}H_{16}$ or $C_{20}H_{32}$ are frequently found in plants.

Other hydrocarbons are found in nature as products of the decomposition of organic matter. Thus methane, $CH_4$, is generally formed during the decay of organic matter in the presence of moisture; the higher members of the methane series are found in crude coal-oil.

**Formation of Hydrocarbons.**—It is difficult to combine the two elements carbon and hydrogen directly; as an instance of such direct combination may be mentioned acetylene, $C_2H_2$, which is formed when electric sparks pass between electrodes of carbon in an atmosphere of hydrogen.

Many hydrocarbons are obtained by destructive distillation of organic matter, and their nature depends on the composition of the material used and upon the degree of heat applied for the decomposition. Hydrocarbons may also be obtained by the decomposition (other than destructive distillation) of numerous organic bodies, such as alcohols, acids, amines, etc., and from derivatives of these substances.

The hydrocarbons found in nature are generally separated from other matter, as well as from each other, by the process known as *fractional distillation.* As the boiling-points of the various compounds differ more or less, they may be separated by carefully distilling off the compounds of lower boiling-points, while noting the temperature of the vapors above the boiling liquid by means of an inserted thermometer, and changing the receiver every time an increase of the boiling-point is noticed. This separation of volatile liquids, known as fractional distillation, is, however, not absolutely complete, because traces of substances having a higher boiling-point are simultaneously volatilized with the distilling substance.

For fractional distillation of small quantities of liquids as well as for the determination of boiling-points, flasks arranged like those shown in Fig. 42 may be used.

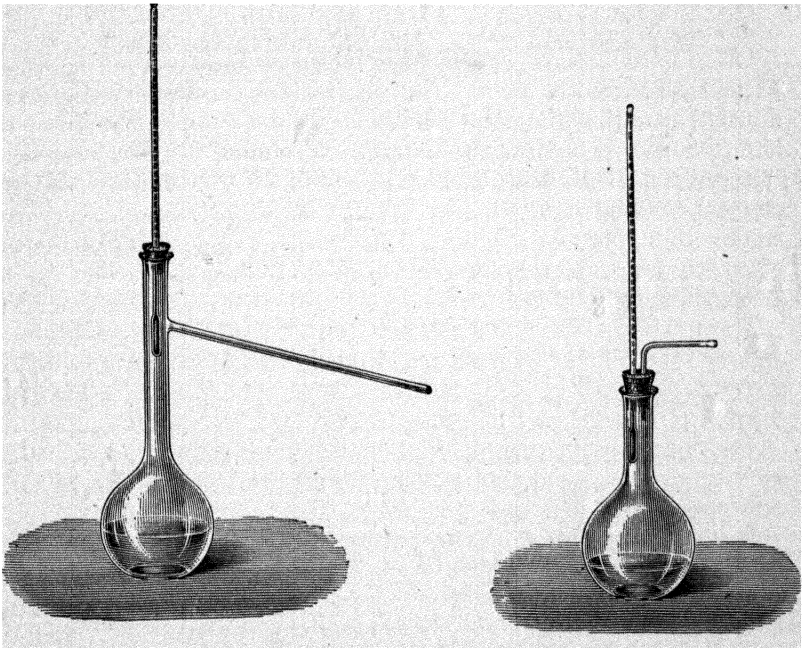
**Properties of Hydrocarbons.**—There are no other two elements which combine together in so many proportions as carbon and hydrogen.

Several hundred hydrocarbons are known, many of which form either homologous series or are metameric or polymeric.

Hydrocarbons occur either as gases, liquids, or solids. If the molecule contains not over 4 atoms of carbon, the compound is generally a gas at the ordinary temperature; if it contains from 4 to 10 or 12 atoms of carbon, it is a liquid; and if it contains a yet higher number of carbon atoms, it is generally a solid.

All hydrocarbons may be volatilized without decomposition, all are colorless substances, and many have a peculiar and often characteristic odor; they are generally insoluble in water but soluble in alcohol, ether, disulphide of carbon, etc.

FIG. 42.



Flasks arranged for fractional distillation.

In regard to chemical properties, the majority of the hydrocarbons are neutral substances, behaving rather indifferently toward most other chemical agents. Many of them are, however, oxidized by the oxygen of the air, by which process liquid hydrocarbons are often converted into solids. The action of halogens on hydrocarbons will be considered later on.

A number of homologous series of hydrocarbons are known, of which the following are the most important:

| | General formula. | First member. |
|---|---|---|
| Methane series or paraffins, | $C_nH_{2n+2}$ | $CH_4$ |
| Ethene series or olefins, | $C_nH_{2n}$ | $C_2H_4$ |
| Ethine series or acetylenes, | $C_nH_{2n-2}$ | $C_2H_2$ |
| Terpenes, | $C_nH_{2n-4}$ | $C_{10}H_{16}$ |
| Benzene series, | $C_nH_{2n-6}$ | $C_6H_6$ |

Of the acetylene series and of the terpenes only a few homologues are known.

The univalent radicals of the members of the methane series are designated by changing the termination *ane* to *yl* (methane, methyl, $CH_3^{I}$); the bivalent radicals by changing *ane* to *ene* (methene, $CH_2^{II}$); and the trivalent radicals by changing the final *e* of ene to *yl* (methenyl, $CH^{III}$). The derivatives of the bivalent radicals are indicated by the termination *ylene*, as methylene iodide, $CH_2I_2$.

## Hydrocarbons of the Paraffin or Methane Series.

The hydrocarbons having the general composition $C_nH_{2n+2}$ are known as paraffins, the name being derived from the higher members of the series which form the paraffin of commerce. The following table gives the composition, boiling-points, etc., of the first sixteen members of this series:

| | | B. P. | Sp. gr. |
|---|---|---|---|
| Methane or methyl hydride, | $CH_4$ | gases. | |
| Ethane or ethyl hydride, | $C_2H_6$ | gases. | |
| Propane or propyl hydride, | $C_3H_8$ | gases. | |
| Butane or butyl hydride, | $C_4H_{10}$ | 1° C. | |
| Pentane or amyl hydride, | $C_5H_{12}$ | 38 | 0.628 |
| Hexane or hexyl hydride, | $C_6H_{14}$ | 70 | 0.669 |
| Heptane or heptyl hydride, | $C_7H_{16}$ | 99 | 0.690 |
| Octane or octyl hydride, | $C_8H_{18}$ | 125 | 0.726 |
| Nonane or nonyl hydride, | $C_9H_{20}$ | 148 | 0.741 |
| Decane or decyl hydride, | $C_{10}H_{22}$ | 166 | 0.757 |
| Undecane or undecyl hydride, | $C_{11}H_{24}$ | 184 | 0.766 |
| Dodecane or dodecyl hydride, | $C_{12}H_{26}$ | 202 | 0.778 |
| Tridecane or tridecyl hydride, | $C_{13}H_{28}$ | 218 | 0.796 |
| Tetradecane or tetradecyl hydride, | $C_{14}H_{30}$ | 236 | 0.809 |
| Pentadecane or pentadecyl hydride, | $C_{15}H_{32}$ | 258 | 0.825 |
| Hexadecane or hexadecyl hydride, | $C_{16}H_{34}$ | 280 | |
| etc. | | | |

The above table shows that the paraffins form an homologous series; the first four members are gases, most of the others liquids, regularly increasing in specific gravity, boiling-point, viscidity, and vapor density, as their molecular weight becomes greater.

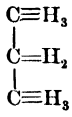
The paraffins are saturated hydrocarbons, the constitution of which has been already explained; they are incapable of uniting directly with monatomic elements or residues, but they easily yield substitution-derivatives when subjected to the action of chlorine or bromine, hydrogen in all cases being given up from the hydrocarbon.

Most of the paraffins are known in two (or even more) modifications; there are, therefore, other homologous series of hydrocarbons of the same composition as the above normal paraffins, which show some difference from the normal paraffins in boiling-points and other properties. In these isomeric paraffins the atoms are arranged differently from those in the normal hydrocarbons, which fact may be proven by the difference in decomposition which these substances suffer when acted upon by chemical agents.

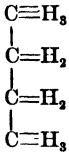
No isomeric hydrocarbons of the first three members of the paraffin series are known, which fact is in accordance with our present theories. Assuming that the quadrivalent carbon atoms exert their full valence, and that they are held together by one bond only, we can arrange the atoms in the compounds, $CH_4$, $C_2H_6$, and $C_3H_8$, not otherwise than thus:

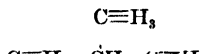






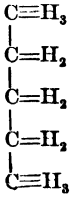
In the next compound, butane, $C_4H_{10}$, we have two possibilities explaining the structure of the molecule, namely, these:

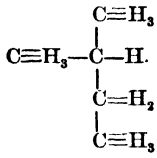


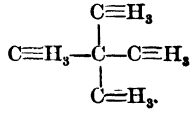


Both these compounds are known, and termed normal butane and isobutane, respectively.

The next member, pentane, $C_5H_{12}$, shows three possibilities of constitution, thus:







These compounds also are known. With the higher members of the paraffins the number of possible isomers rises rapidly according to the law of permutation, so that we have of the seventh member 9, of the tenth 75, and of the thirteenth member 802, possible isomeric hydrocarbons.

**Methane, $CH_4$** (*Marsh-gas, Fire-damp*).—This hydrocarbon has been spoken of in chapter 12, where it was stated that it is a colorless, combustible gas, which is formed by the decay of organic matter in the presence of moisture, during the formation of coal in the interior of the earth, and by the destructive distillation of various organic matters. The fact that methane is a constituent of the gases that arise when vegetable matter undergoes decay in stagnant water gave rise to the name *marsh-gas*. It has been shown that the gas is formed from the cellulose of plant tissues by the action of bacteria.

Intestinal gases formed during imperfect digestion sometimes contain more than 50 per cent. of methane. It often is the cause of explosions in coal mines, for which reason miners call the gas *fire-damp*. Over 90 per cent. of natural gas consists of methane, and coal gas contains about 35 per cent.

Methane can be obtained in the laboratory in a number of ways. It may be made by the action of inorganic substances upon one another; for instance, by the action of water on aluminum carbide, a compound of the metal aluminum, and carbon, $Al_4C_3$, the following change taking place:

$$Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3.$$

Bearing in mind that aluminum carbide, as well as water, may be obtained by direct union of the elements, it is evident that methane may be formed indirectly, by means of the above method, from the elements carbon and hydrogen.

Another method by which methane is formed is to pass a mixture of hydrogen and carbon monoxide or dioxide over finely powdered nickel at about 250° C. Nickel has been found to be an excellent catalytic agent in bringing about reductions of organic compounds by hydrogen gas. The method is far more valuable in other instances than for the production of methane.

A third method which yields methane contaminated with only a small quantity of other substances, is to heat a mixture of anhydrous sodium acetate and soda lime. It will be shown later that acetic acid has the formula $CH_3.COOH$, in other words, that it is derived from methane by replacement of one hydrogen atom by the typical acidifying group, COOH, which is called carboxyl. When the sodium salt is heated with soda lime, the COOH group is removed and the hydrogen replaced, to reform the methane molecule, thus:

$$CH_3.COONa + NaOH = CH_4 + Na_2CO_3.$$

This method is of general application and is important because by means of it organic acids can be converted into the hydrocarbons to which they are related.

*Experiment* 51.—Use apparatus shown in Fig. 5, page 51, omitting the bent tube *B*. Mix in a mortar 20 grams of sodium acetate with 20 grams of potassium (or sodium) hydroxide and 30 grams of calcium hydroxide; fill with this mixture the tube *A*, which should be made of glass fusing with difficulty, or of so-called "combustion tubing;" apply heat and collect the gas over water.

Ignite the gas, and notice that its flame is but slightly luminous. Mix some of the gas in a wide-mouth cylinder, of not more than about 200 c.c. capacity, with an equal volume of air and ignite. Repeat this experiment with mixtures of one volume of methane with 2, 4, 6, 8, and 10 volumes of atmospheric air. Which mixture is most explosive, and why? How many volumes of oxygen and how many volumes of atmospheric air are needed for the complete combustion of one volume of methane?

A fourth method, by which very pure methane may be obtained, is to reduce methyl iodide, $CH_3I$, which is obtained by suitable reactions from methyl alcohol, $CH_3OH$, as will be shown later. Methyl iodide is a heavy, colorless, volatile liquid. The best procedure for reducing it to methane to avoid contamination with hydrogen, etc., is to drop an alcoholic solution of it on a zinc-copper couple. The latter is prepared by heating a mixture of granulated zinc and powdered copper in the proportion of 3 : 1, until the metals begin to alloy. The action consists in the formation of methyl zinc iodide, which is decomposed by alcohol or the water it contains:

$$CH_3I + Zn = CH_3.Zn.I,$$
$$CH_3.Zn.I + H_2O = (HO).Zn.I + CH_4.$$

A slow, steady stream of methane is evolved, containing only a trace of methyl iodide from which it can be freed.

PROPERTIES OF METHANE.—Methane is of special interest because it is the compound from which thousands of other substances may be considered to be derived. It is the simplest of all organic compounds, having but one carbon atom in the molecule. It is a colorless, odorless gas, slightly soluble in water, about 0.6 as heavy as air. Liquefied methane boils at −152° C. and solid methane melts at −186° C. It is the lightest of all compound gases, very stable toward heat, and, like its homologues, is inert toward most chemicals, for example sulphuric and nitric acids, alkalies, strong oxidizing agents, etc. It is often one of the products of the action of heat on other hydrocarbons. The flame of methane is slightly luminous and very hot because of the high per cent. of hydrogen it contains, which is greater than in any other hydrocarbon. The combustion of 16 grams of methane produces 213,500 calories of heat.

Chlorine and bromine act on methane in different ways according to conditions. A mixture of methane and chlorine, when exposed to direct sunlight, explodes, with production of hydrochloric acid, carbon, and other products. When, however, the mixture is exposed to diffused daylight, chlorine substitution products of methane are formed, as illustrated by the following type reaction:

$$CH_4 + 2Cl = CH_3Cl + HCl.$$

A fact worthy of note is that whenever hydrogen is displaced by chlorine or bromine, it does not escape as free hydrogen gas, but is found combined with halogen as hydrochloric or hydrobromic acid. Moreover, the formation of these two acids takes place with the evolution of considerable heat energy, and therefore the action of chlorine and bromine on methane, or other compounds, is exothermic and takes place spontaneously. On the other hand, the union of hydrogen and iodine (see chapter 18) is endothermic, that is, involves an absorption of heat energy, and therefore, iodine does not act spontaneously on methane and other compounds as chlorine and bromine do.

**Ethane, $C_2H_6$,** is a constituent of natural gas and of crude petroleum. It can be obtained from methyl-iodide, $CH_3I$, which, when acted on by sodium, is decomposed thus:

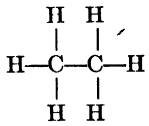
$$CH_3I + CH_3I + 2Na = 2NaI + C_2H_6.$$

This formation of ethane illustrates one of the methods for producing by *synthesis*—*i. e.*, for building up—more complex from simpler hydrocarbons. Another method, accomplishing the same result, depends on the action of a zinc compound of the radicals on the iodides of the radicals. The radicals may be the same or different ones; for instance:

| | | | | | | |
|---|---|---|---|---|---|---|
| $Zn(CH_3)_2$ | + | $2CH_3I$ | = | $ZnI_2$ | + | $2C_2H_6$, |
| Zinc methyl. | | Methyl iodide. | | Zinc iodide. | | Ethane. |
| $Zn(CH_3)_2$ | + | $2C_2H_5I$ | = | $ZnI_2$ | + | $2C_3H_8$, |
| | | Ethyl iodide. | | | | Propane. |

Ethane is most easily prepared, just as in the case of methane, by letting an alcoholic solution of ethyl iodide, $C_2H_5I$, drop on a copper-zinc couple.

Ethane is a colorless, odorless gas, very much like methane in all respects. Liquefied ethane boils at $-90°$ C. The methods of synthesis and the study of its derivatives prove that ethane has the structure



or in other words, that its molecule consists of two methyl radicals in union.

The succeeding members of the methane series, propane, butane, pentane, etc., can be prepared by the methods described above. Beginning with butane, isomeric hydrocarbons are also known. A normal and isobutane, three pentanes, five hexanes, five of nine possible heptanes, etc., are known. These hydrocarbons are similar in chemical behavior to methane and ethane, and for the purposes of this book, need not be further considered.

**Coal.**—As methane is one of the products generated during the formation of coal, it may be well to consider this process here briefly.

The various substances classed together under the name of *coal* consist principally of carbon, associated with smaller quantities of hydrogen, oxygen, nitrogen, sulphur, and certain inorganic mineral matters which compose the ash. Coal is formed from buried vegetable matter by a process of decomposition which is partly a fermentation, partly a decay, and chiefly a slow destructive distillation, the heat for this latter process being derived from the interior of the earth, or by the decomposition itself.

The principal constituent of the organic matter furnishing coal is wood (or woody fibre, cellulose), and a comparison of the composition of this substance with the various kinds of coal gradually formed will help to illustrate the chemical change taking place:

| | Carbon | Hydrogen. | Oxygen. |
|---|---|---|---|
| Wood | 100 | 12.18 | 83.07 |
| Peat | 100 | 9.85 | 55.67 |
| Lignite | 100 | 8.37 | 42.42 |
| Bituminous coal | 100 | 6.12 | 21.23 |
| Anthracite coal | 100 | 2.84 | 1.74 |

This table shows a progressive diminution in the proportions of hydrogen and oxygen during the passage from wood to anthracite. These two elements must, therefore, be eliminated in some form of combination which allows them to move, viz., as gases or liquids. The gases formed are chiefly carbon dioxide (which finds its way through the rocks and soils to the surface either in the gaseous state or after having been absorbed by water in the form of carbonic acid springs) and methane, known to coal-miners as fire-damp, frequently causing the formation of explosive gas mixtures in the coal mines; or escaping, like carbon dioxide, through fissures to the surface of the earth, where it may be ignited.

**Natural Gas.**—While methane and other combustible gases are undoubtedly formed during the formation of coal, the gas mixture now generally termed natural gas (a mixture of methane, ethane, propane, hydrogen, and a few other gases), and used largely for heating and illuminating purposes, is most likely a product of the complete decomposition of vegetable and animal matter which has been precipitated from water, simultaneously with inorganic matter, during the formation of certain rocks, chiefly slate and limestone. The decomposition of this organic matter has been so complete that the gaseous decomposition-products only are left, but no, or very little of, solid residue similar to coal.

**Coal-oil, Petroleum.**—Similar to natural gas, coal-oil is a product of the decomposition of organic matter, most likely of the fats and oils of fish and other aquatic animals. While the albuminous constituents of dead animal matter decompose rapidly, fats are comparatively stable. These oils and fats, after being precipitated simultaneously with other organic and inorganic matter from water, have formed by their decomposition (which was chiefly a destructive distillation) the liquid we call coal-oil or petroleum.[1]

Coal-oil is a mixture of the various liquid paraffins, containing often in solution the gaseous and solid members of this group, as also small quantities of coloring and other matter. The boiling-points of the constituents of coal-oil lie between 0° and 300° C. (32° and 572° F.), or even higher. The crude oil is purified, by treating it with sulphuric acid, followed by other processes of refining, and finally by fractional distillation, in order to separate the members of low boiling-points from those of higher boiling-points.

[1] Another view of the origin of petroleum is that it is the result of the action of water on carbides deep down in the earth, whereby hydrocarbons are formed, which under high temperature and pressure produce the complex mixtures called petroleum.

The hydrocarbons of low boiling-points, chiefly a mixture of $C_5H_{12}$ and $C_6H_{14}$, are known under the name of *petroleum-benzin*, which name must not be confounded with benzene or benzol, $C_6H_6$. Benzin should have a specific gravity from 0.638 to 0.660 at 25° C., and a boiling-point of 45° to 60° C. (113° to 140° F.).

Other similar liquids are sold in the market under the name of *rhigoline*, B. P. about 21° C. (70° F.) and *gasoline*, B. P. about 75° C. (167° F.); they are highly inflammable.

The paraffins distilling between 150° and 250° C. (302° and 408° F.) constitute the common *illuminating oil*, various kinds of which are sold as refined petroleum, kerosene, mineral sperm oil, etc. The danger which arises in the use of coal-oil as an illuminating agent is caused by the use of oils which have not been sufficiently freed from the more volatile members of the series, which, when but slightly heated (or even at ordinary temperature) will vaporize, and upon mixing with atmospheric air, form explosive mixtures. An oil to be safely used for illuminating purposes in common lamps should not give off inflammable vapors (or flash) below 49° C. (120° F.).

*Experiment* 52.—Various forms of apparatus are used for the exact determination of the flashing-point; students may determine it approximately by operating as follows: Fill a cylinder (about one inch in diameter and six inches high) two-thirds with coal-oil, suspend in the oil a thermometer, place the cylinder in a vessel with water (water-bath), keeping the level of the oil even with that of the water, and heat the latter slowly. Cover the cylinder loosely with a piece of pasteboard, and when the thermometer indicates a rise in temperature pass a small flame quickly over the mouth of the cylinder after having removed the pasteboard. Repeat this operation, from degree to degree, until a bluish flame is noticed running down to the surface of the oil. The temperature at which this takes place indicates the flashing-point.

After the illuminating oil has been distilled off, a mixture of substances passes over, which is used for lubricating purposes or furnishes, after having been purified, the *petrolatum* of the U. S. P. When further purified by treatment with bone-black the *white petrolatum* is obtained. Both are fat-like masses, more or less fluorescent, varying in color from white to yellowish or yellow, and almost without odor or taste. The article sold as *vaseline* is practically identical with soft petrolatum.

*Liquid petrolatum* of the U. S. P. is a petroleum of a specific gravity 0.87 to 0.94.

A mixture of the highest and solid members of the paraffin series distilling at a temperature about 350° C. (662° F.) is known as *paraffin*, *paraffinum*, a white crystalline substance used for candles, etc.; it fuses at about 52° to 57° C.

**Illuminating Gas.**—Illuminating gas is a mixture of gases obtained by the destructive distillation of coal (or wood) in iron retorts, with subsequent purification of the gases generated. The constituents of coal have been mentioned above. The products formed from it dur-

ing its destructive distillation are very numerous; the following are the most important:

| | | | | B. P. |
|---|---|---|---|---|
| Gases | | Hydrogen | H. | |
| | | Methane | $CH_4$. | |
| | | Ethene | $C_2H_4$. | |
| | | Acetylene | $C_2H_2$. | |
| | | Nitrogen | N. | |
| | | Ammonia | $NH_3$. | |
| | | Carbonic oxide | CO. | |
| | | Carbon dioxide | $CO_2$. | |
| | | Hydrogen sulphide | $H_2S$. | |
| | | Hydrocyanic acid | HCN. | |
| Coal-tar | Liquids | Benzene | $C_6H_6$ | 80° |
| | | Toluene | $C_7H_8$ | 110 |
| | | Aniline | $C_6H_5NH_2$ | 182 |
| | | Acetic acid | $C_2H_4O_2$ | 117 |
| | | Water | $H_2O$ | 100 |
| | Solids | Carbolic acid (Phenol) | $C_6H_6O$ | 188 |
| | | Kresylic acid | $C_7H_8O$ | 201 |
| | | Naphthalene | $C_{10}H_8$ | 220 |
| | | Anthracene | $C_{14}H_{10}$ | 360 |
| | | Paraffin | $C_{16}H_{34}$ | 280 |

Solid residue: Coke, chiefly carbon and inorganic matter.

The gases are purified by condensing ammonia (and some other gases) in water, carbon dioxide and hydrogen sulphide in calcium hydroxide. The following is the composition of a purified illuminating gas obtained from cannel-coal:

| | |
|---|---|
| Hydrogen | 46 volumes. |
| Methane | 41 " |
| Ethene | 6 " |
| Carbon monoxide | 4 " |
| Carbon dioxide | 2 " |
| Nitrogen | 1 volume. |

The poisonous properties of illuminating gas are due chiefly to carbon monoxide, all other constituents being more or less harmless.

*Experiment* 53.—Use the apparatus as shown in Fig. 5, page 51. Fill the combustion-tube *A* with sawdust (almost any other non-volatile organic matter may be used), apply heat and continue it as long as gases are evolved. Notice that by this process of *destructive distillation* are formed a gas (or gas mixture), which may be ignited, a dark, almost black liquid (tar), which condenses in the tube *B*, and that a residue is left which is chiefly carbon. The tarry liquid shows an acid reaction, due to acetic and other acids present.

**Coal-tar.**—Coal-tar, obtained as a by-product in the manufacture of illuminating gas, contains, as shown by the above table, many valuable substances, such as benzene, aniline, carbolic acid, paraffin,

etc., which are separated from each other by making use of the difference in their boiling-points and specific gravities, or of their solubility or insolubility in various liquids, or, finally, of their basic, acid, or neutral properties.

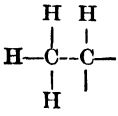
**Unsaturated Hydrocarbons.**—The terms saturated and unsaturated compounds are used for inorganic and organic substances. A compound is said to be unsaturated when it has the power to enter directly into combination with elements or compounds. Thus, carbon monoxide and phosphorus trichloride are unsaturated, as they combine directly with a number of substances; for instance, with chlorine, thus:

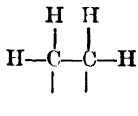
$$CO + 2Cl = COCl_2,$$
$$PCl_3 + 2Cl = PCl_5.$$

The hydrocarbons of the methane series are saturated; they cannot be made to enter directly into combination with other substances, because there are no bonds left unprovided for.

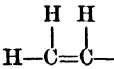
On the other hand, we have several homologous series of hydrocarbons which are unsaturated. The olefins belong to this kind, and the reason is found in the structure of the molecules.

Looking at the graphic formulas of the normal hydrocarbons of the methane series on page 433, we find all affinities completely saturated. The structure of ethylene, $C_2H_4$, the first member of the olefines, may be represented by either of the following formulas:





Each of these representations shows that two bonds are left unsaturated, and as certain considerations lead us to assume that two hydrogen atoms are in combination with one carbon atom the second representation is the one agreeing with our views. Instead of leaving the affinities unsaturated in our formulas as above, we use *double linkage*, and give to ethylene the formula

 or $H_2C{=}CH_2$.

Whenever direct combination between ethylene and another substance occurs the double linkage is broken and the bonds are utilized for holding the respective atoms, or radicals, thus:

$$H_2C{=}CH_2 + 2Br = H_2C(Br)\text{–}CH_2(Br).$$

As the higher members of the ethylene series are obtained by replacement of hydrogen atoms by hydrocarbon radicals in ethylene, which replacement does not alter the double linkage of its carbon atoms, all members behave like unsaturated compounds.

In a similar manner we represent the unsaturated hydrocarbon acetylene $C_2H_2$, by the formula $HC \equiv CH$, showing triple linkage between the carbon atoms. That this view is in keeping with the facts is shown by the action of bromine or of hydrobromic acid on acetylene, thus:

$$HC \equiv CH + 4Br = Br_2HC—CHBr_2.$$
$$HC \equiv CH + 2HBr = BrH_2C—CH_2Br.$$

**Olefins.**—The hydrocarbons of the general formula $C_nH_{2n}$ are termed olefins. To this series belong:

| | |
|---|---|
| Ethylene or ethene . . . . . | $C_2H_4$. |
| Propylene or propene . . . . . | $C_3H_6$. |
| Butylene or butene . . . . . | $C_4H_8$. |
| Amylene or pentene . . . . . | $C_5H_{10}$. |
| Hexylene or hexene . . . . . | $C_6H_{12}$. |

Methene, $CH_2$, the lowest term of this series, is not known. The hydrocarbons of this series are not only homologous, but also polymeric with one another.

**Ethylene, $C_2H_4$** (*Ethene, Olefiant Gas*).—Ethylene the first member of the olefins, is of special interest on account of its normal occurrence in illuminating gas made from coal, as also in most common flames, the luminosity of which depends largely on the quantity of this compound present in the burning gas.

Besides destructive distillation there are several reactions by which ethylene can be obtained. Of these two are of interest. The first one depends on the action of an alcoholic solution of potassium hydroxide on ethyl chloride, bromide, or iodide:

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O.$$

This reaction shows the possibility of preparing an unsaturated compound of the ethylene series from a saturated hydrocarbon; and as the method is applicable to compounds of other classes it furnishes the means to pass from any saturated compound to the corresponding unsaturated compound of the ethylene series.

The second method for preparing ethylene depends on the dehydrating action of sulphuric acid on ethyl alcohol when a mixture is heated at about 175° C.

$$C_2H_5OH - H_2O = C_2H_4.$$

Ethylene combines directly with an equal volume of chlorine forming ethylene dichloride, $C_2H_4Cl_2$, an oily liquid, whence the name of olefiant gas. This action is so energetic that it must be carried out in the dark and at low temperature, otherwise other products are formed, including free carbon, as in the case of the action of chlorine on marsh-gas in sunlight. Bromine acts much less energetically and iodine unites only slowly when ethylene is passed into warm alcoholic solution of iodine. In the case of the halogen acids, the order of activity is reversed. Ethylene acts readily with a concentrated solution of hydriodic acid at 100° C., more slowly with hydrobromic acid, and not at all with hydrochloric acid.

$$C_2H_4 + HBr = C_2H_5Br,$$
$$C_2H_4 + HI = C_2H_5I.$$

Ethylene combines with concentrated sulphuric acid, forming ethyl sulphuric acid, $C_2H_5HSO_4$. This action is also shown by other unsaturated hydrocarbons.

Unlike the paraffin hydrocarbons, ethylene and its homologues are oxidized by chromic acid and other oxidizers.

**Acetylene, $C_2H_2$.**—Acetylene is the first member of a hydrocarbon series of the general composition $C_nH_{2n-2}$. It has been stated before that acetylene is formed by direct union of the elements when an electric current passes between two carbon poles in an atmosphere of hydrogen. It is also formed during the incomplete combustion of coal-gas, such as takes place when the flame of a Bunsen burner "strikes back"—*i. e.*, burns at the base of the burner.

The method now extensively used in the manufacture of acetylene for illuminating purposes depends on the decomposition of calcium carbide by water:

$$C_2Ca + H_2O = CaO + C_2H_2.$$

Pure acetylene is a gas of agreeable ethereal odor, while the gas as ordinarily prepared possesses an unpleasant odor, due to impurities. With an ordinary burner acetylene burns with a luminous but sooty flame, while by the use of specially constructed burners flames may be obtained giving a very pure, intensely luminous white light. Like ethene, it combines directly with halogens, and when heated to a sufficiently high temperature it is converted into the polymeric compounds, benzene, $C_6H_6$, and styrene, $C_8H_8$.

A characteristic property of acetylene is the readiness with which its hydrogen may be replaced by metals; thus, by treating acetylene with sodium, either *monosodium acetylid*, $C_2HNa$, or *disodium acetylid*, $C_2Na_2$, may be obtained. *Silver acetylid*, $C_2Ag_2$, a white crystalline compound, and *cuprous acetylid*, $C_2Cu_2$, a red powder, may be obtained by passing the gas through ammoniacal solutions of silver and cuprous salts, respectively. When dry, both compounds explode violently when heated, the silver compound even when rubbed with a glass rod.

## Halogen Derivatives of Hydrocarbons.

**Substitution Products.**—When a mixture of methane and chlorine is exposed to diffused daylight chemical action takes place gradually, resulting in the successive substitution of hydrogen by chlorine, thus:

$$\begin{aligned} CH_4 + 2Cl &= CH_3Cl + HCl. \\ CH_3Cl + 2Cl &= CH_2Cl_2 + HCl. \\ CH_2Cl_2 + 2Cl &= CHCl_3 + HCl. \\ CHCl_3 + 2Cl &= CCl_4 + HCl. \end{aligned}$$

These reactions between methane and chlorine are more or less characteristic of the general interaction between the halogens and hydrocarbons, most of the latter being very susceptible to the action of halogens. The 4 substitution products formed are designated respectively as *monochlor-methane* or *chlor-methane*, *dichlor-methane*,

*trichlor-methane,* and *tetrachlor-methane* or *carbon tetrachloride.* These compounds may also be looked upon as chlorides of the radicals $CH_3^{i}$, *methyl;* $CH_2^{ii}$, *methylene*; $CH^{iii}$, *methenyl;* and of carbon $C^{iiii}$. The univalent radicals such as methyl, ethyl, propyl are called *alkyl* or alcohol radicals, while the term *alkylene* designates bivalent radicals such as methylene, ethylene, propylene, etc.

A characteristic feature of these halogen derivatives is the behavior of the halogens towards such reagents as silver nitrate. Chlorine and iodine when in combination with hydrogen or metals readily form with a soluble silver salt insoluble chloride or iodide. The halogens which have replaced hydrogen in organic compounds are, as a general rule, not affected by silver salts in solution. This behavior shows that the substitution products are not dissociable —*i. e.*, there are no halogen ions present. While above a general method has been given by which the halogen compounds can be made, there are usually employed other processes for their manufacture. Also the names given above are not always those in general use. Thus, trichlor-methane or methenyl chloride is generally called chloroform and the corresponding bromine and iodine compounds bromoform and iodoform.

Of the normal monosubstitution products, the iodides are most active toward other substances, the chlorides least active; also the halides of small hydrocarbon-radicals are more active than those of larger radicals.

**Methyl Chloride, $CH_3Cl$** (*Monochlor-methane*). Methyl chloride is readily obtainable by the action of hydrochloric acid gas on methyl alcohol containing anhydrous zinc chloride as dehydrating agent.

$$CH_3OH + HCl = CH_3Cl + H_2O.$$

It is a colorless, inflammable gas which can be liquefied by pressure. This liquid which produces an intense cold by its evaporation has been used locally for neuralgia.

**Dichlor-methane, $CH_2Cl_2$** (*Methylene chloride*), is obtained by the action of nascent hydrogen on chloroform:

$$CHCl_3 + 2H = CH_2Cl_2 + HCl.$$

It is a colorless, oily liquid, boiling at 40° C. (104° F.); sp. gr. 1.344. It has an odor similar to that of chloroform, and has been employed as an anæsthetic.

**Tetrachlor-methane, $CCl_4$** (*Carbon tetrachloride*), is obtained by the action of chlorine on carbon disulphide, or by treating chloroform with iodine chloride:

$$CHCl_3 + ICl = CCl_4 + HI.$$

It is a colorless liquid possessing anæsthetic properties, but, like the previous compound, is dangerous.

By far the most important halogen derivatives of methane are the trisubstitution products: *chloroform, bromoform* and *iodoform.* The gaseous chlorine and the liquid bromine convert through their substitution the gaseous methane into colorless, heavy, volatile liquids, while the solid iodine confers the solid state upon the compound.

**Chloroform** (*Chloroform*), $CHCl_3 = 119.39$ (*Trichlor-methane*).—Chloroform is obtained by the action of bleaching-powder and calcium hydroxide on alcohol. The three substances named, after being mixed with a considerable quantity of water, are heated in a retort until distillation commences; the crude product of distillation is an impure chloroform, which is purified by mixing it with strong sulphuric acid and allowing the mixture to stand; the upper layer of chloroform is removed and treated with sodium carbonate (to remove any acids) and distilled over calcium chloride (to remove water).

A full explanation of the formation of chloroform by the above process will be given later on in connection with the consideration of chloral, where it will be shown that alcohol is converted by the action of chlorine first into aldehyde and subsequently into chloral, which, upon being treated with alkalies, is decomposed into an alkali formate and chloroform.

The action of the chlorine of the calcium hypochlorite (which is the active principle in bleaching-powder) upon the alcohol is similar to that of free chlorine upon alcohol; in both cases aldehyde, and afterward chloral, are formed, which latter, in the manufacture of chloroform, is decomposed by the calcium hydroxide into chloroform and calcium formate. The last-named salt is, however, not found in the residue of the distillation, because it is decomposed by bleaching-powder and calcium hydroxide into calcium carbonate, chloride, and water:

$$Ca(CHO_2)_2 + Ca(ClO)_2 + Ca(OH)_2 = 2CaCO_3 + CaCl_2 + 2H_2O$$

If the various intermediate steps of the decomposition are not considered, the process may be represented by the following equation:

$$\underset{\text{Alcohol.}}{4C_2H_6O} + \underset{\text{Calcium hypochlorite.}}{8Ca(ClO)_2} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\text{Calcium formate.}}{3[Ca(CHO_2)_2]} + \underset{\text{Calcium chloride.}}{5CaCl_2} + \underset{\text{Water.}}{8H_2O}.$$

Chloroform is now made extensively by the action of bleaching-powder upon acetone; the reaction takes place thus:

$$\underset{\text{Acetone.}}{2CO(CH_3)_2} + \underset{\text{Calcium hypochlorite.}}{3Ca(ClO)_2} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\text{Calcium hydroxide.}}{2Ca(OH)_2} + \underset{\text{Calcium acetate.}}{Ca(C_2H_3O_2)_2}$$

Pure chloroform is a heavy, colorless liquid, of a characteristic ethereal odor, a burning, sweet taste, and a neutral reaction; it is but very sparingly soluble in water, but miscible with alcohol and ether in all proportions; the specific gravity of pure chloroform is 1.50, but a small quantity of alcohol (from 0.5 to 1 per cent.), allowed to be present by the U. S. P., causes the specific gravity to be about 1.476, boiling-point 61° C. (141.8° F.), but rapid evaporation takes place at all temperatures.

Chloroform or its vapors do not ignite readily, but at a high temperature chloroform burns with a green flame. When kept in a partially filled bottle exposed to daylight it decomposes with the formation of the highly irritating carbonyl chloride:

$$CHCl_3 + O = COCl_2 + HCl.$$

Chloroform containing some alcohol is less apt to undergo this oxidation, but the latter also takes place when chloroform is used for inhalation near an exposed flame.

**Analytical Reactions for Chloroform.**—1. Dip a strip of paper into chloroform and ignite. The flame has a green mantle and emits vapors of hydrochloric acid, rendered more visible upon the approach of a glass rod moistened with ammonia-water.

2. Add a drop of chloroform and a drop of aniline to some alcoholic solution of potassium hydroxide and heat gently: a peculiar penetrating, offensive odor of benzo-isonitrile, $C_6H_5NC$, is noticed. (Chloral shows the same reaction.)

$$CHCl_3 + 3KOH + C_6H_5.NH_2 = C_6H_5NC + 3KCl + 3H_2O.$$

3. Add some chloroform to Fehling's solution and heat: red cuprous oxide is precipitated.

4. Vapors of chloroform, when passed through a glass tube heated to redness, are decomposed into carbon, chlorine, and hydrochloric acid. The two latter should be passed into water, and may be recognized by their action on silver nitrate (white precipitate of silver chloride) and on mucilage of starch, to which potassium iodide has been added (blue iodized starch is formed.)

5. Heat some chloroform with solution of potassium hydroxide and a little alcohol. Chloroform is decomposed into potassium chloride and formate:

$$CHCl_3 + 4KOH = 3KCl + KCHO_2 + 2H_2O.$$

Divide solution into two portions. Acidulate one portion with nitric acid, boil, and add silver nitrate: white precipitate of silver chloride. To second portion add a little ammonia-water and a crystal of silver nitrate: a mirror of metallic silver will be formed after heating slightly.

6. Add to 1 c.c. of chloroform about 0.3 gram of resorcin in solution, and 3 drops of solution of sodium hydroxide; boil strongly: a yellowish-red color is produced, and the liquid shows a beautiful yellow-green fluorescence. (Chloral shows the same reaction.)

In cases of poisoning chloroform is generally to be sought for in the lungs and blood, which are placed in a flask connected with a tube of difficultly fusible glass. By heating the flask the chloroform is expelled and decomposed in the heated glass tube, as stated above in reaction 4. Another portion of chloroform should be distilled without decomposing it, and the distillate tested as above stated.

There is no chemical antidote which may be used in cases of poisoning by chloroform, and the treatment is therefore confined to the use of the stomach-pump, to the maintenance of respiration with oxygen inhalation, and to the use of strychnine hypodermically.

**Bromoform** (*Bromoformum*), **$CHBr_3$** (*Tribrom-methane*).—Bromoform is an extremely heavy, colorless mobile liquid, with an ethereal

odor, and a penetrating, sweet taste, resembling chloroform, specific gravity 2.884; B. P. 148° C. It is sparingly soluble in water, soluble in alcohol and ether. Its physiological action is similar to that of chloroform.

Bromoform may be obtained by gradually adding bromine to a cold solution of potassium hydroxide in ethyl alcohol until the color is no longer discharged, and rectifying over calcium chloride. It is also made by the action of an alkali hypobromite on acetone.

**Iodoform** (*Iodoformum*), **$CHI_3$ = 393.77** (*Triiodo-methane*).—This compound is analogous in its constitution to chloroform and bromoform. It is made by heating together an aqueous solution of an alkali carbonate, iodine, and alcohol until the brown color of iodine has disappeared; on cooling, iodoform is deposited in yellow scales, which are well washed with water and dried between filtering paper. (For an explanation of the chemical changes taking place see Chloral and Chloroform.)

Iodoform occurs in small, lemon-yellow, lustrous crystals, having a peculiar, penetrating odor, and an unpleasant, sweetish taste; it is nearly insoluble in water and acids, soluble in alcohol, ether, fatty and essential oils. It contains 96.7 per cent. of iodine.

Iodoform digested with an alcoholic solution of potassium hydroxide imparts, after acidulation with nitric acid, a blue color to starch solution. (See reaction in Test 5 under Chloroform.)

*Experiment* 54.—Dissolve 4 grams of crystallized sodium carbonate in 6 c.c. of water: add to this solution 1 c.c. of alcohol; heat to about 70° C. (158° F.), and add gradually 1 gram of iodine. A yellow crystalline deposit of iodoform separates.

**Ethyl Chloride** (*Æthylis Chloridum*), **$C_2H_5Cl$ = 64.5** (*Chlor-ethane*).—Ethyl chloride is prepared analogously to methyl chloride by the action of hydrochloric acid gas upon absolute ethyl alcohol:

$$C_2H_5OH + HCl = C_2H_5Cl + H_2O.$$

In place of hydrochloric acid phosphorus pentachloride may be used:

$$C_2H_5OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$$

Ethyl chloride is a gas at ordinary temperature, but by pressure it is converted into a colorless, mobile, very volatile liquid which boils at 12.5° C. The compressed liquid is sold in tubes, from which it is permitted to escape through a small opening when used as a local anæsthetic. It is highly inflammable. It is known also as kelene or chelene.

**Ethyl bromide, $C_2H_5Br$** (*Brom-ethane, Hydrobromic ether*), is obtained by the same reactions as ethyl chloride, substituting bromine for chlorine. It is a colorless, heavy, volatile liquid. Specific gravity 1.473; B. P. 40° C. When inhaled it rapidly produces anæsthesia, followed by quick recovery.

*Somnoform* is said to be a mixture of 60 parts of ethyl chloride, 35 parts of methyl chloride, and 5 parts of ethyl bromide. It is used to some extent in dentistry as an anæsthetic.

**Ethyl iodide, $C_2H_5I$,** may be obtained similarly to the chlorine or bromine compound. It is a colorless liquid with the boiling-point of 72° C.

**Compounds of hydrocarbon (alkyl) radicals with other elements.** Some metals, as zinc, magnesium, cadmium, aluminum, etc., can form compounds with alkyl radicals; for example, $Zn(CH_3)_2$, $Sn(C_2H_5)_4$. Likewise, alkyl radicals can be substituted for one or more atoms of hydrogen in ammonia ($NH_3$), arsine ($AsH_3$), and phosphine ($PH_3$); for example, $NH_2.CH_3$, $AsH(CH_3)_2$, $P(CH_3)_3$. The alkyl derivatives of ammonia are treated in chapter 49. One of the arsenic compounds possesses some interest because of its use in medicine, although its employment is limited. When arsenous oxide and potassium acetate are distilled together, a heavy, horribly-smelling, poisonous, fuming oil is formed, the principal constituent of which has the composition, $[(CH_3)_2As]_2O$. The reaction is, $As_2O_3 + 4CH_3COOK = 2K_2CO_3 + 2CO_2 + [(CH_3)_2As]_2O$. Dimethyl arsine oxide is known best as *cacodyl oxide*, the word cacodyl having been adopted in allusion to the disgusting odor of the compound. It contains the univalent radical, $(CH_3)_2As$—, which acts like an atom of a univalent metal. Cacodyl itself, $(CH_3)_2As—As(CH_3)_2$, also exists. The oxide has a strong affinity for oxygen, and inflames in oxygen gas, but not in air. By oxidizing cacodyl oxide with mercuric oxide, *cacodylic acid* is formed, $(CH_3)_2AsO.OH$, which yields odorless prisms, easily soluble in water. *Sodium cacodylate*, $(CH_3)_2AsO.ONa + 3H_2O$, also called sodium dimethyl arsenate, is evidently closely related to mono-sodium arsenate. It is a white odorless powder, very soluble in water, forming needle-shaped crystals, which are hygroscopic, but otherwise very stable. The aqueous solution is alkaline to litmus, but nearly neutral to phenolphthalein. Its action is similar to that of other arsenic compounds, but it is said to be much less toxic, and also less apt to cause undesirable side-effects. It is official as *Sodii cacodylas*.

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QUESTIONS.—How do hydrocarbons occur in nature, and by what processes are they formed in nature or artificially? State the general physical and chemical properties of hydrocarbons. State the composition and properties of methane, and also the conditions under which it is formed in nature. What is coal, what are its constituents, from what is it derived, and by what process has it been formed? What is crude coal-oil, what is petroleum-benzin, and what is petrolatum? How is illuminating gas manufactured, and what are its chief constituents? Mention some of the important substances found in coal-tar. State of chloroform: composition, properties, two processes for its manufacture, and method of detection. Explain the action of chlorine on methane and name the products. How is iodoform made and what are its properties?

## 43. ALCOHOLS.

**Constitution of Alcohols.**—The old term "alcohol" originally indicated but one substance (ethyl alcohol), but it is now applied to a large group of substances which may be looked upon as being derived from hydrocarbons by replacement of one, two, or more hydrogen atoms by hydroxyl, OH. In other words, alcohols are hydrocarbon radicals in combination with hydroxyl.

If hydroxyl replaces but one atom of hydrogen in a hydrocarbon, the alcohol is termed monatomic; diatomic and triatomic alcohols are formed by replacement of two or three hydrogen atoms respectively. (Diatomic alcohols are also termed *glycols*.) As an instance of a diatomic alcohol may be mentioned ethylene alcohol, $C_2H_4(OH)_2$, while glycerin, $C_3H_5(OH)_3$, is a triatomic alcohol. Tetratomic, pentatomic, and hexatomic alcohols are also known.

It has been shown before that the higher members of the paraffin series are capable of forming a number of isomeric compounds. Running parallel to the various series of hydrocarbons (and their isomers) we have homologous series of alcohols. The isomeric alcohols also show properties different from one another, and yield different decomposition products.

Normal alcohols are those with a straight carbon chain derived from normal hydrocarbons. Alcohols are also divided, according to the linkage between the hydroxyl groups and a carbon atom, into primary, secondary, and tertiary alcohols.

A *primary* alcohol is one in which the hydroxyl group is linked to a carbon atom which is united to but one other carbon atom, or, in other words, it is one containing the univalent group, $—CH_2—OH$. For instance, ethyl alcohol, $CH_3—CH_2—OH$, represents a primary alcohol. Primary alcohols yield by oxidation aldehydes and acids.

A *secondary* alcohol is one in which the hydroxyl group is linked to a carbon atom which is joined to two other carbon atoms—*i. e.*, the hydroxyl forms a side chain and the bivalent group characteristic of secondary alcohols is $>CH—OH$. For instance, iso-propyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH—OH$. Secondary alcohols yield ketones by oxidation.

A *tertiary* alcohol is one in which the hydroxyl group is linked to a carbon atom which is joined to three other carbon atoms, or one containing the trivalent group $\begin{matrix}\diagdown\\—C—OH\\\diagup\end{matrix}$. For instance, tertiary butyl alcohol, $\begin{matrix}CH_3\diagdown\\CH_3—C—OH\\CH_3\diagup\end{matrix}$. Tertiary alcohols by oxidation yield decomposition products.

By saturating with hydrogen the three bonds in the above triatomic radical, methyl alcohol, $H_3C—OH$, is obtained. Methyl alcohol is also known as *carbinol*, and the term *carbinols* is used for the hydrocarbon derivatives of methyl alcohol; for instance, ethyl alcohol may be called methyl carbinol.

$$\begin{matrix}CH_3\diagdown\\H—C—OH.\\H\diagup\end{matrix}$$

Alcohols correspond in their composition to the hydroxides of inorganic substances; both classes of compounds containing hydroxyl, OH, which, in the case of alcohols, is in combination with radicals containing carbon and hydrogen, in the case of inorganic hydroxides with metals, as, for instance, in potassium hydroxide, KOH.

If we represent any hydrocarbon radical by R, the general formula of the alcohols will be:

| Monatomic alcohol. | Diatomic alcohol. | Triatomic alcohol. |
|---|---|---|
| $R^{i}—OH$ | $R^{ii}\begin{matrix}OH\\OH\end{matrix}$ | $R^{iii}\begin{matrix}OH\\—OH\\OH\end{matrix}$ |
| or | | |
| $R^{i}OH$ | $R^{ii}(OH)_2$ | $R^{iii}(OH)_3$ |
| corresponding to | | |
| KOH | $Ca^{ii}(OH)_2$ | $Bi^{iii}(OH)_3$. |

Of the many reactions which justify our views regarding the structure of alcohols, a few may be mentioned. We believe that hydroxyl exists in metallic hydroxides, because they can be made by the action of metals on water, and similarly, by acting with potassium on an alcohol, we obtain a potassium compound and free hydrogen:

$$K + O\begin{matrix}H\\H\end{matrix} = H + O\begin{matrix}K\\H\end{matrix},$$

$$K + O\begin{matrix}H\\CH_3\end{matrix} = H + O\begin{matrix}K\\CH_3\end{matrix}.$$

Also, when we act on a metallic hydroxide with an acid a salt is formed and water produced; the corresponding reaction takes place between alcohols and acids:

$$K.OH + HCl = KCl + H_2O,$$

$$CH_3.OH + HCl = CH_3Cl + H_2O$$

Many other reactions might be mentioned which furnish proof that each oxygen atom contained in an alcohol molecule is in combination with an atom of hydrogen—*i. e.*, that alcohols are hydroxides of hydrocarbon radicals.

**Occurrence in Nature.**—Alcohols are not found in nature in a free or uncombined state, but generally in combination with acids as compound ethers. Some plants, for instance, contain compound ethers mixed with volatile oils. The triatomic alcohol glycerin is a normal constituent of all fats or fatty oils, and is therefore found in many plants and in most animals.

**Formation of Alcohols.**—Alcohols are often produced by fermentation (ethyl alcohol from sugar), sometimes by destructive distillation (methyl alcohol from wood): they are obtained from compound ethers (which are compounds of acids and alcohols) by treating them with the

alkali hydroxides, when the acid enters into combination with the alkali, while the alcohols are liberated according to the general formula:

$$\begin{matrix} R. \\ R.CO \end{matrix}\!\!>\!O + KOH = \begin{matrix} K \\ R.CO \end{matrix}\!\!>\!O + R.OH.$$

Alcohols may be obtained artificially by various processes, as, for instance, by treating hydrocarbons with chlorine, when the chloride of a hydrocarbon residue is formed, which may be decomposed by alkali hydroxides in order to replace the chlorine by hydroxyl, when an alcohol is formed. For instance:

$$\underset{\text{Ethane.}}{C_2H_6} + 2Cl = \underset{\text{Ethyl chloride.}}{C_2H_5Cl} + HCl.$$

$$\underset{\text{Ethyl chloride.}}{C_2H_5Cl} + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Potassium chloride.}}{KCl} + \underset{\text{Ethyl alcohol.}}{C_2H_5OH}.$$

Another method by which alcohols can be obtained depends on the action of nitrous acid on amines containing radicals of the methane series. For instance:

$$\underset{\text{Ethyl amine.}}{C_2H_5NH_2} + \underset{\text{Nitrous acid.}}{NOOH} = \underset{\text{Ethyl alcohol.}}{C_2H_5OH} + 2N + H_2O.$$

**Properties of Alcohols.**—Alcohols are generally colorless, neutral liquids; some of the higher members are solids, none is gaseous at the ordinary temperature. Most alcohols are specifically lighter than water; the lower members are soluble in or mix with water in all proportions; the higher members are less soluble, and, finally, insoluble. Most alcohols are volatile without decomposition; some of the highest members, however, decompose before being volatilized.

Although alcohols are neutral substances, it is possible to replace the hydrogen of the hydroxyl by metals, as has been shown above. The oxygen of alcohols may be replaced by sulphur, when compounds are formed known as *hydrosulphides* or *mercaptans;* these bodies may be obtained by treating the chlorides of hydrocarbon radicals with potassium sulphydrate.

$$C_2H_5Cl + KSH = KCl + C_2H_5SH.$$

By replacement of the hydrogen of the hydroxyl in alcohols by alcohol radicals ethers are formed; by replacing the same hydrogen with acid radicals compound ethers are produced. Suitable oxidizing agents convert primary alcohols first into aldehydes then into acids.

**Monatomic Normal Alcohols of the General Composition $C_nH_{2n+1}$-OH or $C_nH_{2n+2}O$.**

| | | B. P. |
|---|---|---|
| Methyl alcohol . . . . . | $CH_3OH$ | 67° C. |
| Ethyl " . . . . . | $C_2H_5OH$ | 78 |
| Propyl " . . . . . | $C_3H_7OH$ | 97 |
| Butyl " . . . . . | $C_4H_9OH$ | 115 |

| | | | B. P. |
|---|---|---|---|
| Amyl | alcohol | $C_5H_{11}OH$ | 132° C. |
| Hexyl | " | $C_6H_{13}OH$ | 150 |
| Heptyl | " | $C_7H_{15}OH$ | 168 |
| Octyl | " | $C_8H_{17}OH$ | 186 |
| Nonyl | " | $C_9H_{19}OH$ | 204 |
| Cetyl | " | $C_{16}H_{33}OH$ | 50 |
| Ceryl | " | $C_{27}H_{55}OH$ | 79 |
| Melissyl | " | $C_{30}H_{61}OH$ | 85 |

Fusing-point.

**Methyl Alcohol, $CH_3OH$** (*Methyl Hydroxide, Carbinol, Wood-spirit, Wood-naphtha*).—Methyl alcohol exists in nature as methyl salicylate which is practically the sole constituent of oil of wintergreen and oil of birch. When either of these oils is boiled with a solution of sodium hydroxide, it is decomposed (saponified) into sodium salicylate and methyl alcohol, which latter can be distilled off, and from the residue salicylic acid can be precipitated by addition of an acid.

Methyl alcohol is one of the many products obtained by the destructive distillation of wood, and commercially it is made by this process. When wood is heated in retorts between 160° and 275° C. an aqueous distillate (pyroligneous acid) is formed, which consists of water, acetic acid, acetone, methyl alcohol, tar and small quantities of many other substances. Above 275° C. methane, ethane, ethylene, carbon monoxide and dioxide, and higher hydrocarbons are given off. Finally at about 450° C. a residue of charcoal remains. The methyl alcohol and acetic acid are recovered from the pyroligneous acid as described under Acetic Acid.

Pure methyl alcohol can be prepared from the impure commercial article by several methods, one of which consists in treating the alcohol with anhydrous calcium chloride, by which a crystalline compound of the composition $CaCl_2.4CH_3OH$ is obtained. This is heated to 100° C. to drive off volatile substances such as acetone, and then mixed with water and distilled. The alcohol passes over together with some water vapor, which can subsequently be removed by distillation from quick-lime. It is a colorless mobile liquid, similar in odor and taste to ordinary alcohol, boiling at 66° C., and miscible with water in all proportions. It is an excellent solvent, and burns with a pale blue flame free from soot. Impure methyl alcohol is used to dissolve shellac, in making varnish, aniline dyes, formaldehyde, etc. One of the formulas for denaturing ordinary alcohol uses crude methyl alcohol.

Crude wood-spirit, which contains many impurities, has an offensive odor, a burning taste, and is strongly poisonous. A more or less impure article is sold under the name of *Columbian spirit*, while *methylated spirit* is ordinary alcohol containing 10 per cent. of methyl alcohol.

The physiological, intoxicating and poisonous properties of methyl alcohol are similar to those of ordinary alcohol, but more pronounced. Cases of poisoning, if recovery takes place, may be followed by more or less blindness, due to atrophy of the optic nerve.

For method of detecting methyl alcohol in ethyl alcohol, see under Formaldehyde.

**Ethyl Alcohol, $C_2H_5OH$ = 46.05** (*Common Alcohol, Ethyl Hydroxide, Spirit*).—Ethyl alcohol may be obtained from ethene, $C_2H_4$, by addition of the elements of water, which may be accomplished by agitating ethene with strong sulphuric acid, when direct combination takes place and ethyl sulphuric acid is formed:

$$\underset{\text{Ethene}}{C_2H_4} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Ethyl sulphuric acid.}}{C_2H_5HSO_4}.$$

Ethyl sulphuric acid mixed with water and distilled yields sulphuric acid and ethyl alcohol:

$$C_2H_5HSO_4 + H_2O = H_2SO_4 + C_2H_5OH.$$

Ethyl alcohol may also be obtained, as already mentioned, by treating ethyl chloride with potassium hydroxide:

$$C_2H_5Cl + KOH = KCl + C_2H_5OH.$$

While the above methods for obtaining alcohol are of scientific interest, there is but one mode of manufacturing it on a large scale, namely, by the fermentation of certain kinds of sugar, especially grape-sugar or glucose, $C_6H_{12}O_6$. A diluted solution of grape-sugar under the influence of certain ferments (yeast) suffers decomposition, yielding carbon dioxide and alcohol:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} = \underset{\text{Carbon dioxide.}}{2CO_2} + \underset{\text{Ethyl alcohol.}}{2C_2H_5OH}.$$

From 94 to 96 per cent. of the sugar is decomposed, according to the above reaction, the rest forming glycerin (3 per cent.), succinic acid (0.6 per cent.), and higher alcohols designated "fusel oil."

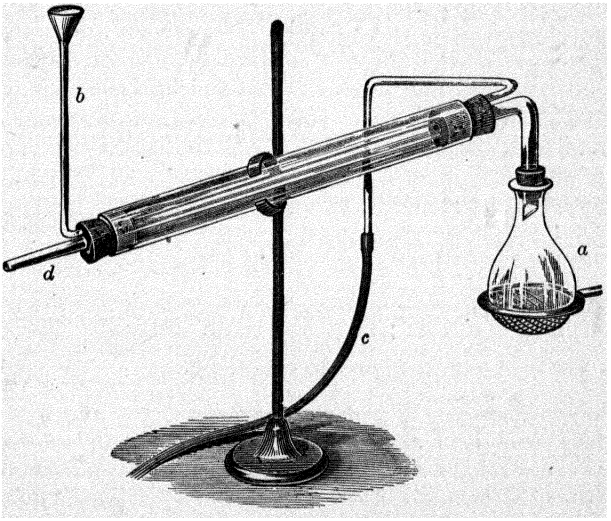
*Experiment* 55.—To a solution of 25 grams of commercial glucose (grape-sugar) in 1000 c.c. of water, add a little brewer's yeast and introduce this mixture into a flask. Attach to the flask, by means of a perforated cork, a bent glass tube leading into clear lime-water, contained in a small flask. After standing (a warm place should be selected in winter for this operation) a few hours, fermentation will commence, which can be noticed by the evolution of carbon dioxide, which, in passing through the lime-water, causes the precipitation of calcium carbonate.

After fermentation ceases connect the flask with a condenser and distil over 50 to 100 c.c. of the liquid. Verify in the distilled portion the presence of alcohol by applying the tests mentioned below. For condensation of the distilling vapors a Liebig's condenser, represented in Fig. 43, may be used.

Some alcohol is manufactured at the present time from wood (sawdust). Sawdust, water and sulphur dioxide are heated in a digester until a pressure of about 100 pounds is reached which is maintained for some time. Cellulose is converted into dextrin and sugars. The heat is cut off and sulphur dioxide recovered. The material is passed into a separator and acetic acid, formed in the digestion, is driven off by a steam jet and collected. The residue is placed in a mash tank, neutralized, mashed, fermented, and distilled.

The alcoholic strength of fermented sugar solutions is never over 14 per cent., since above this point the yeast ceases to act. On the large scale this liquid is distilled in apparatus so arranged that the vapors are repeatedly condensed and vaporized, thus yielding by a single distillation an alcohol of about 90 per cent. This is further purified by treatment with charcoal and rectifying in so-called column stills, when alcohol containing as much as 94 to 95 per cent. is obtained. To remove the last portions of water the liquid is distilled over calcium oxide, which forms calcium hydroxide. The last portions of water cannot be removed from alcohol by fractional distillation, because a 95.57 per cent. (by weight) alcohol boils constantly at 78.15° C. Water in alcohol is detected by adding some anhydrous (white) copper sulphate, which turns blue by combining with the water. The alcohol does not dissolve the salt.

FIG. 43.




Liebig's condenser with distilling-flask.

The alcohol thus obtained, and containing not more than 1 per cent. of water, is known as *pure, absolute,* or *real alcohol* (*alcohol dehydratum*). The *alcohol of the U. S. P.* contains 92.3 per cent. by weight or 94.9 per cent. by volume of real alcohol, and has a specific gravity of 0.816 at 15.6° C. (60° F.). *The diluted alcohol* is made by mixing equal volumes of water and alcohol, and has a specific gravity of 0.936; it is identical with the *proof-spirit* of the U. S. Custom-house and Internal Revenue service.

Pure alcohol is a transparent, colorless, mobile, and volatile liquid, of a characteristic, rather agreeable odor, and a burning taste; it boils at 78° C. (172° F.), has a specific gravity of 0.797, is of a neutral

reaction, becomes syrupy at —110° C. (—166° F.), and solidifies at —130° C. (—202° F.); it burns with a non-luminous flame; when mixed with water a contraction of volume occurs, and heat is liberated; the attraction of alcohol for water is so great that strong alcohol absorbs moisture from the air or abstracts it from membranes, tissues, and other similar substances immersed in it; to this property are due its coagulating action on albumin and its preservative action on animal substances. The solvent powers of alcohol are very extensive, both for inorganic and organic substances; of the latter it readily dissolves essential oils, resins, alkaloids, and many other bodies, for which reason it is used in the manufacture of the numerous official tinctures, extracts, and fluidextracts.

The alcohol in a moderately dilute solution separates as a layer on the surface when the solution is saturated with potassium carbonate or citrate. The separated alcohol contains about 9 per cent. of water.

Alcohol taken internally in a dilute form has intoxicating properties; pure alcohol acts poisonously; it lowers the temperature of the body from 0.5° to 2° C. (0.9° to 3.6° F.), although the sensation of warmth is experienced. Alcohol is not a food in the ordinary sense of the word. Small quantities of diluted alcohol are oxidized in the system to carbon dioxide and water; larger amounts are eliminated, for the most part unchanged, by the lungs and kidneys.

The treatment of acute alcohol poisoning is chiefly restricted to the evacuation of the stomach, warm applications to the extremities, and possibly hypodermic injections of strychnine to sustain the heart.

**Denatured alcohol.** Alcohol may be withdrawn from bond without the payment of internal revenue tax for use in the arts and industries, and for fuel, light, and power, provided said alcohol shall have been mixed, under certain prescribed regulations, with specified denaturing material, whereby it is rendered unfit for beverage or medicinal purposes.

Completely denatured alcohol must contain either methyl alcohol and benzin, or methyl alcohol and pyridine bases. Tax-free alcohol may also be used for manufacturing chemicals, where the alcohol is changed into some other chemical substance and does not appear in the finished product as alcohol, Inasmuch as the agents present in completely denatured alcohol render it unfit for use in many chemical industries, special denaturants have been authorized by the Commissioner of Internal Revenue where absolutely necessary. About thirty special denaturing formulas are in use at the present time.

Hospitals are allowed to denature alcohol with substances which render it unfit as a beverage, but not for external use. For this purpose such substances as camphor, thymol, boric acid, etc., may be used.

For a full account of the subject of denatured alcohol, and the various formulas for this purpose, see the article on Alcohol in the *National Standard Dispensatory.*

**Analytical Reactions for Ethyl Alcohol.**—1. Dissolve a small crystal of iodine in about 2 c.c. of alcohol; add to the cold solution potassium

hydroxide until the brown color of the solution disappears; a yellow precipitate of iodoform, $CHI_3$, forms. Many other alcohols, aldehyde, acetone, etc., show the same reaction.

2. Add to about 1 c.c. of alcohol the same volume of sulphuric acid; heat to boiling and add gradually a little more alcohol: the odor of ethyl ether will be noticed distinctly on further heating.

3. Add to a mixture of equal volumes of alcohol and sulphuric acid, a crystal (or strong solution) of sodium acetate: acetic ether is formed and recognized by its odor.

4. To about 2 c.c. of potassium dichromate solution add 0.5 c.c. of sulphuric acid and 1 c.c. of alcohol: upon heating gently the liquid becomes green from the formation of chromic sulphate, while aldehyde is formed and may be recognized by its odor.

**Alcoholic Liquors.**—Numerous substances containing sugar or starch (which may be converted into sugar) are used in the manufacture of the various alcoholic liquors, all of which contain more or less of ethyl alcohol, besides coloring matter, ethers, compound ethers, and many other substances.

*White* and *red wines* are obtained by the fermentation of the grape-juice; the so-called *light wines* contain from 10 to 12, the *strong wines*, such as *port* and *sherry*, from 19 to 25 per cent. of alcohol; if the grapes contain much sugar, only a portion of it is converted into alcohol, while another portion is left undecomposed; such wines are known as *sweet wines*. *Effervescent wines*, as champagne, are bottled before the fermentation is complete; the carbonic acid is disengaged under pressure and retained in solution in the liquid.

*Beer* is prepared by fermentation of germinated grain (generally barley) to which much water and some hops have been added; the active principle of hops is *lupulin*, which confers on the beer a pleasant, bitter flavor, and the property of keeping without injury. *Light beers* have from 2 to 4, *strong beers*, as *porter* or *stout*, from 4 to 6 per cent. of alcohol.

*Spirits* differ from either wines or beers in so far as the latter are not distilled, and therefore contain also non-volatile organic and inorganic substances, such as salts, etc., not found in the spirits, which are distilled liquids containing volatile compounds only. Moreover, the quantity of alcohol in spirits is very much larger, and varies from 45 to 55 per cent. Of distilled spirits may be mentioned: *American whiskey*, made from fermented rye or Indian corn; *Irish whiskey*, from potatoes; *Scotch whiskey*, from barley; *brandy* or *cognac*, by distilling French wines; *rum*, by fermenting and distilling molasses; *gin*, from various grains flavored with juniper berries.

**Amyl alcohol, $C_5H_{11}OH$.** Theoretically eight amyl alcohols are possible, and all are known.. The common amyl alcohol is iso-butyl-carbinol, $(CH_3)_2$-$CH.CH_2.CH_2OH$. It is frequently formed in small quantities during the fermentation of corn, potatoes, and other substances. When the alcoholic liquors are distilled, amyl alcohol passes over toward the end of the distillation, generally accompanied by propyl, butyl, and other alcohols, and by certain ethers and compound ethers. A mixture of these substances is known as *fusel oil*, and from this liquid amyl alcohol may be obtained in a pure state. It is an oily, colorless liquid, having a peculiar odor and a burning, acrid taste; it is soluble in alcohol, but not in water. By oxidation of amyl alcohol valerianic acid is obtained.

*Amylene hydrate, Ethyl-dimethyl-carbinol,* $(CH_3)_2.COH.C_2H_5$, is an alcohol isomeric with the above amyl alcohol, but yielding only acetic acid on oxidation. It is a colorless liquid, having a pungent, ethereal odor, and a boiling-point of 100° C. (212° F.). It has been used as an hypnotic.

**Allyl alcohol,** $C_3H_5OH$, is an unsaturated monatomic alcohol which can be obtained from glycerin by several reactions. It is most readily obtained by distilling a mixture of glycerin and oxalic acid between 220° and 230° C., when allyl alcohol, $CH_2 = CH - CH_2OH$, passes over. When glycerin is treated with iodide of phosphorus, allyl iodide, $CH_2 = CH.CH_2I$, is obtained. This reacts with silver hydroxide, forming silver iodide and allyl alcohol. Allyl iodide is employed in the artificial preparation of oil of mustard, or allyl iso-sulpho-cyanate, and oil of garlic, or allyl sulphide. These products are found in nature and are salts of allyl alcohol.

By oxidation with potassium permanganate allyl alcohol is reconverted into glycerin.

Allyl alcohol is a colorless liquid possessing a disagreeable penetrating odor. It is soluble in water in all proportions; B. P. 96.5° C.

**Glycerin** (*Glycerinum*), $C_3H_5(OH)_3 = 92.06$ (*Glycerol*).—This is a triatomic alcohol, in which three OH groups have replaced three hydrogen atoms in propane, $CH_3.CH_2.CH_3$. Synthetic methods have shown the glycerin to be $CH_2OH.CHOH.CH_2OH$.

It is a rather odd and interesting fact that, with very few exceptions, organic molecules do not exist in which there are more than one hydroxyl group attached to the same carbon atom. Attempts made to prepare compounds having the group $= C\begin{matrix}OH\\OH\end{matrix}$ result in failure, for water splits off from the hydroxyl groups, leaving the radical $= CO$, which is called the carbonyl group. This behavior reminds one of what takes place when it is attempted to obtain anhydrous carbonic or chromic acid. These do not exist because water is immediately split off, thus, $O = C\begin{matrix}OH\\OH\end{matrix} = CO_2 + H_2O$. As a result of this tendency to split off water, the simplest diatomic alcohol is found to be $\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$ and not $CH_2(OH)_2$, and the simplest triatomic alcohol $CH_2OH—CHOH—CH_2OH$ and not $CH(OH)_3$. In other words, the polyatomic alcohols contain at least as many carbon atoms in the molecule as there are hydroxyl groups in it.

Glycerin is a normal constituent of all fats, which are glycerin, in which the three atoms of hydrogen of the hydroxyl have been replaced by radicals of fat acids. It is obtained as a by-product in the manufacture of soap, but it is also largely manufactured by passing steam under 120 to 150 pounds pressure into fats contained in large copper digesters. By this treatment the fats are decomposed into glycerin, which remains dissolved in the water; non-volatile

fatty acids, floating on the surface of the solution; and volatile fatty acids, which escape with the steam. The aqueous solution of glycerin is first concentrated by evaporation, and then treated with superheated steam, with which glycerin volatilizes and is condensed in suitably constructed vessels.

Pure glycerin is a clear, colorless, odorless liquid of a syrupy consistence, smooth to the touch, hygroscopic, very sweet, and neutral in reaction, soluble in water and alcohol in all proportions, but insoluble in ether, chloroform, benzol, and fixed oils; its specific gravity is 1.246 at 25° C.; it cannot be distilled by itself without decomposition, but is volatilized in the presence of water or when steam is passed through it.

Glycerin is a good solvent for a large number of organic and inorganic substances; the solutions thereby obtained are often termed *glycerites;* official are the glycerites of starch, carbolic acid, and a few others.

*Boroglycerin* is made by heating a mixture of boric acid and glycerin, when an ester of the composition $C_3H_5BO_3$ is obtained. It is used as a mild antiseptic agent.

**Analytical Reactions.**—1. A borax bead immersed for a few minutes in a solution of glycerin (made slightly alkaline with potassium hydroxide) imparts a green color to a non-luminous flame, owing to the liberation of boric acid.

2. Glycerin slightly warmed with an equal volume of sulphuric acid should not turn dark, but, on further heating, the characteristic, irritating odor of acrolein is noticed.

**Glycerin Trinitrate, $C_3H_5(NO_3)_3$** (*Nitro-glycerin, Glonoin*).—When glycerin is treated with nitric acid, or, better, with a mixture of concentrated sulphuric and nitric acids, chemical action takes place resulting in the formation of glyceryl mono-nitrate, or tri-nitrate, substances belonging to the group of compound ethers the constitution of which will be explained later.

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O.$$

The trinitro-glycerin is the common nitro-glycerin, a pale yellow, oily liquid, which is nearly insoluble in water, soluble in alcohol, crystallizes at —20° C. (—4° F.) in long needles, and explodes very violently by concussion; it may be burned in an open vessel, but explodes when heated over 180° C. (356° F.).

**Spirit of Glyceryl Trinitrate** (*Spiritus glycerylis nitratis; Spirit of glonoin*).—Spirit of glyceryl trinitrate is an alcoholic solution of nitro-glycerin, containing 1 per cent. of this substance.

**Dynamite.**—One kilogram of nitro-glycerin yields after explosion 713 liters of gas, measured at normal temperature and pressure. As the gas temperature is raised by explosion to about 7000° C. (13,000° F.), the volume is comparatively larger, and the explosive power of nitro-glycerin compared with that of gunpowder is about 13 to 1. Indeed, the explosions of pure nitro-glycerin are so violent that it is generally mixed with inert substances, such as clay, sawdust,

infusorial (diatomaceous) earth, etc. When mixed with the latter it forms the extensively used dynamite, which is more useful and less dangerous to handle than pure nitro-glycerin. While it is not readily exploded by pressure or jar, it is by percussion; for instance, by fulminating mercury explosion.

Mixtures of nitro-glycerin and gun-cotton form *explosive gelatine*, or *gelatine-dynamite.*

**Glycerophosphoric Acid, $C_3H_5(OH)_2O.PO(OH)_2$.**—Compounds of this acid are met with in blood, flesh, the brain, and the nerves. It also occurs together with cholin, as a result of the splitting up of lecithin.

The absolute acid is very unstable, decomposing easily into glycerin and phosphoric acid. The commercial article is a 20 per cent. aqueous solution. It is obtained by dissolving gradually glacial phosphoric acid in an equal weight of 95 per cent. glycerin with moderate heat, and subsequently heating the mixture for several hours at 110° C. Union takes place thus:

$$C_3H_5(OH)_3 + HPO_3 = C_3H_5(OH)_2O.PO(OH)_2.$$

The tenacious mass is dissolved in water, neutralized with milk of lime, and filtered. The excess of lime is precipitated by a current of carbon dioxide and filtered off. The filtrate is concentrated in a vacuum and precipitated with alcohol or evaporated to dryness. The calcium salt is washed with alcohol to remove glycerin, dissolved in water, and decomposed with a calculated amount of diluted sulphuric acid. (The filtrate is evaporated to the proper concentration.)

Glycerophosphoric acid is a clear, colorless liquid which gradually turns yellow, and decomposes slowly in the cold, more rapidly when heated. It is a dibasic acid of decidedly acid taste and reaction. The normal salts are soluble in water, but insoluble in alcohol, and generally have an alkaline reaction. The usual reagents for phosphoric acid do not affect the solution of glycerophosphoric acid in the cold. The calcium, potassium, sodium, lithium, iron, and quinine salts of the acid have been introduced into medicine.

**Calcium Glycerophosphate** (*Calcii Glycerophosphas*), $C_3H_5(OH)_2CaPO_4.H_2O$, is a white crystalline powder, soluble in 50 parts of water, but less soluble in hot water. It is odorless and practically tasteless, somewhat hygroscopic, alkaline to litmus and phenolphthalein, and above 170° C. decomposes with evolution of inflammable vapors. It loses its water of crystallization at 130° C.

**Sodium Glycerophosphate** (*Sodii Glycerophosphas*), $C_3H_5(OH)_2.Na_2PO_4 + H_2O$, occurs as white plates or scales, or as a white powder. It is odorless, very soluble in water, alkaline to litmus and phenolphthalein. In most respects it is like the calcium salt. *Liquor sodii glycerophosphatis* is a solution containing 50 per cent. of the anhydrous salt.

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QUESTIONS.—What is the general constitution of alcohols, and what is the difference between monatomic, diatomic, and triatomic alcohols? How do alcohols occur in nature? By what processes may alcohols be formed artificially,

## 44. ALDEHYDES. KETONES.

### Aldehydes.

The name aldehyde is derived from alcohol dehydrogenatum, referring to its method of formation, viz., by the removal of hydrogen from alcohols, as, for instance:

$$C_2H_6O - 2H = C_2H_4O.$$

Ethyl alcohol. Acetic aldehyde.

This removal of hydrogen may be accomplished by various methods, as, for instance, by oxidation of alcohols, when one atom of oxygen combines with two atoms of hydrogen, forming water, while an aldehyde is formed at the same time. Aldehydes, when further oxidized, are converted into acids; aldehydes are, consequently, the intermediate products between alcohols and acids, and are frequently looked upon as the hydrides of the acid radicals. The constitution of acetic acid may be represented by the formula $CH_3.CO.OH$; the radical of acetic acid or acetyl is the group $CH_3.CO$, and the hydride of acetyl is acetic aldehyde, $CH_3.C\diagup\!\!\!\diagdown^{H}_{O}$. It is the group $-C\diagup\!\!\!\diagdown^{H}_{O}$ which is characteristic of, and found in, all aldehydes. Only a few aldehydes are of practical interest, as, for instance, formaldehyde, acetic aldehyde, paraldehyde, and benzoic aldehyde.

It has been stated that the saturated hydrocarbons are unaffected by oxidizing agents. But when once a hydrogen atom in the molecule has been replaced by another atom or group of atoms, particularly the (OH) radical, the resulting compounds are more readily oxidized. The point of attack in the oxidation of alcohols is the hydrogen united with the carbon atom to which the (OH) group is attached. Although, by a comparison of the formulas, aldehydes seem to be derived from alcohols by removal of 2 atoms of hydrogen from the molecule, the formation of the aldehydes is really more complex. Just as the oxidation of a hydrogen atom in a hydrocarbon to hydroxyl gives rise to an alcohol, so the oxidation of a second hydrogen atom to hydroxyl would theoretically give rise to a diatomic alcohol, thus:

$$R.CH_2OH + O = R.CH(OH)_2.$$

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and how may they be separated from their combinations? State the general properties of alcohols. Mention names and composition of the first five members of alcohols of the general composition $C_nH_{2n+1}OH$. By what process is methyl alcohol obtained, under what other names is it known, and what are its properties? Describe the manufacture of pure alcohol from sugar. Give the alcoholic strength of the alcohol and diluted alcohol of the U. S. P., and also of spirit of wine, proof-spirit, light wines, heavy wines, beers, and spirits. What are the general properties of common alcohol? How is alcohol denatured? What is glycerin, how is it found in nature, how is it obtained, and what are its properties.

But such compounds with two (OH) groups attached to the same carbon atom do not exist, a molecule of water being split off, thus:

$$R.CH(OH)_2 = R.C\begin{matrix}H\\O\end{matrix} + H_2O.$$

It will be seen that oxidation of primary alcohols gives rise to compounds containing the group $-C\begin{matrix}H\\O\end{matrix}$ which are called aldehydes, whereas secondary alcohols give rise to compounds of the type R.CO.R, thus:

$$R.CHOH.R + O = R.C(OH)_2.R = R.CO.R + H_2O.$$

Compounds of this type are called *ketones*. They evidently are closely related to aldehydes, being considered derivatives of aldehydes by replacement of the hydrogen atom in the $-C\begin{matrix}H\\O\end{matrix}$ group by hydrocarbon radical. The relationship is like that between methyl alcohol and the other alcohols, thus:

$$H.CH_2OH \text{ and } R.CH_2OH.$$

Ketones behave in some respects like aldehydes, which is only to be expected. Because of the hydrogen atom in the $-C\begin{matrix}H\\O\end{matrix}$ group, which can be oxidized to hydroxyl, aldehydes act as reducing agents, whereas ketones do not. The presence of the $>C = O$ group, which contains a double bond, is responsible for the fact that both aldehydes and ketones act like unsaturated compounds and have the property of combining directly with certain substances, for example hydrocyanic acid, acid sodium sulphite, etc.

$$R.C\begin{matrix}H\\O\end{matrix} + HCN = R.CH\begin{matrix}OH\\CN.\end{matrix}$$

$$R.C=O.R + NaHSO_3 = \begin{matrix}R\\R\end{matrix}>C\begin{matrix}OH\\SO_3Na.\end{matrix}$$

Aldehydes are named with respect to the acids formed by their oxidation. Thus, $CH_3.C\begin{matrix}H\\O\end{matrix}$ is called acetaldehyde because it forms acetic acid, $CH_3.COOH$, by oxidation. Ketones are named with respect to the radicals combined with the carbonyl group, $= C = O$. Thus, $CH_3.CO.CH_3$ is called dimethyl ketone, and $CH_3.CO.C_2H_5$, methyl-ethyl ketone.

**Formic Aldehyde, $CH_2O$ or $H.C\begin{matrix}H\\O\end{matrix}$** (*Formaldehyde, Methyl Aldehyde*).—This is obtained by the dry distillation of calcium formate, or by gentle oxidation of methyl alcohol. The latter process is carried out by passing vapors of methyl alcohol with air over a

heated spiral of platinum or copper. The condensed vapors are formaldehyde dissolved in undecomposed methyl alcohol.

Formaldehyde is a colorless gas, possessing a strong, penetrating odor; it may be condensed to a liquid which boils at −20° C. (−4° F.).

**Solution of Formaldehyde** (*Liquor Formaldehydi*).—Formaldehyde is readily soluble in water, and a solution containing 37 per cent. by weight is official. It is a colorless liquid which has a pungent odor and caustic taste; its vapors act as an irritant upon the mucous membrane. Sometimes on standing, always on slow evaporation, white, solid paraformaldehyde separates. With ammonio-silver nitrate the solution gives a precipitate of metallic silver. The solution is a strong antiseptic, and when diluted to 4 or 5 per cent. it is one of the best hardening and preserving agents for tissues. It is known in trade as *formalin*.

In the presence of dilute alkali, formaldehyde is oxidized quantitatively by hydrogen dioxide to formate according to this reaction:

$$2CH_2O + H_2O_2 + 2NaOH = 2HCOONa + 2H_2O + 2H.$$

on which is based the official assay of solution of formaldehyde.

In general, one molecule of an aldehyde unites directly with one molecule of ammonia, but formaldehyde is a marked exception in its action. Six molecules unite with four molecules of ammonia, with elimination of water, thus,

$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

This product is official under the name hexamethylenamine.

Aldehydes in general are polymerized to so-called aldehyde resin when treated with alkali solutions, but formaldehyde again is an exception in its behavior, for in the presence of alkali in aqueous solution, it reacts with water, giving methyl alcohol and formic acid,

$$2CH_2O + H_2O = CH_3OH + H.COOH.$$

Formaldehyde shows a marked tendency to react with other substances and a number of very delicate tests have been devised for the detection of small quantities. One of these is employed in the U. S. P. as the basis for *the detection of methyl alcohol in common alcohol*, which is carried out as follows: The alcohol is diluted with distilled water until it contains about 10 per cent. by volume of alcohol. To 5 c.c. of this dilution are added 2 c.c. of a 3 per cent. solution of potassium permanganate and 2 or 3 drops of concentrated sulphuric acid. After five minutes sulphurous acid is added drop by drop until the precipitate of manganese dioxide is dissolved, then 1 c.c. of concentrated sulphuric acid and 5 c.c. of fuchsin-sulphurous acid (Schiff's) reagent (see U. S. P.). A colorless liquid after standing ten minutes means that no noteworthy amount of methyl alcohol was present. If present in appreciable quantity, the formaldehyde formed by oxidation will produce a purplish-red color with the fuchsin reagent.

The presence of formaldehyde as a preservative in milk may be detected as follows: Float a mixture of 5 c.c. of milk and 5 c.c. of water on the surface

of 5 c.c. of concentrated sulphuric acid made very pale yellow with tincture of ferric chloride. The development after a time of a blue to violet color at the junction between the two liquids shows the presence of formaldehyde. Pure milk gives a pale greenish color.

**Paraformaldehyde** (*Paraformaldehydum*) **($CH_2O)_3 = 90.05$** (*Paraform, trioxymethylene*).—On slow evaporation of a solution of formaldehyde in methyl alcohol polymerization takes place, and paraformaldehyde separates in colorless crystals which are slowly soluble in cold water, more readily in hot water with formation of formaldehyde, insoluble in alcohol or ether, but soluble in caustic alkalies. On heating the compound, which is now found on the market in the form of tablets, it splits up into formaldehyde, which, escaping as a gas, is used for disinfecting purposes. It acts powerfully on all germs, and has the advantage over chlorine and sulphur dioxide that it does not act injuriously on the fabric or color of household goods.

Formaldehyde gas is now very generally used for disinfecting rooms, etc., and has practically displaced the method of burning sulphur to obtain sulphur dioxide. The simplest method of filling a closed space with the gas is to pour the commercial solution of formaldehyde upon small crystals of potassium permanganate, contained in a spacious metallic vessel. A vigorous reaction takes place, with destruction of a portion of the formaldehyde, approximately according to this reaction:

$$4KMnO_4 + 3HCOH + H_2O = 4MnO(OH)_2 + 2K_2CO_3 + CO_2.$$

The great heat produced causes nearly all the remaining solution to vaporize and fill the space with formaldehyde gas and water vapor, which latter is an essential factor in the disinfection. The temperature of the room should be not less than 10° C. (50° F.), but a higher temperature is better. The proportions adopted by some Boards of Health are 500 c.c. of formaldehyde solution and 237 grams of potassium permanganate per 1000 cubic feet of space. It is well known that formaldehyde is mainly a surface disinfectant, having very little power to penetrate objects, as clothing, etc.

The formaldehyde odor clinging for days to rooms which have been disinfected by it may be quickly removed by evaporation of some ammonia water, hexamethylenamine $(CH_2)_6N_4$, being formed.

**Acetic Aldehyde, $C_2H_4O$ or $CH_3.C\langle^{H}_{O}$** (*Ethyl Aldehyde*).—Alcohol may be converted into aldehyde by the action of various oxidizing agents; the one generally used is potassium dichromate in the presence of sulphuric acid, which oxidizes two hydrogen atoms of the alcohol molecule, converting it into aldehyde:

$$C_2H_6O + O = C_2H_4O + H_2O.$$

*Experiment* 56.—Place in a 500 c.c. flask, provided with a funnel-tube and connected with a Liebig's condenser, 6 grams of potassium dichromate. Pour upon this salt through the funnel-tube, very slowly, a previously prepared and cooled mixture of 5 c.c. of sulphuric acid, 24 c.c. of water and 6 c.c. of alcohol. Chemical action begins generally without application of heat, and often becomes

so violent that the liquid boils up, for which reason a large flask is used. The escaping vapors, which are a mixture of aldehyde, alcohol, and water, are collected in a receiver kept cold by ice. From this mixture pure aldehyde may be obtained by repeated distillation. Use the distillate for silvering a test-tube by adding some ammoniated silver nitrate. How much potassium dichromate is needed for the conversion of 5 grams of pure alcohol into aldehyde?

Aldehyde is a neutral, colorless liquid, having a strong and characteristic odor; it mixes with water and alcohol in all proportions and boils at 21° C. (69.8° F.). The most characteristic chemical property of aldehyde is its tendency to combine *directly* with a great number of substances; thus it combines with hydrogen to form alcohol, with oxygen to form acetic acid, with ammonia to form *aldehyde-ammonia*, $C_2H_4O.NH_3$, a beautifully crystallizing substance, with hydrocyanic acid to form *aldehyde hydrocyanide*, $C_2H_4O.HCN$, with acid sulphites and with many other substances. In the absence of such other substance it unites often with itself, forming polymeric modifications, such as paraldehyde and metaldehyde.

Aldehyde is a strong reducing agent, which property is used in the silvering of glass, which is done by adding aldehyde to an ammoniacal solution of silver nitrate, when metallic silver is deposited on the walls of the vessel or upon substances immersed in the solution.

**Paraldehyde, $C_6H_{12}O_3$.**—When a few drops of concentrated sulphuric acid are added to aldehyde, this becomes hot and solidifies on cooling to 0° C. (32° F.). This solid crystalline mass of paraldehyde, which liquefies at 10.5° C. (51° F.), has been formed by the direct union of three molecules of common aldehyde. Paraldehyde is soluble in 8.5 parts of water, boils at 124° C. (253° F.), and is reconverted into common aldehyde by boiling it with dilute sulphuric or hydrochloric acid. It is official as *Paraldehydum* and a hypnotic.

*Metaldehyde* $(C_2H_4O)_3$ is stereo-isomeric with paraldehyde; it is obtained by a process similar to the one mentioned for paraldehyde, but at a lower temperature. It is a solid crystalline substance, insoluble in water, but slightly soluble in alcohol, ether, and chloroform.

**Trichloraldehyde, Chloral, $C_2HCl_3O$ or $CCl_3.C\langle^{H}_{O}$** (*Trichloracetyl Hydride*).—This substance may be looked upon as acetic aldehyde, $C_2H_4O$, in which three atoms of hydrogen have been replaced by chlorine. It is made by passing a rapid stream of dry chlorine into pure alcohol to saturation, keeping the alcohol cool during the first few hours, and warming it gradually until the boiling-point is reached. According to the quantity of alcohol operated on, the conversion requires several hours or even days. The crude liquid product separates into two layers; the lower is removed and shaken with three times its volume of strong sulphuric acid and distilled, the distillate is mixed with calcium oxide and again distilled; the portion passing over between 94° and 99° C. (201° and 210° F.) is collected.

The decomposition taking place between alcohol and chlorine may be explained by the formation of aldehyde:

$$C_2H_6O + 2Cl = C_2H_4O + 2HCl,$$

and by the subsequent replacement of hydrogen by chlorine:

$$C_2H_4O + 6Cl = CCl_3.CHO + 3HCl.$$

The actual decomposition is, however, somewhat more complicated, numerous intermediate bodies and other decomposition products being formed at the same time.

Chloral is a colorless, oily liquid, having a penetrating odor and an acrid, caustic taste; its specific gravity is 1.5, and its B. P. 95° C. (202° F.).

**Hydrated Chloral** (*Chloralum Hydratum*), $\mathbf{CCl_3.CH(OH)_2 = 166.4}$.—When water is added to chloral the two substances combine, heat is disengaged, and the hydrate of chloral is formed, which is a crystalline, colorless substance, having an aromatic, penetrating odor, a bitter, caustic taste, and a neutral reaction; it is freely soluble in water, alcohol, and ether, also soluble in chloroform, carbon disulphide, benzene, fatty and essential oils, etc.; it liquefies when mixed with carbolic acid or with camphor; it melts at 58° C. (136° F.), and boils at 95° C. (203° F.), and also volatilizes slowly at ordinary temperature.

Chloral, and its hydrate, are decomposed by weak alkalies into chloroform and a formate of the alkali metal:

| $CCl_3.CHO$ | + | $KHO$ | = | $KCHO_2$ | + | $CHCl_3$ |
|---|---|---|---|---|---|---|
| Chloral. | | Potassium hydroxide | | Potassium formate | | Chloroform. |

This decomposition was believed to take place in the animal body, and especially in the blood, whenever chloral was given internally, but recent investigations seem to contradict this assumption. There is no chemical antidote which may be used in cases of poisoning by chloral, and the treatment is therefore confined to the use of the stomach-pump and to the maintenance of respiration.

**Analytical Reactions for Chloral.**—1. Chloral or hydrated chloral heated with potassium hydroxide is converted into potassium formate and chloroform, which latter may be recognized by its odor. (See explanation above.)

2. Heated with silver nitrate and ammonium hydroxide a silver mirror is formed on the glass.

3. Heated with Fehling's solution a red precipitate is formed.

See also reactions 2 and 6 for chloroform.

**Acrylic Aldehyde, $\mathbf{CH_2 = CH.C\langle^{H}_{O}}$** (*Acrolein*).—Acrylic aldehyde may be obtained by the careful oxidation of allyl alcohol, or by the dehydrating action of potassium acid sulphate on glycerin:

$$C_3H_8O_3 - 2H_2O = C_3H_4O.$$

It is also formed by the destructive distillation of glycerin, which is a constituent of fats. Hence, acrolein is formed when fats are heated to a point of decomposition, and its presence is noticed by the peculiar penetrating odor.

Acrolein is a highly volatile liquid, boiling at 52.4° C. It has a characteristic, penetrating odor and its vapors act on the eyes, causing the secretion of tears. Acrolein shows in its chemical behavior its aldehydic nature. It takes up oxygen forming *acrylic acid;* combines with hydrogen forming allyl alcohol; combines directly with hydrochloric acid, ammonia, etc.

**Geranial** (*Citral*).—Geranial is another example of an aldehyde derived from an unsaturated hydrocarbon, but, unlike acrolein, it contains two double bonds. It is a constituent of some essential oils, for example, lemon, geranium, rose, etc. It is a liquid having an agreeable odor. Synthetic methods of producing the aldehyde and a study of its reactions lead to the conclusion that it has the formula, $(CH_3)_2C{:}CH.CH_2.CH_2.C(CH_3){:}CH.CHO$.

## Ketones or Acetones.

These are compounds containing the bivalent radical carbonyl, CO<, to which two hydrocarbon radicals are attached. The relation existing between carbonic acid, organic acids, aldehydes, and ketones is best shown by the following formulas, in which R stands for any hydrocarbon radical:

| $CO\begin{matrix}OH\\OH\end{matrix}$ | $CO\begin{matrix}R\\OH\end{matrix}$ | $CO\begin{matrix}R\\H\end{matrix}$ | $CO\begin{matrix}R\\R\end{matrix}$ |
|---|---|---|---|
| Carbonic acid. | Organic acid. | Aldehyde. | Ketone. |

While aldehydes are obtained by the oxidation of primary alcohols, ketones are the first product of the oxidation of secondary alcohols. For instance:

$$\underset{\text{Primary propyl alcohol.}}{C_2H_5CH_2.OH} + O = \underset{\text{Propionic aldehyde.}}{C_2H_5.COH} + H_2O.$$

$$\underset{\text{Secondary propyl alcohol.}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.OH} + O = \underset{\text{Dimethyl ketone.}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CO} + H_2O.$$

Ketones are neutral substances which resemble aldehyde in so far as they have the power to unite directly with many substances with which aldehydes combine; as, for instance, with the acid sulphites. On the other hand, while aldehydes readily take up oxygen directly and form acids, ketones are decomposed by oxidizing agents.

**Acetone** (*Acetonum*), $\mathbf{CH_3.CO.CH_3 = 58.05}$ (*Dimethyl-ketone*).—This compound is obtained by the destructive distillation of acetates (and of a number of other substances). The decomposition which calcium acetate suffers may be shown by the equation:

$$\underset{\text{Calcium acetate.}}{\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\!\!>\!Ca} = \underset{\text{Acetone.}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CO} + CaCO_3.$$

The acetone is freed from impurities by treatment with a solution of acid sodium sulphite, by which a crystalline addition product is formed. When the latter is heated with a solution of sodium carbonate, acetone is distilled off. It is fractionally distilled to remove water, dried over calcium chloride, and again distilled.

Acetone is a colorless liquid, boiling at 56.5° C. (133.7° F.), miscible with water, alcohol, and ether in all proportions; it has a peculiar ethereal, somewhat mint-like odor, and burns with a luminous non-sooty flame. It is an excellent solvent for resins, gums, varnishes, alkaloids, etc., and is used in the preparation of chloroform, iodoform, sulphonal, smokeless powder, etc.

In many of its chemical behaviors, actone is like aldehyde, but it shows some marked differences. It does not form a simple addition product with ammonia, but complex condensation products. It does not polymerize, but when treated with hydrochloric acid gas, two or three molecules of acetone condense with elimination of water, to form complex ketones containing double bonds. Acetone, as well as other ketones, does not reduce Fehling's solution or ammonio-silver nitrate solution, and gives a color reaction with fuchsin-sulphurous acid reagent only on long standing.

Most ketones which do not contain the simple group, $CH_3.CO—$, do not form an addition product with acid sodium sulphite.

**Methyl nonyl ketone,** $CH_3.CO.C_9H_{19}$, is the chief constituent of oil of rue.

**Chloretone,** or *Trichlor-tertiary-butyl-alcohol,* $(CH_3)_2.C\begin{matrix}OH\\CCl_3\end{matrix}$, is a condensation product of chloroform and acetone under the influence of caustic alkalies. It forms snow-white crystals with camphor-like odor and taste, very soluble in alcohol, ether, and chloroform, and freely so in glycerin, fixed and volatile oils, and acetone. It gives about a 1 per cent. solution in water, and is a stable, non-irritant, non-toxic hypnotic and local anesthetic, without effect upon the heart.

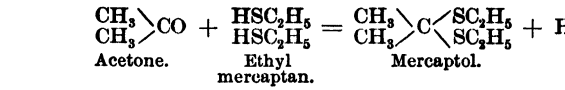
**Sulphur Derivatives.**—A comparison of such inorganic compounds as $H_2S$, $CS_2$, $NH_4SH$, with $H_2O$, $CO_2$, $NH_4OH$, shows that sulphur often replaces oxygen. Correspondingly, sulphur frequently replaces oxygen in organic compounds. When this replacement takes place in alcohols compounds are formed, called *mercaptans, sulpho-alcohols,* or *thio-alcohols;* when it takes place in aldehydes sulph-aldehydes are formed. These bodies, as a general rule, are ill-smelling compounds, some of which are the result of putrefaction in proteins.

When mercaptans are treated with oxidizing agents three atoms of oxygen are taken up and compounds are formed which are called sulphonic acids, thus:

$$\underset{\substack{\text{Ethyl}\\\text{mercaptan.}}}{C_2H_5SH} + 3O = \underset{\substack{\text{Ethyl sulphonic}\\\text{acid.}}}{C_2H_5.SO_2OH}.$$

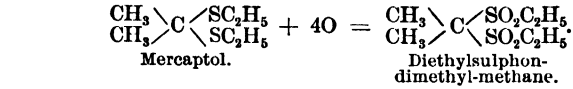
Sulphonic acids correspond to sulphorous acid in which a hydrogen atom has been replaced by a hydrocarbon radical.

Ketones form condensation products with mercaptans, thus:



Acetone. Ethyl mercaptan. Mercaptol.

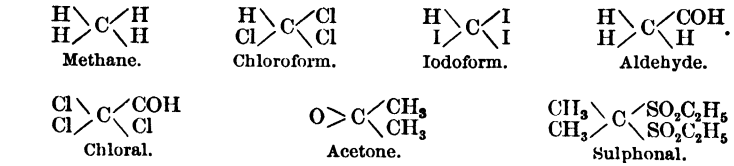
By oxidizing mercaptol with potassium permanganate it takes up oxygen (similar to mercaptans), with the result that a compound is formed containing sulphonic acid:



Mercaptol. Diethylsulphon-dimethyl-methane.

This compound is used medicinally under the name of sulphonal.

The relations between methane and some of its derivatives, which have been considered in this chapter, may be shown graphically thus:



Methane. Chloroform. Iodoform. Aldehyde.

Chloral. Acetone. Sulphonal.

**Sulphonmethane** (*Sulphonmethanum, Sulphonal*), $(CH_3)_2C(C_2H_5SO_2)_2 = 228.27$ (*Diethylsulphon-dimethyl-methane*). Sulphonal is a white crystalline substance, having neither odor nor taste; it is soluble in 15 parts of boiling and 360 parts of cold water, soluble with difficulty in alcohol; it fuses at 125.5° C. (258° F.), and volatilizes at about 300° C. (572° F.), with partial decomposition. A mixture of sulphonal with either wood charcoal or with potassium cyanide evolves, on heating, the characteristic odor of mercaptan. It is used as an hypnotic and soporific.

**Sulphonethylmethane, Trional,** $CH_3(C_2H_5)C(C_2H_5SO_2)_2$ (*Diethylsulphon-methyl-ethyl-methane*), and **Tetronal,** $(C_2H_5)_2C(C_2H_5SO_2)_2$ (*Diethylsulphon-diethyl-methane*), are both colorless solids, forming lustrous crystals, soluble in hot water and in alcohol and ether. The therapeutic action of these bodies is similar to that of sulphonal.

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QUESTIONS.—What is an aldehyde, and what are its relations to alcohols and acids? Give composition, mode of manufacture, and properties of formaldehyde. Explain the action of chlorine upon alcohol. Give the composition and properties of chloral and hydrated chloral. What decomposition takes place when alkalies act upon chloral? Under what conditions is acrolein formed and what are its properties? Give the general composition of ketones and a general method of obtaining them. How is acetone prepared? Which compounds are called mercaptans, and how are they converted into sulphonic acids? Give method for preparing sulphonal, and state its properties.

## 45. MONOBASIC FATTY ACIDS.

**General Constitution of Organic Acids.**—When hydroxyl, OH, replaces hydrogen in hydrocarbons, alcohols are formed; when the univalent group, $CO_2H$, known as *carboxyl*, replaces hydrogen in hydrocarbons, acids are formed; and all acids containing this radical are termed *carboxylic acids*. Monatomic, diatomic, and triatomic alcohols are formed by introducing hydroxyl once, twice, or three times respectively into hydrocarbon molecules; monobasic, dibasic, and tribasic acids are formed by substituting one, two, or three hydrogen atoms by carboxyl. For instance:

| *Hydrocarbons.* | *Monobasic acids.* | *Dibasic acids.* |
|---|---|---|
| $CH_4$ | $CH_3CO_2H$ | $CH_2{<}^{CO_2H}_{CO_2H}$. |
| Methane. | Acetic acid. | Malonic acid. |
| $C_2H_6$ | $C_2H_5CO_2H$ | $C_2H_4{<}^{CO_2H}_{CO_2H}$. |
| Ethane. | Propionic acid. | Succinic acid. |

As stated before, organic acids may also be considered as carbonic acid in which one of the hydroxyl groups has been replaced by a hydrocarbon radical, thus:

$CO{<}^{OH}_{OH}$ Carbonic acid.

$CO{<}^{CH_3}_{OH}$ Acetic acid

$CO{<}^{OH}_{CH_2}{>}CO{<}^{OH}$ Malonic acid.

This shows that carboxyl, $CO_2H$, is made up of hydroxyl, OH, and the bivalent radical, CO, termed *carbonyl*. By replacement of the hydrogen of the hydroxyl (or of the carboxyl, which is the same) by metals the various salts are formed.

What is termed the *acyl radical* is the group of the total number of atoms present in the molecule, with the exception of the hydroxyl. In acetic acid, $C_2H_4O_2$, for instance, the radical is $CH_3CO$, or $C_2H_3O$, which group of atoms, known as acetyl, is characteristic of acetic acid, and of all acetates, and may often be transferred from one compound into another without decomposition.

The difference between alcohol or alkyl, and acyl radicals may also be stated by saying that the first contain carbon and hydrogen only, while acyl radicals contain carbon, hydrogen and oxygen.

In a similar manner, as there are homologous series of alcohols corresponding to the various series of hydrocarbons, there are also homologous series of organic acids running parallel with the corresponding series of hydrocarbons or alcohols.

**Occurrence in Nature.**—Organic acids are found and formed both in vegetables and animals, and are present either in the free state, or (and more generally) in combination with bases as salts, or with

alcohols as compound ethers. Uncombined or as salts are found, for instance, citric, tartaric, and oxalic acids in plants, formic acid in some insects, uric acid in urine, etc.; as compound ethers are found many of the fatty acids in the various fats.

Some organic acids are also found as products of the decomposition of organic matter in nature.

**Formation of Acids.**—Many acids are produced by oxidation of alcohols. As intermediate products are formed aldehydes, which may be looked upon (as stated in the last chapter) as alcohols from which two atoms of hydrogen have been removed.

The change of a primary alcohol into an aldehyde, and of this into an acid, takes place according to the general formulas:

$$\underset{\text{Alcohol}}{R.CH_2OH} + O = R.C\begin{matrix}H\\(OH)_2\end{matrix} = \underset{\text{Aldehyde}}{R.C\begin{matrix}H\\O\end{matrix}} + H_2O,$$

$$\underset{\text{Aldehyde}}{R.C\begin{matrix}H\\O\end{matrix}} + O = \underset{\text{Acid.}}{R.C\begin{matrix}OH\\O\end{matrix}}$$

Acids are obtained from compound ethers by boiling them with alkalies, when salts are formed, which may be decomposed by sulphuric or other acids. For instance:

$$\underset{\text{Ethyl acetate}}{\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}>O} + \underset{\substack{\text{Potassium}\\\text{hydroxide}}}{KOH} = \underset{\substack{\text{Potassium}\\\text{acetate.}}}{\begin{matrix}C_2H_3O\\K\end{matrix}>O} + \underset{\text{Ethyl alcohol.}}{C_2H_5OH.}$$

$$\underset{\substack{\text{Potassium}\\\text{acetate}}}{2C_2H_3O_2K} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\text{Acetic acid}}{2C_2H_4O_2} + \underset{\substack{\text{Potassium}\\\text{sulphate}}}{K_2SO_4.}$$

Acids are formed also by destructive distillation (acetic acid); by fermentation (lactic acid), by putrefaction (butyric acid); by oxidation of many organic substances (oxalic acid by oxidation of starch), etc.

**Properties.**—Organic acids show the characteristics mentioned of inorganic acids, viz., when soluble, they have an acid or sour taste, redden litmus, and contain hydrogen replaceable by metals, with the formation of salts.

Most organic acids, and especially the higher members, show these acid properties in a less marked degree than inorganic acids; in fact, they become so weak that the acid properties can often scarcely be recognized. As stated above, mono-, di-, and tri-basic organic acids are known, the latter two being capable of forming normal, acid, or double salts.

Most organic acids are colorless, some of the lower and volatile acids have a characteristic odor, but most of them are odorless; most organic acids are solids, some liquids, scarcely any gaseous at the ordinary temperature. Any salt formed by the union of an organic acid and a non-volatile metal (especially alkali metal) leaves the carbonate

of this metal after the salt has suffered combustion. It is for this reason that ashes contain metals largely in the form of carbonates.

While the hydrogen of the hydroxyl may be replaced by metals or by other residues, the hydrogen of the acyl radical may often be replaced by chlorine, and the oxygen of the hydroxyl by sulphur. The acids formed by this last reaction are known as *thio acids*, for instance, thio-acetic acid, $C_2H_4OS$.

When the hydrogen of the hydroxyl is replaced by a second acyl radical (of the same kind as the one forming the acid) the so-called *anhydrides* are produced, which correspond to the inorganic anhydrides. For instance:

| $HNO_3$ or $NO_2.OH$ | $C_2H_4O_2$ or $C_2H_3O.OH$. |
|---|---|
| Nitric acid. | Acetic acid. |
| $\begin{matrix}NO_2\\NO_2\end{matrix}\!\!>\!O$ | $\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\!\!>\!O.$ |
| Nitric anhydride. | Acetic anhydride. |

It is evident from the above that, while acids are hydroxides of acyl radicals, the anhydrides are oxides. They are often formed by abstracting water from two molecules of an acid, thus:

$$\left.\begin{matrix}C_2H_3O.OH\\C_2H_3O.OH\end{matrix}\right\} = \begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\!\!>\!O + H_2O.$$

*Amino-acids* are compounds obtained from acids by replacement of a hydrogen atom of the acyl radical by $NH_2$; these compounds will be spoken of later in connection with amides.

**Fatty Acids of the General Composition, $C_nH_{2n}O_2$ or $C_nH_{2n+1}CO_2H$.**

| | | *Fusing-point.* | *Boiling-point.* | *Occurs in:* |
|---|---|---|---|---|
| Formic acid, | $H\,CO_2H$ | + 8°C. | 101°C. | Red ants and some plants, etc. |
| Acetic acid, | $C\,H_3\,CO_2H$ | +17 | 118 | Vegetable and animal fluids. |
| Propionic acid, | $C_2\,H_5\,CO_2H$ | −21 | 140 | Sweat, fluids of the stomach, etc. |
| Butyric acid, | $C_3\,H_7\,CO_2H$ | −20 | 162 | Butter. |
| Valeric acid, | $C_4\,H_9\,CO_2H$ | −16 | 185 | Valerian root. |
| Caproic acid, | $C_5\,H_{11}CO_2H$ | − 2 | 205 | Butter. |
| Œnanthylic acid, | $C_6\,H_{13}CO_2H$ | −10 | 224 | Castor oil. |
| Caprylic acid, | $C_7\,H_{15}CO_2H$ | +14 | 236 | Butter; cocoanut oil. |
| Pelargonic acid, | $C_8\,H_{17}CO_2H$ | 18 | 254 | Leaves of geranium. |
| Capric acid, | $C_9\,H_{19}CO_2H$ | 30 | 270 | Butter. |
| Lauric acid, | $C_{11}H_{23}CO_2H$ | 43 | ..... | Cocoanut oil. |
| Myristic acid, | $C_{13}H_{27}CO_2H$ | 54 | ..... | |
| Palmitic acid, | $C_{15}H_{31}CO_2H$ | 62 | ..... | Palm oil, butter. |
| Margaric acid, | $C_{16}H_{33}CO_2H$ | 60 | ..... | (Obtained artificially.) |
| Stearic acid, | $C_{17}H_{35}CO_2H$ | 70 | ..... | Most solid animal fats. |
| Arachidic acid, | $C_{19}H_{39}CO_2H$ | 75 | ..... | Oils of certain plants. |
| Behenic acid, | $C_{21}H_{43}CO_2H$ | 76 | ..... | |
| Hyænic acid, | $C_{24}H_{49}CO_2H$ | 77 | ..... | |
| Cerotic acid, | $C_{26}H_{53}CO_2H$ | 80 | ..... | Beeswax. |
| Melissic acid, | $C_{29}H_{59}CO_2H$ | 90 | ..... | |

The name fatty acids has been given to these acids on account of their frequent occurrence in fats, and also in allusion to the somewhat fatty appearance of the higher members of the series.

The gradual change of properties which the members of an homologous series show, is well marked in the series of fatty acids, thus:

| *First member.* | *Last member.* |
|---|---|
| Is liquid. | Is solid. |
| Volatilized at 100° C. | Not volatilized without decomposition. |
| Strongly acid. | Scarcly acid. |
| Strongly odoriferous. | Odorless. |
| Easily soluble in water. | Insoluble in water. |
| Produces no grease spot. | Produces a grease spot. |
| Forms salts easily soluble without decomposition. | Forms salts which are insoluble or decomposed by water. |

The intermediate members of the series show intermediate properties, and this change in properties is in proportion to the gradual change in molecular weight.

**Formic Acid, $H.CO_2H$ or HCO.OH.**—This acid is found in the red ant and in other insects, which eject it when irritated. It is also contained in some plants, as, for instance, in the leaves of the stinging nettle.

It is formed by the oxidation of methyl alcohol:

$$\underset{\text{Methyl alcohol.}}{CH_4O} + O_2 = \underset{\text{Formic acid.}}{CH_2O_2} + H_2O,$$

by the action of carbonic oxide on potassium hydroxide under heat and pressure:

$$KOH + CO = \underset{\text{Potassium formate.}}{KCHO_2},$$

by the action of potassium hydroxide on chloroform:

$$CHCl_3 + 4KOH = 3KCl + 2H_2O + KCHO_2,$$

by the action of potassium on moist carbon dioxide:

$$2CO_2 + H_2O + 2K = KHCO_3 + KCHO_2,$$

by heating equal parts of glycerin and oxalic acid, when the latter is split up into carbon dioxide and formic acid, which may be separated from the glycerin by distillation:

$$\underset{\text{Oxalic acid}}{C_2H_2O_4} = CO_2 + \underset{\text{Formic acid}}{CH_2O_2}.$$

It is also a product of the decomposition of sugar, starch, etc. Formic acid is a colorless liquid having a penetrating odor, and a strongly acid taste; it produces blisters on the skin; it is a powerful deoxidizer, being, when thus acting, converted into carbon dioxide and water:

$$CH_2O_2 + O = CO_2 + H_2O.$$

When pure, formic acid melts at 8.5° C., boils at 101° C., and at 0° C. has the specific gravity 1.241. An aqueous solution containing 77.5 per cent. of the acid boils constantly at 107.1° C.; hence water cannot be separated from the acid by fractional distillation. Formic acid does not decompose when distilled, but when heated with dehydrating agents, as sulphuric acid, it decomposes into water and carbon monoxide. Formates show the same action. Formic acid and its salts do not reduce an aqueous solution of silver nitrate or copper sulphate; in fact beautifully crystallized silver formate or copper formate can be made. But when a formate is heated with ammoniacal silver nitrate, or alkaline copper sulphate (Fehling's) solution, reduction takes place quickly to metallic silver, or red cuprous oxide, while the formate is oxidized to carbonate.

**Acetic Acid, $H.C_2H_3O_2$, or $C_2H_3O.OH$, or $CH_3.CO_2H$ = 60.03.**— The most important alcohol is ethyl alcohol, and the most largely used organic acid is acetic acid, obtained from ethyl alcohol by oxidation. Acetic acid is found in combination with alkali metals in the juices of many plants, also in the secretions of some glands, etc.

There are many reactions by which acetic acid can be obtained similar to formic acid. For all practical purposes, however, it is made either by the oxidation of alcohol (and aldehyde) or by the destructive distillation of wood. It is produced commercially on a large scale as follows: A diluted alcohol (8 to 10 per cent.) is allowed to trickle down slowly through wood shavings contained in high casks having perforated sides in order to allow a free circulation of the air; the temperature is kept at about 24° to 30° C. (75° to 86° F.), and the liquid having passed through the shavings is repeatedly poured back in order to cause complete oxidation. When the latter object has been accomplished the liquid is a diluted acetic acid.

It appears that the conversion of alcohol into acetic acid is greatly facilitated by the presence of a microscopic organism (mycoderma aceti) commonly termed "mother of vinegar." This serves in some unexplained way to convey the atmospheric oxygen to the alcohol. The term "acetic fermentation" is often applied to this conversion, although it is not a true fermentation, since no splitting up of the alcohol molecule into other less complex compounds, but a process of slow oxidation, takes place.

The second process for manufacturing acetic acid is the heating of wood to a red heat in iron retorts, when numerous products (gases, aqueous and tarry substances) are formed. The aqueous products contain, besides other substances, methyl alcohol and acetic acid. The liquid is neutralized with calcium hydroxide and distilled, when methyl alcohol, water, etc., evaporate and a solid residue is left, which is an impure calcium acetate. From this latter, acetic acid is obtained by distilling with sulphuric (or hydrochloric) acid, calcium sulphate (or chloride) being formed and left in the retort, while acetic acid distils over.

*Experiment* 57.—Add to 54 grams of sodium acetate contained in a small flask which is connected with a Liebig's condenser, 40 grams of sulphuric acid. Apply heat and distil over about 35 c.c. Determine volumetrically the amount of pure acetic acid in this liquid.

Pure acetic acid, or *glacial acetic acid*, is solid at or below 15° C. (59° F.); at higher temperatures it is a colorless liquid having a characteristic, penetrating odor, boiling at 118° C. (244.4° F.), and causing blisters on the skin; its specific gravity is 1.049 at 25° C.; it is miscible with water, alcohol, and ether, is strongly acid, forming salts known as acetates, which are all soluble in water.

*Vinegar* is dilute acetic acid (about 6 per cent.), containing often other substances, such as coloring matter, compound ethers, etc. Vinegar was formerly obtained exclusively by the oxidation of fermented fruit-juices (wine, cider, etc.), the various substances present in them imparting a pleasant taste and odor to the vinegar; today vinegar is often made artificially by adding various coloring and odoriferous substances to dilute acetic acid. Vinegar should be tested for sulphuric and hydrochloric acids, which are sometimes fraudulently added.

*Acidum aceticum*, *Acidum aceticum dilutum*, and *Acidum aceticum glaciale* are the three official forms of acetic acid. The first-named acid contains 36 per cent., the second 6 per cent., the third at least 99 per cent. of pure acetic acid.

Acetic acid shows an exceptional behavior in regard to the specific gravity of its aqueous solutions. The highest specific gravity of 1.0748 belongs to an acid of 78 per cent., which is equal to an acid containing one molecule of water and one of acetic acid, or $C_2H_4O_2.H_2O$. When the acid and water are mixed in this proportion, a maximum rise in temperature and contraction in volume takes place, which fact indicates the existence of ortho-acetic acid, $CH_3C(OH)_3$, some ethereal salts of which are known. The addition of either acetic acid or of water causes the liquid to become lighter. For instance, the specific gravity of an acid containing 95 per cent. is equal to that containing 56 per cent. of pure acid, both solutions having a specific gravity of 1.066.

The specific gravity of dilute acetic acid cannot, therefore, be used as a means of determining the amount of pure acid; this is done by exactly neutralizing a weighed portion of the acid with an alkali; from the quantity of the latter used, the quantity of actual acid present may be easily calculated. (See also Volumetric Methods in chapter 39.)

Water can be separated from acetic acid by repeated fractional distillation, but the glacial acid is prepared by distilling anhydrous sodium acetate with concentrated sulphuric acid. To remove small amounts of water, the acid is frozen, partly melted, the liquid drained off, and the residue melted and frozen again. By repeating this process a very pure and nearly absolute acid is obtained. At the

boiling-point, the glacial acid burns with a slightly luminous flame. It is an excellent solvent, for many organic compounds and some inorganic ones, as iodine and sulphur.

Acetic acid is very stable toward oxidizing agents, such as permanganic and chromic acids, in which respect it is in sharp contrast to formic acid. The reason for this is the fact that formic acid, H.COOH, has a hydrogen atom attached to a carbon atom that is in combination with substituting groups and, accordingly, is easily oxidized to hydroxyl, whereas acetic acid, $CH_3$.COOH and the others of the series, have a hydrocarbon radical in place of the hydrogen, such radicals being difficult to oxidize.

The vapor density of absolute acetic acid at just a little above its boiling-point is twice as great as that corresponding to the formula, $C_2H_4O_2$. At 200° C. or above, the vapor density is normal. This kind of behavior has been observed in the case of other substances.

While vinegar is used in our diet, it should be remembered that acetic acid acts as an irritant and corrosive, having caused in some instances perforation of the stomach, and death in six to fifteen hours. Milk of magnesia should be given as an antidote with a view to neutralize the acid -

**Analytical Reactions.** (Sodium acetate, $NaC_2H_3O_2$, may be used.)—1. Any acetate heated with sulphuric acid evolves acetic acid, which may be recognized by its odor.

2. Acetic acid or acetates heated with sulphuric acid and alcohol give a characteristic odor of acetic ether.

3. A solution containing acetic acid, or an acetate carefully neutralized, turns deep red on the addition of solution of ferric chloride, and forms, on boiling, a reddish-brown precipitate of an oxyacetate of iron.

**Potassium Acetate** (*Potassii Acetas*) $\mathbf{KC_2H_3O_2 = 98.12}$. **Sodium Acetate** (*Sodii Acetas*), $\mathbf{NaC_2H_3O_2.3H_2O = 136.07}$. **Zinc Acetate,** (*Zinci Acetas*) $\mathbf{Zn(C_2H_3O_2)_2.2H_2O = 219.45}$.—These three salts may be obtained by neutralizing the respective carbonates with acetic acid and evaporating the solution; they are white salts, easily soluble in water.

**Ammonium Acetate, $NH_4C_2H_3O_2$.**—Ammonium acetate is official in the form of a 7 per cent. solution, which is known as *Spirit of Mindererus*.

**Iron Acetates.**—Both the *ferrous acetate*, $Fe(C_2H_3O_2)_2.4H_2O$, and the *ferric acetate*, $Fe(C_2H_3O_2)_3$, are known. The latter is formed by adding sodium acetate to the solution of a ferric salt, as is indicated by the deep red color which the solution assumes. As stated above in reaction 3, on boiling, decomposition of the salt takes place. The separation of manganese and some other metals from iron depends on this reaction.

**Lead Acetate** (*Plumbi Acetas*), $\mathbf{Pb(C_2H_3O_2)_2 3H_2O = 379.19}$ (*Sugar of Lead*).—Lead acetate is made by dissolving lead oxide in diluted acetic acid. It forms colorless, shining, transparent crystals, easily soluble in water; on heating, it melts and then loses water of crystal-

lization; at yet higher temperatures it is decomposed; it has a sweetish, astringent, afterward metallic taste. Commercial sugar of lead contains often an excess of lead oxide in the form of basic salts; such an article when dissolved in spring water gives generally a turbid solution, in consequence of the formation of lead carbonate; the addition of a few drops of acetic acid renders the liquid clear by dissolving the precipitate.

When a mixture of lead acetate and lead oxide is digested or boiled with water, the acetate combines with the oxide, forming a *basic lead acetate*, approximately $Pb(C_2H_3O_2)_2.PbO$, a 25 per cent. solution of which is the *Liquor plumbi subacetatis*, or *Goulard's extract*, while a solution containing about 1 per cent. is the *Liquor plumbi subacetatis dilutus*, or *lead-water*. Other more basic compounds are known. So-called *tribasic lead acetate* has the formula $Pb(C_2H_3O_2)_2.2PbO$.

**Cupric Acetate, $Cu(C_2H_3O_2)_2H_2O$.**—The commercial *verdigris* is a basic acetate of copper, $Cu(C_2H_3O_2)_2CuO$, made by the action of dilute acetic acid and atmospheric air on metallic copper. By adding to this basic acetate more acetic acid, the neutral acetate is obtained, but this may be made directly also by dissolving cupric hydroxide or carbonate in acetic acid. It forms deep green, prismatic crystals, which are soluble in water.

By boiling verdigris with arsenous oxide, *cupric aceto-arsenite*, $3CuAs_2O_4 + Cu(C_2H_3O_2)_2$, is formed, which is the chief constituent of *emerald green* or *Schweinfurt green*, a substance often used as a coloring matter. *Paris green* is of a similar composition, but less pure.

**Chlorine Substitution Products of Acetic Acid.**—The action of chlorine gas and of phosphorus trichloride on acetic acid furnishes an additional proof of the correctness of our views regarding its constitution and, consequently, of the constitution of organic acids in general. It has been shown that chlorine in acting on a hydrocarbon (methane) will successively replace all hydrogen present. Similarly we can, by treatment with chlorine, replace that hydrogen in acetic acid which is derived from the hydrocarbon, with the result that *monochlor*, *dichlor*, and *trichlor-acetic acids* are formed.

$$CH_3.COOH + 2Cl = CH_2Cl.COOH + HCl,$$
$$CH_2Cl.COOH + 2Cl = CHCl_2.COOH + HCl,$$
$$CHCl_2.COOH + 2Cl = CCl_3.COOH + HCl.$$

The fourth atom of hydrogen cannot be directly replaced by chlorine. As it is this carboxyl hydrogen atom to which the acid properties are due the above three compounds have acid properties.

The action of phosphorus trichloride on water, on methyl alcohol, and on acetic acid takes place thus:

$$3\,{}^{H}_{H}{>}O + PCl_3 = 3HCl + P(OH)_3,$$
$$3\,{}^{CH_3}_{H}{>}O + PCl_3 = 3CH_3Cl + P(OH)_3,$$
$$3\,{}^{C_2H_3O}_{H}{>}O + PCl_3 = 3C_2H_3OCl + P(OH)_3.$$

In all three cases the hydroxyl group is replaced by chlorine, with the result that hydrogen chloride (hydrochloric acid), methyl chloride, and *acetyl chloride* are formed.

**Trichlor-acetic Acid** (*Acidum Trichloraceticum*), $CCl_3.CO_2H = 163.39$. —As shown in the previous paragraph, this acid may be obtained by the direct action of chlorine on acetic acid, but it is usually made by the oxidation with nitric acid of chloral (trichlor-aldehyde), which requires but one atom of oxygen for its conversion into trichlor-acetic acid.

Trichlor-acetic acid is a white, deliquescent, crystalline substance. It has a slight, characteristic odor, is readily soluble in water, alcohol, and ether. The aqueous solution, on boiling, is decomposed into chloroform and carbon dioxide. It is used as a local caustic and as a reagent for albumin. It melts at 55° C. and boils at 195° C.

**Monochlor-acetic acid, $CH_2Cl.COOH$** can be made by passing chlorine in direct sunlight into acetic acid containing a little iodine, which acts as a halogen carrier, or by the action of chlorine on boiling acetic acid containing about 10 per cent. of sulphur, and purifying by fractional distillation. The acid melts at 63° C., boils at about 186° C., is readily soluble in water, and blisters the skin. When boiled with water chlorine is replaced by (OH) group, and when treated with ammonia, chlorine is replaced by the amine group, $NH_2$. It is used in large quantity in making synthetic indigo.

**Dichlor-acetic acid, $CHCl_2.COOH$,** is best prepared by boiling hydrated chloral with an aqueous solution of potassium cyanide,

$$CCl_3.CH(OH)_2 + KCN = CHCl_2.COOH + KCl + HCN.$$

The acid melts at −4° C., and boils at about 190° C.

**Acetyl chloride, $CH_3.COCl$,** is obtained by distilling a mixture of 9 parts of glacial acetic acid and 6 parts of phosphorus trichloride on a water-bath at a slightly elevated temperature. It is a colorless liquid, having a suffocating odor, boiling-point of 55° C., and specific gravity 1.13 at 0° C. It fumes in the air, and acts on water energetically, thus:

$$CH_3COCl + H_2O = CH_3COOH + HCl.$$

It is a valuable reagent for testing for alcoholic hydroxyl groups in organic compounds, which may be illustrated by its action on ordinary alcohol, thus:

$$CH_3COCl + C_2H_5OH = CH_3COOC_2H_5 + HCl.$$

Acetates are thus formed by the replacement of hydrogen of hydroxyl by the acetyl radical.

**Acetic anhydride or acetyl oxide, $(CH_3CO)_2O$,** is formed by distilling a mixture of anhydrous sodium acetate and acetyl chloride:

$$CH_3COONa + CH_3COCl = (CH_3CO)_2O + NaCl.$$

It is a colorless liquid with a disagreeable odor, boiling at 137° C., and having a specific gravity of 1.073 at 20° C. It is soluble in about 10 parts of water, the solution decomposing slowly with formation of acetic acid. Like acetyl chloride, it unites with hydroxyl groups in organic compounds, forming ace-

tates. This process of making acetates from alcoholic compounds is called *acetylization*, and is often used in analysis of substances.

**Butyric acid, $HC_4H_7O_2$.** Among the glycerides of butter those of butyric acid are found; they exist also in cod-liver oil, croton oil, and a few other fatty oils; some volatile oils contain compound ethers of butyric acid; free butyric acid occurs in sweat and in cheese. It may be obtained by a peculiar fermentation of lactic acid (which itself is a product of fermentation), and is also generated during the putrefaction of albuminous substances. Butyric acid is a colorless liquid, having a characteristic, unpleasant odor; it mixes with water in all proportions.

**Valeric Acid, $HC_5H_9O_2$** (*Valerianic Acid*).—This acid occurs in valerian root and angelica root, from which it may be separated; it is, however, generally obtained by oxidation of amyl alcohol by potassium dichromate and sulphuric acid. After oxidation has taken place the mixture is distilled, when valeric acid with some valerate of amyl distils over. The change of amyl alcohol into valeric acid is analogous to the conversion of ethyl alcohol into acetic acid.

$$\underset{\text{Amyl alcohol}}{C_5H_{11}OH} + 2O = \underset{\text{Valeric acid}}{HC_5H_9O_2} + H_2O.$$

Pure valeric acid is an oily, colorless liquid, having a penetrating, highly characteristic odor; it is slightly soluble in water, but soluble in alcohol; it boils at 185° C. (365° F.).

*Ammonium valerate* and *zinc valerate* are official. Both are white solids having the odor of valeric acid. The ammonium salt is readily, the zinc salt sparingly soluble in water.

**Stearic Acid** (*Acidum Stearicum*), **$HC_{18}H_{35}O_2$ = 284.29.**—The official stearic acid is the commercial, more or less impure article made from solid fats, chiefly tallow. It is a hard, white, somewhat glossy solid without odor or taste. It is insoluble in water, but soluble in alcohol, ether and alkalies. Both stearic acid and *palmitic acid*, $HC_{16}H_{31}O_2$, occur largely in solid fats. The general properties of palmitic acid are nearly identical with those of stearic acid. (See Analytical Reactions of Fats.)

**Oleic Acid** (*Acidum Oleicum*), **$HC_{18}H_{33}O_2$ = 282.27.**—As shown by its formula, oleic acid does not belong to the above-described series of fatty acids of the composition $C_nH_{2n}O_2$, but to a series having the general composition $C_nH_{2n-2}O_2$.

These acids belong to the ethylene series, *i. e.*, they contain two carbon atoms held together by a double bond, in virtue of which they are oxidized more readily than the corresponding saturated acids. They also form addition products; oleic acid, for instance, combines directly with 2 atoms of hydrogen, forming stearic acid, and with bromine to form dibrom-stearic acid.

Oleic acid is a constituent of most fats, especially of fat oils. Thus, olive oil is mainly oleate of glyceryl. By boiling olive oil with

potassium hydroxide, potassium oleate is formed, which may be decomposed by tartaric acid, when oleic acid is liberated.

Oleic acid is a nearly colorless, yellowish, or brownish-yellow, neutral, oily liquid, having a peculiar, lard-like odor and taste. It is insoluble in water, soluble in alcohol, chloroform, oil of turpentine, and fat oils, crystallizing near the freezing-point of water; exposed to the air it decomposes and shows then an acid reaction. Lead oleate is soluble in ether, lead palmitate and lead stearate are not.

The official *oleate of mercury* is obtained by dissolving the yellow mercuric oxide in oleic acid.

**Dissociation of Formic Acid and its Homologues.**—In chapter 13 it is stated that the "strength" or relative activity of acids and bases is proportional to their degree of dissociation in solution. Organic acids in solution are dissociated only to a small degree and are much "weaker" than such mineral acids as hydrochloric, nitric, and sulphuric, which are almost completely dissociated in very dilute solutions. The following table shows the percentage of molecules dissociated in aqueous solutions containing the molecular weight in grams of the respective acids diluted to 8 liters:

| Formic acid. | Acetic acid. | Propionic acid. | Normal butyric acid. |
|---|---|---|---|
| 4.05 | 1.193 | 1.016 | 1.068 |

Further dilution does not increase the percentage of dissociation very much. For example, the molecular weight of acetic acid in 16 liters of solution dissociates only to the extent of 1.673 per cent., whereas in a similar solution of hydrochloric acid the dissociation is 95.5 per cent. Formic acid dissociates more than the others of the series, and is, therefore, the strongest acid of the series. The salts of organic acids are dissociated much more than the acids are. Thus, in a normal solution of acetic acid only 0.4 per cent. of the molecules are dissociated, while in normal solutions of sodium and potassium acetate 53 per cent. and 64 per cent., respectively, of the molecules are dissociated.

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QUESTIONS.—What is the constitution of organic acids, what group of atoms is found in all of them, and how does an alcohol radical differ from an acyl radical? Give some processes by which organic acids are formed in nature or artificially. Mention the general properties of organic acids. Which series of acids is known as fatty acids, and why has this name been given to them? Mention names, composition, and occurrence in nature of the first five members of the series of fatty acids. By what processes may formic acid be obtained, and what are its properties? Describe the processes of manufacturing acetic acid from alcohol and from wood. What is vinegar, and what is glacial acetic acid? Give tests for acetic acid and for acetates. Describe the processes for making the acetates of potassium, zinc, iron, lead, and copper, and also of Goulard's extract and lead-water; state their composition and properties. Where and in what form of combination is oleic acid found in nature, and what are its properties?

## 46. POLYBASIC AND HYDROXY-ACIDS.

### Dibasic Acids of the General Composition $C_nH_{2n-2}O_4$.

| | |
|---|---|
| Oxalic acid . . . . . | $H_2C_2O_4$ or $(CO_2H)_2$. |
| Malonic acid . . . . . | $H_2C_3H_2O_4$ or $CH_2(CO_2H)_2$. |
| Succinic acid . . . . . | $H_2C_4H_4O_4$ or $C_2H_4(CO_2H)_2$. |
| Pyrotartaric acid . . . . . | $H_2C_5H_6O_4$ or $C_3H_6(CO_2H)_2$. |
| Adipic acid . . . . . | $H_2C_6H_8O_4$ or $C_4H_8(CO_2H)_2$. |

These acids crystallize well, and those containing four or more carbon atoms in the molecule distil undecomposed under reduced pressure. Heated under atmospheric pressure, they eliminate water and form anhydrides. They are not volatile with steam, as the lower fatty acids are.

Of these acids, only the first member is of general interest.

**Oxalic Acid, $H_2C_2O_4.2H_2O$.**—This acid may be looked upon as a direct combination of two carboxyl groups, $CO_2H—CO_2H$, both atoms of hydrogen being replaceable by metals.

Oxalic acid is distributed largely in the vegetable kingdom in the form of potassium, sodium, or calcium salts. Thus, we find it in all varieties of oxalis (sorrel), in rhubarb, tomatoes, and many other plant juices. It may be obtained from vegetables, or by the oxidation of many organic substances, chiefly fats, sugars, starch, etc., by nitric acid or other strong oxidizing agents.

*Experiment* 58.—Pour 120 grams of nitric acid (sp. gr. 1.42) upon 20 grams of sugar contained in a 500 c.c. flask. Apply heat gently until the reaction begins. When red fumes cease to escape pour the solution into a porcelain dish and evaporate to about 30 c.c. on a water-bath. Crystals of oxalic acid separate on cooling; use them for making the analytical reactions mentioned below. Filter off the crystals on a perforated plate, but not on paper.

Oxalic acid is manufactured on the large scale by heating sawdust with potassium or sodium hydroxide to about 250° C. (482° F.), when the oxalate of these metals is formed; by the addition of calcium hydroxide to the dissolved alkali oxalate, insoluble calcium oxalate is formed which is decomposed by sulphuric acid.

Oxalic acid crystallizes in large, transparent, colorless prisms, containing two molecules of water; it is soluble in water and alcohol, and has poisonous properties. When heated slowly, it sublimes at a temperature of about 155° C. (311° F.); but if heated higher or with sulphuric acid it is decomposed into water, carbonic oxide, and carbon dioxide:

$$H_2C_2O_4 = H_2O + CO + CO_2.$$

Oxalic acid acts as a reducing agent, decolorizing solutions of the permanganates, and precipitating gold and platinum from their solutions:

$$PtCl_4 + 2H_2C_2O_4 = Pt + 4CO_2 + 4HCl.$$

In a decinormal solution of oxalic acid, 50 per cent. of the acid is dissociated.

**Analytical Reactions.** (*Sodium Oxalate*, $Na_2C_2O_4$, may be used.)—1. Oxalic acid or oxalates when heated with strong sulphuric acid evolve carbonic oxide and carbon dioxide (see above).

2. Neutral solutions of an oxalate give with calcium chloride a white precipitate of calcium oxalate, $CaC_2O_4$, which is insoluble in acetic, soluble in hydrochloric acid.

3. Silver nitrate produces a white precipitate of silver oxalate, $Ag_2C_2O_4$.

4. A dry oxalate (containing a non-volatile metal) heated in a test-tube evolves carbonic oxide, while a carbonate is left which shows effervescence with acids. Scarcely any charring takes place.

*Antidotes to Oxalic Acid.*—Calcium carbonate or lime-water should be administered, but no alkalies, as in cases of poisoning by mineral acids, because the alkali oxalates are soluble and also poisonous.

Crystals of oxalic acid resemble very much those of magnesium sulphate and zinc sulphate in appearance, and have been administered in mistake for the latter salts. The acid can readily be distinguished from these two sulphates by the following facts: It has a sour taste and very acid reaction on litmus paper, sublimes when heated, causes effervescence when mixed with a solution of sodium carbonate, but gives no precipitate, bleaches iron ink, and is easily soluble in alcohol.

**Oxalates.**—Of the simple salts of oxalic acid, only those of the alkali metals are soluble in water. *Calcium oxalate*, $CaC_2O_4.2H_2O$, is, in small quantities, a normal constituent of urine, and often leads to the formation of urinary calculi. Acid oxalates and tetroxalates (quadroxalates) are also known. *Acid potassium oxalate*, $KHC_2O_4.H_2O$, exists as a white powder or crystals having a sour taste, and soluble in 40 parts of water. *Potassium tetroxalate*, $KHC_2O_4.H_2C_2O_4.2H_2O$, exists in certain plants and is called *salt of sorrel*. When made artificially, it is a fine white powder, difficultly soluble in water. Both of these acid potassium oxalates are known popularly as *salt of lemon* or salt of sorrel, and are used for removing rust and ink stains from fabrics, bleaching straw, cleaning metal surfaces, etc., but at present oxalic acid is usually sold as salt of lemon.

Many complex oxalates exist. Most of these contain alkali metals, and are soluble in water and used in electro-analysis. An example of such complex salts is *potassium ferrous oxalate*, $K_2Fe(C_2O_4)_2$, which gives a yellow solution. This fact indicates that the iron is held in a complex ion, $Fe(C_2O_4)_2''$, since the color of simple ferrous salts in solution is usually pale green. The salt has strong reducing properties and is used as a developer in photography.

*Potassium ferric oxalate*, $K_3Fe(C_2O_4)_3$, gives a green solution, and the iron is probably held in a complex ion, $Fe(C_2O_4)_3'''$. It is rapidly reduced by sunlight, thus,

$$2K_3Fe(C_2O_4)_3 = 2K_2Fe(C_2O_4)_2 + K_2C_2O_4 + 2CO_2,$$

and therefore is useful in making platinotypes in photography.

**Malonic Acid, $CH_2(COOH)_2$.**—Malonic acid was first obtained as a product of the oxidation of malic acid, hence its name. The acid may be considered as a carboxyl substitution product of acetic, and can readily be built up from the latter. When monochlor- or monobrom-acetic acid is heated with potassium cyanide, cyanacetic acid is obtained. When this is heated with a solution of an alkali, the (CN) radical is hydrolyzed to the (COOH) group, thus:

$$CH_2\begin{matrix}CN\\COOH\end{matrix} + 2H_2O = CH_2\begin{matrix}COOH\\COOH\end{matrix} + NH_3.$$

This is a general and important reaction for introducing carboxyl radical into compounds and thus building up organic acids.

Malonic acid forms laminated crystals which melt at about 133° C. Heated at about 145° C. it decomposes quantitatively into acetic acid and carbon dioxide, thus,

$$CH_2(COOH)_2 = CH_3.COOH + CO_2.$$

This kind of decomposition is characteristic for acids which have two (COOH) groups united to the same carbon atom in the molecule, and is similar in character to the splitting off of water from two (OH) groups attached to the same carbon atom.

It will be noted that the behavior of malonic and other similar acids gives a method for obtaining monobasic from dibasic acids.

**Succinic Acid,** $\begin{matrix}CH_2—COOH\\|\\CH_2—COOH\end{matrix}$.—Succinic acid, thus named because it occurs in amber (the Latin name of which is succinum), is of interest because of its occurrence in some plants, in the urine of rabbits, goats and horses, and its close relationship to malic and tartaric acids which are hydroxyl derivatives, and to aspartic acid and asparagine which are amino derivatives. It can be obtained by distilling amber or by bacterial action on calcium malate, and by synthetic methods. It is a colorless crystalline substance which melts at 182° C., and boils at 235° C. with partial decomposition, the decomposition product being succinic anhydride $\begin{matrix}CH_2—CO\\|\quad\quad\rangle O\\CH_2—CO\end{matrix}$. Other dibasic acids in which the (COOH) groups are not attached to the same carbon atom in the molecule form acid anhydrides when heated alone or with dehydrating agents. The difference in action, in this respect, between these acids, and those of the type of malic acid should be noted.

*Isosuccinic acid*, $CH_3.CH(COOH)_2$, is methyl malonic acid, which, like the latter, loses carbon dioxide when heated above its melting-point, 130° C., and forms propionic acid.

## Hydroxy-acids.

In the acids heretofore considered, the hydrogen is derived either from the hydrocarbon radical or from carboxyl. There are, however, compounds containing as a third radical hydroxyl, *i. e.*, that radical

characteristic of alcohols. Consequently we may look upon these compounds as acids into which alcoholic hydroxyl has been introduced, or as alcohols into which carboxyl has been introduced. The acid properties of these compounds are so predominating that the compounds are spoken of as acids, and according to the number of carboxyl groups present we have monobasic, dibasic, etc., acids. The hydrogen of the carboxyl is, of course, replaceable by metals, while the hydrogen of the alcoholic hydroxyl can be replaced by hydrocarbon radicals. In order to indicate this difference in the function of the hydrogen the number of the respective groups present is given in the name. Thus, tartaric acid, which contains 2 hydroxyl and 2 carboxyl groups, is designated as a dibasic dihydroxy-acid, or as dihydroxy-dicarboxylic acid, while citric acid, which contains 1 hydroxyl and 3 carboxyl groups, is a monohydroxy-tribasic acid or hydroxy-tricarboxylic acid.

Of the several methods known for obtaining hydroxy-acids only one shall be mentioned. It corresponds to one of the methods used for the introduction of hydroxyl into hydrocarbons; in one case the halogen of a hydrocarbon, in the other case the halogen of an acid is replaced by hydroxyl:

$$CH_3Br + H_2O = CH_3OH + HBr,$$

$$CH_2{<}^{Br}_{CO_2H} + H_2O = CH_2{<}^{OH}_{CO_2H} + HBr.$$

Brom-acetic acid. Hydroxy-acetic acid.

It is evident from what has been said that we have running parallel to every series of acids another series of hydroxy-acids. For instance thus:

| *Fatty acids.* | *Hydroxy-acids.* |
|---|---|
| Formic acid, $H.CO_2H$. | Hydroxy-formic acid, $HO.CO_2H$. |
| Acetic acid, $CH_3.CO_2H$. | Hydroxy-acetic acid, $CH_2OH.CO_2H$. |
| Propionic acid, $C_2H_5.CO_2H$. | Hydroxy-propionic acid, $C_2H_4OH.CO_2H$. |
| etc. | etc. |

The first member of these hydroxy-acids designated as hydroxy-formic acid is simply carbonic acid and does not partake of the general character of hydroxy-acids.

The position of the (OH) group in the molecule is indicated by Greek letters, $\alpha$, $\beta$, $\gamma$, etc. The carbon atom next to the (COOH) radical is called the $\alpha$ position, the next one the $\beta$ position, etc. The $\alpha$-hydroxy-acids when heated lose water between two molecules of the acid, the (OH) group of each molecule acting with the (COOH) group of the other. This may be illustrated by the following equation for hydroxy-acetic (glycollic) acid:

$$2CH_2{<}^{OH}_{COOH} = \begin{matrix} OC—O—CH_2 \\ | \quad\quad | \\ H_2C—O—CO \end{matrix} + 2H_2O.$$

Glycollide

The product, when heated with water or alkali, takes up water again and reforms the acid.

The $\beta$-hydroxy-acids also readily lose water but in a different way, forming acids with a double bond, thus:

$$\underset{\beta\text{-Hydroxy-propionic acid.}}{CH_2OH.CH_2.COOH} = \underset{\text{Acrylic acid.}}{CH_2 : CH.COOH} + H_2O.$$

The $\gamma$- and $\delta$-hydroxy-acids lose water very easily, sometimes spontaneously, forming so-called *lactones*, which are inner salts (esters), thus:

$$\underset{\gamma\text{-Hydroxy-butyric acid}}{CH_2OH.CH_2.CH_2COOH} = \underset{\text{Lactone.}}{CH_2.CH_2.CH_2.CO\text{—}O} + H_2O.$$

## Monohydroxy-monobasic Acids.

**Glycollic Acid, $CH_2.OH.CO_2H$** (*Hydroxy-acetic Acid*).—Glycollic acid is found in unripe grapes and in the leaves of the wild grape. It can be obtained synthetically, as shown in the previous paragraph. It may also be made by the oxidation of *ethylene alcohol or glycol*, $C_2H_4(OH)_2$ thus:

$$C_2H_4(OH)_2 + 2O = CH_2.OH.CO_2H + H_2O.$$

Glycollic acid is a white deliquescent, crystalline substance, easily soluble in water, alcohol, and ether.

**Lactic Acid** (*Acidum lacticum*), **$C_2H_4.OH.CO_2H = 90.05$** (*Hydroxy-propionic Acid*).—Lactic acid occurs in many plant-juices; it is formed from sugar by a peculiar fermentation known as "lactic fermentation," which causes the presence of this acid in sour milk and in many sour, fermented substances, as in ensilage, sauer-kraut, etc. The formation of lactic acid from sugar may be expressed by the equation:

$$\underset{\text{Sugar.}}{C_6H_{12}O_6} = \underset{\text{Lactic acid.}}{2HC_3H_5O_3}.$$

For practical purposes lactic acid is made by mixing a solution of sugar with milk, putrid cheese, and chalk, and digesting this mixture for several weeks at a temperature of about 30° C. (86° F.). The bacteria in the cheese act as a ferment, and the chalk neutralizes the acid generated during the fermentation. The calcium lactate thus obtained is purified by crystallization and decomposed by oxalic acid, which forms insoluble calcium oxalate.

Lactic acid is a colorless, syrupy liquid, of strongly acid properties; it mixes in all proportions with water and alcohol. The official lactic acid contains 75 per cent. of absolute acid.

Lactic acid decomposes when distilled at ordinary pressure, but it can be distilled in a vacuum. The liquid obtained can be frozen to crystals, which melt at 18° C.

It is $\alpha$-hydroxy-propionic acid, and, accordingly, forms lactide when heated at 150° C., thus:

$$\underset{\text{Lactic acid.}}{2CH_3.CH.OH.COOH} = \underset{\text{Lactide.}}{\begin{matrix} CH_3.CH\text{—}O\text{—}CO \\ | \qquad\quad | \\ OC\text{—}O\text{—}HC.CH_3 \end{matrix}} + 2H_2O.$$

Lactide melts at 124° C. and when boiled with water, reverts to lactic acid.

Three isomeric lactic acids are known:

(a) *Fermentation lactic acid*, obtained as described above from milk, is optically inactive.

(b) *Sarcolactic* or *paralactic acid* is dextrorotatory and occurs in muscle and other parts of the body. It forms a constituent of meat-juice, and, therefore, of meat extract.

(c) *Lævolactic acid* is lævorotatory, and is obtained from cane-sugar by fermentation by a special microorganism.

**Calcium Lactate** (*Calcii lactas*), $Ca(C_3H_5O_3)_2.5H_2O = 308.23$.—It occurs as white, odorless, nearly tasteless, granular masses or powder, somewhat efflorescent soluble in twenty times its weight of water, almost insoluble in alcohol. It loses all water when heated at 120° C. Its solution is practically neutral to litmus and phenolphthalein.

**Hydracrylic Acid** (*β-hydroxy-propionic Acid*), $CH_2OH.CH_2.COOH$.—Hydracrylic acid is an isomer of lactic acid, which can be made from a β-halogen derivative of propionic acid in the usual way. It is a thick liquid, which, upon heating, loses water, thus:

$$\underset{\text{Hydracrylic acid}}{CH_2OH.CH_2.COOH} = \underset{\text{Acrylic acid}}{CH_2 : CH.COOH.} + H_2O.$$

By oxidation, it forms malonic acid:

$$CH_2OH.CH_2.COOH + 2O = CH_2(COOH)_2 + H_2O.$$

## Dibasic and Tribasic Hydroxy-acids.

**Mono-hydroxy-succinic acid, or malic acid =**

$C_4H_6O_5$ or $C_2H_3(OH)(CO_2H)(CO_2H)$ or $\begin{matrix} CH.OH.CO_2H \\ | \\ CH_2.CO_2H \end{matrix}$

**Di-hydroxy-succinic acid, or tartaric acid =**

$C_4H_6O_6$ or $C_2H_2(OH)_2(CO_2H)(CO_2H)$ or $\begin{matrix} CH.OH.CO_2H \\ | \\ CH.OH.CO_2H \end{matrix}$

**Malic Acid, $H_2C_4H_4O_5$.**—Malic acid occurs in the juices of many fruits, as apples, currants, cherries, etc. It may be extracted from these fruits or prepared synthetically. The unripe berries of the mountain ash is the most suitable natural source of the acid, and the procedure is much like that used in extracting citric acid from lemons. Malic acid is difficult to crystallize, being very soluble in water.

**Tartaric Acid** (*Acidum Tartaricum*), $H_2C_4H_4O_6 = 150.05$.—Frequently found in vegetables, and especially in fruits, sometimes free, generally as the potassium or calcium salt; grapes contain it chiefly as potassium acid tartrate, which is obtained in an impure state as a by-product in the manufacture of wine. During the fermentation of grape-juice, its sugar is converted into alcohol; potassium acid tartrate is less soluble in alcoholic fluids than in water, and therefore

is deposited gradually, forming the *crude tartar*, or *argol*, of commerce, a substance containing chiefly potassium acid tartrate, but also calcium tartrate, some coloring matter, and traces of other substances. Crude tartar is the source of tartaric acid and its salts.

Tartaric acid is obtained from potassium acid tartrate by neutralizing with calcium carbonate, and decomposing the remaining neutral potassium tartrate by calcium chloride:

$$\underset{\text{Potassium acid tartrate}}{2(KHC_4H_4O_6)} + \underset{\text{Calcium carbonate.}}{CaCO_3} = \underset{\text{Calcium tartrate}}{CaC_4H_4O_6} + \underset{\text{Potassium tartrate.}}{K_2C_4H_4O_6} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon dioxide.}}{CO_2}.$$

$$\underset{\text{Potassium tartrate}}{K_2C_4H_4O_6} + \underset{\text{Calcium chloride.}}{CaCl_2} = \underset{\text{Calcium tartrate.}}{CaC_4H_4O_6} + \underset{\text{Potassium chloride.}}{2KCl}.$$

The whole of the tartaric acid is thus converted into calcium tartrate, which is precipitated as an insoluble powder; this is collected, well washed, and decomposed by boiling with sulphuric acid, when calcium sulphate is formed as an almost insoluble residue, while tartaric acid is left in solution, from which it is obtained by evaporation and crystallization:

$$\underset{\text{Calcium tartrate.}}{CaC_4H_4O_6} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Tartaric acid}}{H_2C_4H_4O_6} + \underset{\text{Calcium sulphate}}{CaSO_4}.$$

Tartaric acid crystallizes in colorless, translucent prisms; it has a strongly acid, but not disagreeable taste; it is readily soluble in water and alcohol, and fuses at about 169° C.

The presence of (OH) groups in the molecule of tartaric acid causes it to exhibit alcoholic or basic properties in addition to the properties of an acid conferred by the (COOH) groups. The hydrogen of the (OH) groups can be replaced by acyl radicals, for example, acetyl. But the two (COOH) groups in the acid are electronegative in character, and their presence causes the (OH) groups to be less basic than they are in simple alcohols, and even to exhibit slightly acid tendencies. This is illustrated by the fact that copper hydroxide is dissolved by a solution of an alkali tartrate (see Experiment 40) to form a deep blue solution, which with the addition of an alkali constitutes Fehling's solution. A crystalline compound of the composition, $Cu\begin{matrix}O.CH.COONa\\ |\\ O.CH.COONa.2H_2O\end{matrix}$ has been obtained. The evidence that the copper has replaced the hydrogen of the (OH) groups and not ordinary acid hydrogen, as in simple copper salts, is the deep blue color of the compound, that the copper cannot be precipitated by addition of alkali, and that during electrolysis the copper, bound in the tartaric acid ion, travels toward the positive pole (anode) and not toward the negative pole (cathode), as in the case of simple copper salts, such as the sulphate, chloride, etc.

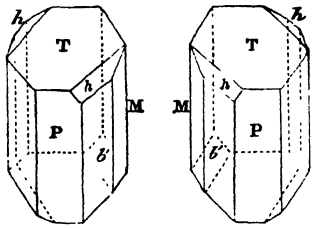
It is a well-known fact in the field of inorganic compounds, that the behavior of an element is determined by the character of the other elements with which it is combined. Thus, the strongly electropositive elements combined with hydroxyl, form bases, such as NaOH, $Bi(OH)_3$, whereas electronegative elements combined with hydroxyl give rise to acids, such as ClOH, $P(OH)_3$. The same influence is noticed among organic compounds. Hydroxyl combined with the more positive

radicals of the paraffin hydrocarbons gives rise to basic compounds (alcohols), but when combined with the less positive radicals of the benzene hydrocarbons, compounds of acid character (phenols) are formed. Hydroxyl hydrogen of ordinary phenol, $C_6H_5OH$, is weakly acidic, but the introduction of negative radicals into phenol causes it to assume a well-marked acid character, for example, trinitrophenol (picric acid), $C_6H_2<^{OH}_{(NO_3)_3}$. Hydrocarbon hydrogen and ammonia hydrogen may become acidic in character by the presence of negative radicals in the molecule. For example, the two hydrogen atoms of the $CH_2$ group in ethyl malonate, $CH_2<^{COOC_2H_5}_{COOC_2H_5}$, may be replaced by sodium, and the ammonia hydrogen in benzosulphinide (saccharin), $C_6H_4<^{CO}_{SO_2}>NH$, is replaceable by metals, the sodium salt, which is much more soluble than saccharin, being now official.

**Isomerism of Tartaric Acid.** Four tartaric acids are known. They are: *dextrotartaric* or *common tartaric acid; lævotartaric acid; mesotartaric* or *inactive tartaric acid;* and *racemic acid.* These four acids have the same composition and show the same chemical reactions, proving that they are built up from the same radicals; but in some respects they possess different physical properties. Thus, mesotartaric and racemic acids are optically inactive; the others, as indicated by their names, are active, one turning polarized light to the right, the other to the left.

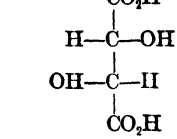
Pasteur first observed that the spontaneous evaporation of a solution of ammonium sodium racemate yields two kinds of stereo-isomeric crystals. These crystals (Fig. 44) are rectangular prisms P, M, T, having the lateral edges replaced by the faces $b'$, and the intersection of these faces with the face T replaced by a face $h$. The crystals are hemihedral, having four of these $h$ faces placed alternately. In the two kinds of crystals these hemihedral faces occupy opposite positions, so that if one kind of crystal be placed before a mirror its reflection will represent the arrangement of the hemihedral faces of the other kind of crystal. The crystals are called right-handed and left-handed respectively.

FIG 44.

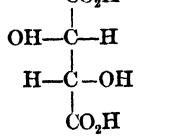



Isomeric salts of tartaric acid.

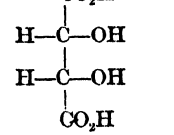
From these two kinds of crystals two tartaric acids can be separated; one is dextrotartaric acid, the other lævotartaric acid. When the two acids are brought together in solution they unite forming racemic acid. These observations, supported by chemical data, have led to assume in tartaric acids the existence of two asymmetric carbon atoms, about which the hydrogen atoms and the radicals are arranged differently. Three of these forms may be represented by the formulas:




Dextrotartaric acid.




Lævotartaric acid.




Mesotartaric acid.

Racemic acid results from the combination of dextrotartaric and lævotartaric acids. Mesotartaric cannot be split up into active varieties of tartaric acid. When ordinary tartaric acid is boiled with water or hydrochloric acid, some racemic acid is formed, and when heated with water in a sealed tube at 175° C., it is almost completely converted into racemic acid.

In a tenth-normal solution of tartaric acid at 25° C., 8.2 per cent. of the acid is dissociated into H. and $H.C_4H_4O_6'$ ions.

**Analytical Reactions** (*Potassium Sodium Tartrate*, $KNaC_4H_4O_6$, may be used.)—1. A neutral solution of a tartrate gives with calcium chloride a white precipitate of calcium tartrate, which, after being quickly collected on a filter and washed, is soluble in potassium hydroxide; from this solution calcium tartrate is precipitated on boiling. (Calcium citrate is insoluble in potassium hydroxide.)

Calcium tartrate is soluble in a solution of an alkali tartrate; hence, unless a sufficient amount of calcium chloride is added, a precipitate will not be obtained.

2. A strong solution of a tartrate, acidulated with acetic acid, gives a white precipitate of potassium acid tartrate on the addition of potassium acetate. The precipitate, which forms slowly, is soluble in alkalies and in mineral acids.

In the case of potassium sodium tartrate, or potassium tartrate, addition of acetic acid alone precipitates potassium acid tartrate.

3. A neutral solution of a tartrate gives with silver nitrate a white precipitate of silver tartrate, $Ag_2C_4H_4O_6$, which blackens on boiling, in consequence of the decomposition of the salt, with separation of silver. If, before boiling, a drop of ammonia-water be added, a mirror of metallic silver will form upon the glass.

Silver tartrate is soluble in a solution of alkali tartrate; hence the silver nitrate solution must be added in sufficient quantity to obtain a permanent precipitate.

4. Sulphuric acid heated with tartrates chars them readily.

5. Tartrates, when heated, are decomposed (blacken), and evolve a somewhat characteristic odor, resembling that of burnt sugar.

The above reaction, 3, can be used to advantage for silvering glass by operating as follows: Dissolve 1 gram of silver nitrate in 20 c.c. of water, add ammonia-water until the precipitate which forms is nearly redissolved, and dilute with water to 100 c.c. Make a second solution by dissolving 0.2 gram of silver nitrate in 100 c.c. of boiling water, add 0.166 gram of potassium sodium tartrate, boil until the precipitate becomes gray, and filter. Mix the two solutions cold and set aside for one hour, when a mirror of metallic silver will be found.

**Potassium Acid Tartrate** (*Potassii Bitartras*), $\mathbf{KHC_4H_4O_6 = 188.14}$ (*Potassium bitartrate, Cream of Tartar*).—The formation of this salt in the crude state (argol) has been explained above. It is purified by dissolving in hot water and crystallizing, when it is obtained in colorless crystals, or as a white, somewhat gritty powder of a pleasant, acidulous taste; it is soluble in about 200 parts of cold, easily soluble in hot water, but insoluble in alcohol.

The name cream of tartar was given to the salt for the reason that small crystals, which float on the liquid, separate on rapidly cooling a hot solution of potassium bitartrate.

**Potassium Tartrate, $2(K_2C_4H_4O_6).H_2O$.**—Obtained by saturating a solution of potassium acid tartrate with potassium carbonate:

$$\underset{\text{Potassium acid tartrate.}}{2KHC_4H_4O_6} + \underset{\text{Potassium carbonate}}{K_2CO_3} = \underset{\text{Potassium tartrate.}}{2K_2C_4H_4O_6} + H_2O + CO_2.$$

Small transparent or white crystals, or a white neutral powder, soluble in less than its own weight of water.

**Potassium Sodium Tartrate** (*Potassii et Sodii Tartras*), $KNaC_4H_4O_6.4H_2O = 282.20$ (*Rochelle salt*). If in the above-described process for making neutral potassium tartrate, sodium carbonate is substituted for potassium carbonate, the double tartrate of potassium and sodium is formed. It is a white powder, or occurs in colorless, transparent crystals which are easily soluble in water.

*Experiment* 59.—Add gradually 24 grams of potassium acid tartrate to a hot solution of 20 grams of crystallized sodium carbonate in 100 c.c. of water. Heat until complete solution has taken place, filter, evaporate to about one-half the volume, and set aside for the potassium sodium tartrate to crystallize. How much crystallized sodium carbonate is required for the conversion of 25 grams of potassium acid tartrate into Rochelle salt?

*Seidlitz powders* (*Compound effervescing powders*) consist of a mixture of 7.75 grams (120 grains) of Rochelle salt with 2.58 grams (40 grains) of sodium bicarbonate (wrapped in blue paper), and 2.25 grams (35 grains) of tartaric acid (wrapped in white paper). When dissolved in water the tartaric acid acts upon the sodium bicarbonate, causing the formation of sodium tartrate, while the escaping carbon dioxide causes effervescence.

**Antimony and Potassium Tartrate** (*Antimonii et Potassii Tartras*), $(2KSbO.C_4H_4O_6).H_2O = 664.7$ (*Potassium Antimonyl Tartrate, Tartar Emetic*). This salt is made by dissolving freshly prepared antimonous oxide (while yet moist) in a solution of potassium acid tartrate. From the solution somewhat evaporated, tartar emetic separates in colorless, transparent rhombic crystals:

$$\underset{\text{Potassium acid. tartrate.}}{2KHC_4H_4O_6} + \underset{\text{Antimonous oxide}}{Sb_2O_3} = \underset{\text{Tartar emetic.}}{2KSbO.C_4H_4O_6} + H_2O.$$

The fact that not antimony itself, but the group SbO, replaces the hydrogen, has led to the assumption of the hypothetical radical SbO, termed antimonyl.

Tartar emetic is soluble in water, insoluble in alcohol; it has a sweet, afterward disagreeable metallic taste.

**Action of Certain Organic Acids upon Certain Metallic Oxides.**—The solution of a ferric salt (or certain other metallic salts) is precipitated by alkali hydroxides, a salt of the alkali and ferric hydroxide being formed. When a sufficient quantity of either tartaric, citric, oxalic, or various other organic acids has been added previously to the iron solution (or to certain other metallic solutions) no such precipitate is produced by the alkali hydroxides, because organic salts or double salts are formed which are soluble, and from which the metallic hydroxides are not precipitated by alkali hydroxides. Upon evaporation no crystals (of the organic salt) form, and in order to obtain the compounds in a dry state, the liquid, after being evaporated to the consistence of a syrup, is spread on glass plates which are exposed to a temperature not exceeding 60° C. (140° F.), when brown, green, yellowish-green, amorphous, shining, transparent scales are formed.

The true chemical constitution of many of these scale compounds has not as yet been determined with certainty.

**Citric Acid** (*Acidum Citricum*), $H_3C_6H_5O_7.H_2O$ = **210.08.**—Citric acid is a tribasic acid containing three atoms of hydrogen replaceable by metals; its constitution may be expressed by the graphic formulas:

$$C_3H_4\begin{cases}OH\\CO_2H\\CO_2H\end{cases} \quad \text{or} \quad \begin{array}{l}CH_2.CO_2H\\|\\COH.CO_2H\\|\\CH_2.CO_2H\end{array}$$

Citric acid is found in the juices of many fruits (strawberry, raspberry, currant, cherry, etc.), and in other parts of plants. It is obtained from the juice of lemons by saturating it with calcium carbonate at ordinary temperature and filtering. The tricalcium citrate contained in the filtrate is readily soluble in cold water, but almost insoluble in boiling water. After boiling the filtrate the precipitate is filtered and washed with boiling water. It is then decomposed with an equivalent amount of sulphuric acid, the calcium sulphate is filtered off, and the filtrate evaporated until the citric acid crystallizes (100 parts of lemons yield about 5 parts of the acid).

Citric acid forms colorless, rhombic prisms, which contain one molecule of water and melt at 100° C. The anhydrous acid, obtained at about 130° C., melts at 153° C.

Citric acid is also obtained commercially by the action of a microorganism, citromycetes pfefferianus, on glucose.

**Analytical Reactions.** (*Potassium Citrate,* $K_3C_6H_5O_7$, may be used.) —1. Neutral solutions of citrates yield with calcium chloride on boiling (not in the cold) a white precipitate of calcium citrate, which is insoluble in potassium hydroxide, but soluble in cupric chloride.

2. Neutral solutions of citrates are precipitated white by silver nitrate. The precipitate does not blacken on boiling, as in the case of tartrates. Silver citrate is soluble in a solution of an alkali citrate; hence, sufficient silver nitrate solution must be added to obtain a permanent precipitate.

3. A solution of citrate made alkaline with a little sodium hydroxide solution, to which a few drops of potassium permanganate solution are added, turns green *slowly*, whereas, a tartrate under the same conditions decolorizes permanganate quickly, with precipitation of brown manganese dioxide.

4. When ignited, it is decomposed without emitting an odor resembling burning sugar. (Difference from tartaric acid.)

5. Tartaric acid in citric acid may be detected by adding about 1 c.c. of an aqueous solution of ammonium molybdate to about 1 gram of the citric acid, then 2 or 3 drops of sulphuric acid, and warming on the water-bath. The presence of 0.1 per cent. or more of tartaric acid gives a blue color to the solution.

**Citrates.**—*Potassium citrate*, $K_3C_6H_5O_7.H_2O$, and *Lithium citrate*, $Li_3C_6H_5O_7.4H_2O$, are official. Both are white deliquescent salts, easily soluble in water, and obtained by dissolving the carbonates in citric acid. *Sodium citrate*, $2Na_3C_6H_5O_7.11H_2O$, is also official.

The official *solution of magnesium citrate* is made by dissolving magnesium carbonate in an excess of citric acid solution to which some syrup is added, and dropping into this mixture, which should be contained in a strong bottle, potassium bicarbonate. The bottle is immediately closed with a cork in order to retain the liberated carbon dioxide.

Bismuth citrate, $BiC_6H_5O_7$, is obtained by boiling a solution of citric acid with bismuth nitrate, when the latter is gradually converted into citrate, while nitric acid is set free; the insoluble bismuth citrate is collected, washed, and dried; it forms a white, amorphous powder, which is insoluble in water, but soluble in ammonia water.

*Bismuth ammonium citrate* is a scale compound obtained by dissolving bismuth citrate in ammonia water and evaporating the solution at a low temperature.

Ferric Citrate. Obtained in transparent, red scales, by dissolving ferric hydroxide in citric acid and evaporating the solution as mentioned heretofore. By mixing solution of ferric citrate with either ammonia-water, quinine, or sodium phosphate, evaporating to the consistence of syrup and drying on glass plates, the following scale compounds are obtained respectively: *Iron and ammonium citrate, iron and quinine citrate, and ferric phosphate.*

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QUESTIONS.—Name the more common organic acids found in vegetables and especially in sour fruits. What is the composition of oxalic acid, how is it manufactured, and what are its properties? Explain the formation of crude tartar during the fermentation of grape-juice, and how is tartaric acid obtained from it? Give properties of and tests for tartaric acid. State the composition and formation of cream of tartar, Rochelle salt, and tartar emetic. What are Seidlitz powders, and what changes take place when they are dissolved? Give the general composition of hydroxy-acids, and state a method for preparing them synthetically. From what and by what process is citric acid obtained? Mention tests by which citric acid may be distinguished from tartaric acid. From what and by what process is lactic acid obtained; what are its properties? How can oxalic acid be distinguished from magnesium or zinc sulphate? What is salt of lemon and salt of sorrel? What is the explanation of the fact that hydrogen of the (OH) radical is basic in some compounds and acidic in others?

## 37. ETHERS AND ESTERS.

**Constitution.**—It has been shown that alcohols are hydrocarbon residues in combination with hydroxyl, OH, and that acids are hydrocarbon residues in combination with carboxyl, CO.OH; it has further been shown that carboxyl may be considered as being composed of CO, and hydroxyl, OH, and that the term acyl radical is applied to that group of atoms in acids which embraces the hydrocarbon residue + CO. If we represent a hydrocarbon radical by R, and an acid radical by R.CO, the general formula of an alcohol is R.OH, or $\begin{matrix}R\\H\end{matrix}\!>\!O$, and of an acid, R.CO.OH, or $\begin{matrix}R.CO\\H\end{matrix}\!>\!O$.

*Ethers* are formed by replacement of the hydrogen of the hydroxyl in alcohols by hydrocarbon residues, and esters, also called *compound ethers*, or ethereal salts are formed by replacement of the hydrogen of the hydroxyl (or carboxyl) in acids by hydrocarbon residues. While alcohols correspond in their constitution to hydroxides, ethers correspond to oxides, and esters to salts. For instance:

| *Hydroxides.* | *Oxides.* | *Acids.* | *Salts.* |
|---|---|---|---|
| $KOH = \begin{matrix}K\\H\end{matrix}\!>\!O$ | $K_2O = \begin{matrix}K\\K\end{matrix}\!>\!O$ | $HNO_3 = \begin{matrix}NO_2\\H\end{matrix}\!>\!O$ | $KNO_3 = \begin{matrix}NO_2\\K\end{matrix}\!>\!O$ |
| Potassium hydroxide. | Potassium oxide. | Nitric acid. | Potassium nitrate. |
| $\begin{matrix}C_2H_5\\H\end{matrix}\!>\!O$ | $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O$ | $\begin{matrix}C_2H_3O\\H\end{matrix}\!>\!O$ | $\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\!>\!O$ |
| Ethyl alcohol. | Ethyl ether. | Acetic acid. | Ethyl acetate, or acetic ether |
| $\begin{matrix}R\\H\end{matrix}\!>\!O$ | $\begin{matrix}R\\R\end{matrix}\!>\!O$ | $\begin{matrix}R.CO\\H\end{matrix}\!>\!O$ | $\begin{matrix}R.CO\\R\end{matrix}\!>\!O.$ |
| Alcohol. | Ether. | Acid. | Ester. |

It is not necessary that the two hydrocarbon residues in an ether should be alike, as in the above ethyl ether, but they may be different, in which case the ethers are termed *mixed ethers*. For instance:

$CH_3.C_2H_5O = \begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!O$ Methyl-ethyl ether. $\qquad C_3H_7.C_5H_{11}.O = \begin{matrix}C_3H_7\\C_5H_{11}\end{matrix}\!>\!O.$ Propyl-amyl ether.

In diatomic or triatomic alcohols, or in dibasic or tribasic acids, containing more than one atom of hydrogen derived from hydroxyl or carboxyl, these hydrogen atoms may be replaced by various other univalent, bivalent, or trivalent residues. This fact shows that the number of ethers or esters which are capable of being formed is very large.

**Formation of Ethers.**—Ethers may be formed by the action of the chloride or iodide of a hydrocarbon residue upon an alcohol, in which the hydroxyl hydrogen has been replaced by a metal. This reaction is of great historical interest, as it first threw light on the structure of ethers and their relation to the corresponding alcohols.

$$\underset{\text{Sodium ethylate.}}{C_2H_5\!\!\searrow\!\!\underset{Na}{\swarrow}O} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Ethyl ether.}}{\overset{C_2H_5}{\underset{C_2H_5}{\searrow\!\!\swarrow}}O} + \underset{\text{Sodium iodide.}}{NaI.}$$

$$\underset{\text{Sodium ethylate.}}{C_2H_5\!\!\searrow\!\!\underset{Na}{\swarrow}O} + \underset{\text{Methyl iodide.}}{CH_3I} = \underset{\text{Ethyl-methyl ether.}}{\overset{C_2H_5}{\underset{CH_3}{\searrow\!\!\swarrow}}O} + \underset{\text{Sodium iodide.}}{NaI.}$$

Ethers are also formed by the action of sulphuric acid upon alcohols; the sulphuric acid removing water in this case, thus:

$$\underset{\text{Ethyl alcohol.}}{2(C_2H_5OH)} = \underset{\text{Ethyl ether.}}{\overset{C_2H_5}{\underset{C_2H_5}{\searrow\!\!\swarrow}}O} + \underset{\text{Water.}}{H_2O.}$$

Esters are formed by the combination of acids with alcohols and elimination of water. (Presence of sulphuric acid facilitates this action.)

$$\underset{\text{Ethyl alcohol.}}{C_2H_5\!\!\searrow\!\!\underset{H}{\swarrow}O} + \underset{\text{Acetic acid.}}{C_2H_3O\!\!\searrow\!\!\underset{H}{\swarrow}O} = \underset{\text{Ethyl acetate.}}{\overset{C_2H_3O}{\underset{C_2H_5}{\searrow\!\!\swarrow}}O} + \underset{\text{Water.}}{H_2O.}$$

They are also formed by the action of hydrocarbon chlorides (or iodides) on salts. For instance:

$$\underset{\text{Amyl chloride}}{C_5H_{11}Cl} + \underset{\text{Potassium formate}}{\overset{HCO}{K}\!>\!O} = \underset{\text{Amyl formate.}}{\overset{C_5H_{11}}{HCO}\!>\!O} + \underset{\text{Potassium chloride}}{KCl.}$$

**Occurrence in Nature.**—Many ethers are products of vegetable life and occur in some essential oils; *wax* contains the compound ether melissyl palmitate, $C_{30}H_{61}.C_{16}H_{31}O.O$, and *spermaceti*, a solid substance found in the head of the whale, is cetyl palmitate, $C_{16}H_{33}.C_{16}H_{31}O.O$. The most important group of esters are the fats and fatty oils, which are distributed widely in the vegetable, but even more so in the animal kingdom.

**General Properties.**—The ethers and esters of the lower members of the monatomic alcohols and fatty acids have generally a characteristic and pleasant odor. Fruit essences consist mainly of such esters, and what is generally known as the "bouquet" or "flavor" of wine and other alcoholic liquors is due chiefly to ethers or compound ethers, which are formed during (and after) the fermentation by the action of the acids present upon the alcohol or the alcohols formed. The improvement which such alcoholic liquids undergo "by age" is caused by a continued chemical action between the substances named.

All esters are neutral substances; those formed by the lower alcohols and acids are generally volatile liquids, those of the higher members are non-volatile solids. When esters are heated with alkalies, the acid combines with the latter, while the alcohol is liberated. (The properties of the esters, termed fats, will be considered farther on.)

One of the chief points of distinction between ethers and esters is that ethers are not acted on by alkalies, while esters are decomposed, an alcohol and a salt of the alkali metal being formed. Esters, being like inorganic salts between weak acids and weak bases, are hydrolyzed to a greater or less extent by water, but the action is much slower than in the case of inorganic salts.

## Ethers.

**Ethyl Ether** (*Æther*) $(C_2H_5)_2O = 74.08$ (*Ether, Sulphuric Ether, Ethyl Oxide*).—The name of the whole group of ethers is derived from this (ethyl) ether, in the same way that common (ethyl) alcohol has given its name to the group of alcohols. The name sulphuric ether was given at a time when its true composition was yet unknown, and for the reason that sulphuric acid was used in its manufacture.

Ether is manufactured by heating to about 140° C. (284° F.) a mixture of 1 part of alcohol and 1.8 parts of concentrated sulphuric acid in a retort, which is so arranged that additional quantities of alcohol may be allowed to flow into it, while the open end is connected with a tube, leading through a suitable cooler, in order to condense the highly volatile product of the distillation.

*Experiment* 60.—Mix 100 grams of alcohol with 180 grams of ordinary sulphuric acid, allow to stand and pour the cooled mixture into a flask which is provided with a perforated cork through which pass a thermometer and a bent glass tube leading to a Liebig's condenser. Apply heat and notice that the liquid commences to boil at about 140° C. (284° F.). Distil about 50 c.c., pour this liquid into a stoppered bottle and add an equal volume of water. Ethyl ether will separate into a distinct layer over the water, and may be removed by means of a pipette. Repeat the washing with water, add to the ether thus freed from alcohol a little calcium chloride and distil it from a dry flask, standing in a water-bath. The greatest care should be exercised and the neighborhood of flames avoided in working with ether, on account of its volatility and the inflammability of its vapors.

The apparatus described above for etherification can be constructed so as to make the process continuous. This may be done by using with the boiling-flask a cork with a third aperture through which a glass tube passes into the liquid. The other end of the tube is connected by means of rubber tubing with a vessel filled with alcohol and standing somewhat above the flask. As soon as distillation commences alcohol is allowed to flow into the flask at a rate equal to that of the distillation, keeping the temperature at about 140° C. (284° F.). The flow of alcohol is regulated by a stop-cock.

The action of sulphuric acid upon alcohol is not quite so simple as described above in connection with the general methods for obtaining ethers, where the final result only was given. An intermediate product, known as *ethyl sulphuric acid* or *sulpho-vinic acid*, is formed, which, by acting upon another molecule of alcohol, forms sulphuric acid and ether, which latter is volatilized as soon as formed. The decomposition is shown by the equations:

$$\underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\text{Sulphuric acid.}}{\begin{matrix}HO\\HO\end{matrix}\!\!>\!SO_2} = \underset{\text{Ethyl-sulphuric acid.}}{\begin{matrix}C_2H_5O\\HO\end{matrix}\!\!>\!SO_2} + H_2O.$$

$$\underset{\text{Ethyl-sulphuric acid.}}{\begin{matrix}C_2H_5O\\HO\end{matrix}\!\!>\!SO_2} + \underset{\text{Alcohol.}}{C_2H_5OH} = \underset{\text{Ether.}}{(C_2H_5)_2O} + \underset{\text{Sulphuric acid.}}{\begin{matrix}HO\\HO\end{matrix}\!\!>\!SO_2}.$$

The liberated sulphuric acid at once attacks another molecule of alcohol, again forming ethyl-sulphuric acid, which is again decomposed, etc. Theoretically, a given quantity of sulphuric acid should be capable, therefore, of converting any quantity of alcohol into ether; practically, however, this is not the case, because secondary reactions take place simultaneously, and because the water which is constantly formed does not all distil with the ether, and therefore dilutes the acid to such an extent that it no longer acts upon the alcohol.

Ether thus obtained is not pure, but contains water, alcohol, sulphurous and sulphuric acids, etc.; it is purified by mixing it with chloride and oxide of calcium, pouring off the clear liquid and distilling it.

The official ether contains 96 per cent. of ethyl ether and 4 per cent. of alcohol. It is a very mobile, colorless, highly volatile liquid, of a refreshing, characteristic odor, a burning and sweetish taste, and a neutral reaction; it is soluble in alcohol, chloroform, liquid hydrocarbons, fixed and volatile oils, and dissolves in ten volumes of water. Specific gravity is 0.716 at 25° C. (77° F.); boiling-point 35° C. (95° F.). It is easily combustible and burns with a luminous flame. When inhaled, it causes intoxication and then loss of consciousness and sensation. The great volatility and combustibility of ether necessitate special care in the handling of this substance near fire or light.

Although ether is an oxide, it is less basic in character than alcohol, and very different in its action from metallic oxides. Warmed with a concentrated solution of hydriodic acid, ethyl iodide is formed, which is analogous to the action between metallic oxides and the acid. Ether dissolves in cold concentrated sulphuric acid without chemical action, but upon gently heating, ethyl sulphuric acid is formed, thus, $(C_2H_5)_2O + 2H_2SO_4 = 2C_2H_5.H.SO_4 + H_2O$. Toward most common reagents and chemicals, ether is inactive. Metallic sodium which acts on alcohol, has no action on ether. Caustic alkalies do not affect ether, but chlorine and bromine form substitution products with ether.

*Spiritus ætheris* is a mixture of about one part of ether and two parts alcohol.

**Methyl Ether,** $(CH_3)_2.O$,—Methyl ether is made from methyl alcohol and sulphuric acid. It is a gas at ordinary temperature, but readily convertible by pressure or cold into a mobile liquid.

**Methyl-ethyl Ether,** $CH_3.C_2H_5.O$.—This is a mixed ether which can be prepared by the action of ethyl iodide upon sodium methylate:

$$C_2H_5I + NaOCH_3 = NaI + C_2H_5.O.CH_3.$$

Methyl-ethyl ether is a colorless, highly volatile, and inflammable liquid of peculiar odor; it boils at 11° C. (52° F.). It has been used as an anæsthetic, and for that purpose is sold in cylinders.

## Esters.

**Ethyl Acetate, $C_2H_5C_2H_3O_2$** (*Acetic Ether*).—Made by mixing dried sodium acetate with alcohol and sulphuric acid, distilling and purifying the crude product by shaking with calcium chloride and rectifying:

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Sodium acetate.}}{NaC_2H_3O_2} + H_2SO_4 = \underset{\text{Acetic ether.}}{C_2H_5C_2H_3O_2} + \underset{\text{Sodium acid sulphate.}}{NaHSO_4} + H_2O.$$

*Experiment* 61.—Add to a mixture of 40 grams of pure alcohol and 100 grams of concentrated sulphuric acid 60 grams of sodium acetate. Introduce this mixture into a boiling-flask, connect it with a Liebig condenser and distil about 50 c.c. Redistil the liquid from a flask, as represented in Fig. 42, and collect the portion which passes over at a temperature of 77° C. (170° F.); it is nearly pure ethyl acetate.

Ethyl acetate is a colorless, neutral, and mobile liquid, of a strong ethereal and somewhat acetous odor, soluble in alcohol, ether, chloroform, etc., in all proportions, and in 17 parts of water. Specific gravity 0.902. Boiling-point about 77° C.

The function of the sulphuric acid in the preparation of ethyl acetate is to combine with water formed in the reaction, thereby making the yield nearly quantitative. When equivalent quantities of alcohol and acetic acid are heated together, only about 65 per cent. of the acid is converted into ester, because at this stage the ester is hydrolyzed by the water liberated, at the same rate at which ester is formed. An equilibrium is reached. While ethyl acetate is prepared by the method described above, it can be made by other methods which are of interest because they are used in the preparation of esters in general. Acid chlorides and acid anhydrides act on alcohols, with formation of esters, thus:

$$\underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\text{Acetyl chloride}}{CH_3COCl} = \underset{\text{Ethyl acetate.}}{CH_3COOC_2H_5} + HCl.$$

$$C_2H_5OH + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} = CH_3COOC_2H_5 + CH_3.COOH.$$

Alkyl halides act on salts of acids, particularly the silver salts, and produce esters, thus:

$$\underset{\text{Silver acetate.}}{CH_3COOAg} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + AgI.$$

**Ethyl Nitrite, $C_2H_5NO_2$ = 75.05** (*Nitrous Ether*).—Can be made by distilling a mixture of alcohol, sulphuric acid, and sodium nitrite:

$$C_2H_5OH + NaNO_2 + H_2SO_4 = C_2H_5NO_2 + NaHSO_4 + H_2O.$$

The distillate, which contains, besides ethyl nitrite, some alcohol and often some decomposition products, is washed with ice-cold water, in which ethyl nitrite is nearly insoluble, and with sodium carbonate to remove traces of acid; finally, it is freed from water by treatment with anhydrous potassium carbonate. It boils at 17° C. (62.6° F.).

The process adopted by the Pharmacopœia differs from the former by dispensing with the distillation and using the insolubility of the ether in ice-cold salt solution for its separation. The process is carried out by pouring a cold solution of sodium nitrite very slowly into an ice-cold mixture of sulphuric acid, alcohol, and water. Decomposition takes place as in the reaction given above. Some sodium-acid sulphate is precipitated and has to be separated from the liquid, which is poured into a separating funnel where two layers form. The lower aqueous solution is drawn off and the remaining nitrous ether is purified like the distillate obtained in the first process. (For assay-method of ethyl nitrite, see paragraph on Gas-analysis.)

*Spirit of nitrous ether, Spiritus ætheris nitrosi, Sweet spirit of niter.* This is a mixture of about 4 parts of ethyl nitrite with 96 parts of alcohol. It is a clear, mobile, volatile, and inflammable liquid, of a pale straw color inclining slightly to green, a fragrant, ethereal odor, and a sharp, burning taste. It is neutral or but very slightly acid to litmus paper but evolves no carbon dioxide with potassium bicarbonate.

**Amyl Nitrite** (*Amylis Nitris*), $C_5H_{11}NO_2$ = **117.09.**—Made by a process analogous to the first one mentioned above for ethyl nitrite, substituting amyl alcohol for ethyl alcohol.

The official amyl nitrite contains about 80 per cent. of this ether, together with variable quantities of undetermined compounds; it is a clear, pale yellowish liquid, of an ethereal, fruity odor, an aromatic taste, and a neutral or slightly acid reaction. Specific gravity 0.865. Boiling-point 96° C. (205° F.). The low boiling-point necessitates special precautions in storing the article. It is best kept in sealed vials and dispensed in sealed glass bulbs, each containing only a few drops of the liquid.

**Methyl Sulphate,** $(CH_3)_2SO_4$.—When methyl alcohol and concentrated sulphuric acid are gently heated together, acid methyl sulphate (methyl sulphuric acid) is formed. When this is distilled under reduced pressure, methyl sulphate is formed, thus:

$$2CH_3.HSO_4 = (CH_3)_2SO_4 + H_2SO_4.$$

It is an oily liquid which boils at 188° C. As the ester is now a comparatively cheap reagent and its use as a methylating agent is very simple, it is replacing the more expensive methyl iodide to a great extent.

A number of esters are manufactured for use in artificial flavoring extracts. Iso-amyl acetate, $C_2H_3O_2.C_5H_{11}$, suggests the odor of pears, methyl butyrate, $C_4H_7O_2.CH_3$, suggests the odor of pine-apples, iso-amyl isovalerate, $C_5H_9O_2.C_5H_{11}$, that of apples, and octyl acetate, $C_2H_3O_2.C_8H_{17}$, that of oranges.

**Fats and Fat Oils.**—All true fats are esters of the triatomic alcohol glycerin, in which the three replaceable hydrogen atoms of the hydroxyl are replaced by three univalent radicals of the higher members of the fatty acids. For instance:

Glycerin $= C_3H_5(OH)_3$ or $C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix}$

Stearic acid $= C_{18}H_{35}O.OH$ or $C_{18}H_{35}O\begin{matrix}\\H\end{matrix}O.$

Stearin or tristearin $= C_3H_5.(C_{18}H_{35}O)_3.O_3$ or $C_3H_5\begin{matrix}(C_{18}H_{35}O).O\\(C_{18}H_{35}O).O\\(C_{18}H_{35}O).O\end{matrix}$

While all natural fats are glycerin in which the three hydrogen atoms are replaced, we may by artificial means introduce but one or two acid radicals, thus forming:

Monostearin $= C_3H_5\begin{matrix}(C_{18}H_{35}O)O\\OH\\OH\end{matrix}$ Distearin $= C_3H_5\begin{matrix}(C_{18}H_{35}O)O\\(C_{18}H_{35}O)O\\(OH)\end{matrix}$

Fats are often termed *glycerides;* stearin being, for instance, the glyceride of stearic acid.

The principal fats consist of mixtures of palmitin, $C_3H_5.(C_{16}H_{31}O_2)_3$, stearin, $C_3H_5(C_{18}H_{35}O_2)_3$, and olein, $C_3H_5.(C_{18}H_{33}O_2)_3$. Stearin and palmitin are solids, olein is a liquid at ordinary temperature; the relative quantity of the three fats mentioned determines its solid or liquid condition. The liquid fats, containing generally olein as their chief constituent, are called *fatty oils* or *fixed oils* in contradistinction to volatile or essential oils.

All fats, when in a pure state, are colorless, odorless, and tasteless substances, which stain paper permanently; they are insoluble in water, difficultly soluble in cold alcohol, easily soluble in ether, disulphide of carbon, benzene, etc. The taste and color of fats are due to foreign substances, often produced by a slight decomposition which has taken place in some of the fat. All fats are lighter than water, and all solid fats fuse below 100° C. (212° F.); fats can be distilled without change at about 300° C. (572° F.), but are decomposed at a higher temperature with the formation of numerous products, some of which have an extremely disagreeable odor, as, for instance, *acrolein,* which has been mentioned before.

Fats being lighter than, and insoluble in, water will float on it, but mechanical mixtures of both substances exist in *emulsions.* These contain finely divided fat globules, suspended in the water, or better in water containing some gum-arabic or a similar substance. Milk and certain plant juices are examples of natural emulsions.

Some fats keep without change when pure; since, however, they generally contain impurities, such as albuminous matter, etc., they suffer decomposition (a kind of fermentation aided by oxidation), which results in a liberation of the fatty acids, which impart their odor and taste to the fats, causing them to become what is generally termed *rancid.*

Some fats, especially some oils, suffer oxidation, which renders them hard. These *drying oils* differ from other oils in being mixtures

of olein with another class of glycerides, containing unsaturated acids with less hydrogen in relation to carbon than oleic acid. Drying oils are prevented from drying by albuminous impurities, which may be removed by treating the oil with 4 per cent. of concentrated sulphuric acid; the acid does not act on the fat, but quickly destroys the albuminous matters, which, with the sulphuric acid, sink to the bottom, while the "refined" oil may be removed by decantation.

Fats are largely distributed in the animal and vegetable kingdoms. They exist in plants chiefly in the seeds, while in animals they are found generally under the skin, around the intestines, and on the muscles.

*Human fat, beef tallow, mutton tallow,* and *lard* are mixtures of palmitin and stearin with some olein. *Butter* consists of the glycerides of butyric acid, caproïc acid, caprylic acid, and capric acid, which are volatile with water vapors, and of myristic, palmitic, oleic, and stearic acids, which are not volatile.

The principal non-drying vegetable oils (consisting chiefly of olein) are *olive oil, cottonseed oil, cocoanut oil, palm oil, almond oil.*

Among the drying oils those of importance are *linseed oil, castor oil, croton oil, hemp oil, cod-liver oil.*

Whenever fats are treated with alkaline hydroxides, or with a number of other metallic oxides, decomposition takes place, the fatty acids combining with the metals, while glycerin is set free. Some of the substances thus formed are of great importance, as, for instance, the various kinds of soap.

The term *saponification,* as used by the chemist, is applied to the decomposition which occurs when neutral fat is split into its constituents, glycerin and fatty acid. This decomposition is a hydrolytic cleavage, and can be produced by the action of boiling alkalies, superheated steam, various enzymes, etc. In other words, the formation of a soap is not an essential part of the process.

**Oleomargarine.**—Oleomargarine is a substitute for butter. It is olein with some stearin and palmitin that has been churned with milk to give it the appearance and flavor of butter. It occurs in the market almost colorless or colored like butter.

**Renovated or "Process" Butter.**—Renovated butter is a product derived from butter of poor quality by a process designed to improve its character. The process in outline is this: Melting of the butter and settling of the curd and brine, skimming off of froth and scum, separation of the curd and brine, blowing of air through the molten fat to remove faulty odors, mixing of milk very thoroughly with the molten fat, rapid cooling and "granulating" of this mixture by running it into ice-cold water, draining and ripening of the granulated mass for a number of hours, salting and working out the excess of milk, packing or making into prints.

There is a marked difference of behavior when butter, oleomargarine and process butter, respectively, are heated in a small tin cup to boiling over a gas flame. Oleomargarine and process butter boil noisily, sputtering more or less like a mixture of grease and water when boiled, and produce no foam, or but very little. Genuine butter boils usually with less noise and *produces an abundance of foam.*

**Waxes.**—These are fat-like substances but differ from true fats in that they contain no glycerin as the basic constituent, but high monatomic saturated alcohols. *Sperm oil*, obtained from the blubber and head cavity of the sperm whale, consists of esters of dodecyl alcohol, $C_{12}H_{25}.OH$, cetyl alcohol, $C_{16}H_{33}.OH$, and others. It is a liquid wax. From it is obtained a crystalline wax called *spermaceti*, which consists chiefly of cetyl palmitate. *Beeswax* consists mainly of myricyl palmitate, $C_{15}H_{31}COOC_{30}H_{61}$, with some cerotic acid, $C_{26}H_{53}COOH$. *Carnauba wax*, of vegetable origin, contains myricyl alcohol, cerotic acid, myricyl cerotate, and other substances.

**Soap.**—Any fat boiled with sodium or potassium hydroxide will form soap. Soft soap is potassium soap, hard soap is sodium soap. The better kinds of hard soap are made by boiling olive oil with sodium hydroxide:

$$\underset{\text{Oleate of glyceryl (olive oil).}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\text{Sodium hydroxide.}}{3NaOH} = \underset{\text{Sodium oleate (hard soap).}}{3NaC_{18}H_{33}O_2} + \underset{\text{Glycerin.}}{C_3H_5(OH)_3}.$$

Soaps are soluble in water and alcohol; they contain rarely less than 30 per cent., but sometimes as much as 70–80 per cent. of water.

Potassium or soft soap is usually yellowish, but it is sometimes tinted green artificially, and is then called "green soap." It contains, besides the potassium salts of the fatty acids, the glycerin liberated in the saponification and relatively much water. Hard or sodium soap is separated from the solution after saponification by adding common salt to the boiling mixture to saturation. The soap, being insoluble in the salt solution, separates as a molten layer, which can be removed after cooling and solidifying. This method of separating the soap is known as the "salting out" process. The soap is free from glycerin, but contains some water.

*Ammonia liniment, Linimentum ammoniæ*, and *lime liniment, Linimentum calcis*, are obtained by mixing cottonseed oil with ammonia-water and lime-water respectively. The oleate of ammonium or calcium is formed, and remains mixed with the liberated glycerin.

*Lead plaster.* Chiefly lead oleate, $Pb(C_{18}H_{33}O_2)_2$. Obtained by boiling lead oxide with olive oil and water for several hours, until a homogeneous, pliable, and tenacious mass is formed. Lead oleate differs from the oleate of the alkalies by its complete insolubility in water.

*Experiment* 62.—Dissolve in a 500 c.c. flask 15 grams of potassium hydroxide in 100 c.c. of alcohol. Melt 50 grams of lard in an evaporating dish and pour the liquefied fat into the flask. Heat over a water-bath, and shake cautiously when the alcohol begins to boil. Saponification takes place very rapidly, and its completion is determined by pouring a few drops of the liquid into a test-tube of water, when any unsaponified fat will float on the surface. When saponification is complete the solution contains soap, glycerin, and any excess of caustic potash.

Pour the contents of the flask into 250 c.c. of hot 5 per cent. sulphuric acid; the fatty acids separate as an oily layer which solidifies on cooling. The solution contains potassium acid sulphate, sulphuric acid, and glycerin. When the solution is neutralized, evaporated to crystallization, and extracted with alcohol, glycerin can be obtained by evaporation of the alcoholic extract.

**Reactions of Fats and Fatty Acids.**—1. Boil 5 grams of suet with 25 c.c. of alcohol and filter while hot. Wash the residue with a little ether, squeeze as dry as possible and then dry in the air. The resulting fibrous mass is the connective-tissue network of the adipose tissue and a little fat. Show the presence of protein in connective tissue by the xanthoproteic and Millon's reactions. On evaporation of the alcoholic filtrate, fat is left.

2. Rub a little fat on glazed white paper. Notice that this "grease-spot" appears dark on a white background in reflected light, but light (transparent) in transmitted light. The stain does not disappear on heating.

3. Heat in a dry test-tube a small quantity of fat with an equal portion of potassium bisulphate. Acrolein is formed and recognized by its odor.

4. Heat about 2 grams of fatty acids with 100 c.c. of water and enough sodium carbonate to dissolve the fatty acids. A solution of sodium soap is formed, of which use a few cubic centimeters for each of the following reactions:

*a.* Heat with an excess of hydrochloric acid; fatty acids are liberated.

*b.* Add calcium chloride solution; insoluble calcium soap is formed, and the solution does not foam on shaking.

*c.* Add lead acetate solution; a white precipitate of an insoluble lead salt (lead plaster) is formed, becoming sticky on heating.

*d.* Add some olive oil and shake well; a homogeneous milk-like mixture—*i. e.*, emulsion—is formed.

**Wool Fat, Lanolin** (*Adeps Lanæ*).—This is the fat, or mixture of fats, found in sheep's wool and obtained by treating the wool with soap-water, and acidifying the wash liquor, when the fats separate unchanged. These fats differ from the fats spoken of above in so far as the alcohol present is not glycerin, but an alcohol, or rather two isomeric alcohols of the composition $C_{26}H_{43}OH$ and known as *cholesterin* and *isocholesterin*. These alcohols, which are white, crystalline, fusible substances, when in combination with fatty acids form the compound ethers known as lanolin.

Lanolin is a yellowish-white (or, when not sufficiently purified, a more or less brownish), fat-like substance, having the peculiar odor of sheep's wool and fusing at about 40° C. (104° F.), forming an oily liquid. Unlike true fats, lanolin is capable of mixing with twice its weight of water or aqueous solutions and yet retaining its fatty consistency; it is, moreover, much less liable to decompose than fats, and it is this property and its power to mix with aqueous solutions which have rendered lanolin a valuable agent in certain pharmaceutical preparations. Official is also *hydrous wool-fat*, the purified fat mixed with not more than 30 per cent. of water.

**Cholesterin, $C_{26}H_{43}.OH$.**—Cholesterin is the only alcohol occurring in the free state in the human body. It is present in small quantity in the blood and many tissues; in abundance in the white matter of the spinal chord and in nerves. It is a constituent of bile, and often makes up nearly the whole mass of gall-stones from which the alcohol can be conveniently extracted. Cholesterin is a

glittering white crystalline substance, soapy to the touch. From hot alcohol, it crystallizes in rhombic tables which are characteristic for recognition. It melts at 145° C. and boils at 360° C. It is soluble in solutions of the bile salts.

**Lecithins, $C_{44}H_{90}NPO_9$ or $C_{42}H_{84}NPO_9$.**—*Lecithin*, one of the constituents of bile, is a member of the group of substances generally termed *phosphorized fats* or *lecithins*. These bodies are highly complex in composition, and may be looked upon as fats formed from glycerophosphoric acid by substitution of hydrogen atoms with two fatty acid radicals and a base, choline. Thus, by introducing the radicals of stearic acid and of choline distearyl-lecithin is obtained of the composition, $C_3H_5(C_{18}H_{35}O_2)_2.HPO_4.C_2H_4N(CH_3)_3OH$.

## 48. CARBOHYDRATES.

**General Remarks.**—The name carbohydrates was originally given to a class of compounds found chiefly in plants, and containing in the molecule 6 atoms of carbon (or a multiple of 6) in combination with hydrogen and oxygen in the proportion to form water, as shown in the formula for grape-sugar, $C_6H_{12}O_6$, cane-sugar, $C_{12}H_{22}O_{11}$, etc. While even formerly the name was not well chosen, because it implies that these substances are carbon in combination with water, today it is still less suitable, because members of the group have been found which do not contain oxygen and hydrogen in the proportion mentioned; as, for instance, a sugar, termed rhamnose, having the composition $C_6H_{12}O_5$. We also know now carbohydrates containing carbon atoms in numbers which have no relation to 6. While, therefore, the term carbohydrate no longer implies what it formerly did, and no longer refers to the restricted number of compounds which it formerly included, yet it is retained for the whole group of compounds now to be considered.

The group includes now, as heretofore, the different sugars, starches, gums, etc., and also a number of compounds obtained by artificial or synthetic processes. In order to show in its name that a substance belongs to the carbohydrates, the ending *ose* is used to distinguish these bodies from the members of other groups.

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QUESTIONS.—Explain the constitution of simple and mixed ethers and esters. To what inorganic compounds are they analogous? State the general processes for the formation of ethers and esters. What is the composition of ethyl ether? Explain the process of its manufacture in words and symbols, and state its properties. How is acetic ether made, and what are its properties? What is sweet spirit of niter, and how is it made? State the general composition of fats and the chief constituents of tallow, butter, and olive oil. What is the solubility of fats in water, alcohol, and ether; how do heat and oxygen act upon them; what is the cause of their becoming rancid? Explain the composition and manufacture of soap, and state the difference between hard and soft soap. How are ammonia liniment, lime liniment, and lead plaster made, and what is their composition? What is the source of lanolin; what are its constituents and properties?

**Constitution.**—While the true atomic structure of many carbohydrates is as yet not fully understood, the structure of others is well known. It appears that some carbohydrates are true aldehydes, while others are closely related to ketones, and yet others are the anhydrides, or condensation products of the former.

Thus, a sugar of the composition $C_3H_6O_3$, termed *glycerose*, is obtained by the action of mild oxidizing agents on glycerin, thus:

$$C_3H_8O_3 + O = C_3H_6O_3 + H_2O.$$

If we bear in mind the fact that glycerin, $C_3H_5(OH)_3$, is a triatomic alcohol, and that alcohols by oxidation yield aldehydes, we realize the analogy existing between the above reaction and that leading to the formation of the aldehydes, previously considered.

In a manner similar to the one producing glycerose from glycerin, a sugar of the composition $C_4H_8O_4$, and called *erythrose*, is obtained from the tetratomic alcohol *erythrite*, $C_4H_6(OH)_4$, while a sugar of the composition $C_6H_{12}O_6$ is obtainable from the hexatomic alcohol *mannite*, $C_6H_8(OH)_6$. In both cases two atoms of hydrogen are split off from the alcohol molecules.

The relationship existing between the sugars of the composition $C_6H_{12}O_6$ and other carbohydrates having the composition $C_6H_{10}O_5$ or $C_{12}H_{22}O_{11}$ can be readily shown by the equations:

$$x(C_6H_{12}O_6 - H_2O) = (C_6H_{10}O_5)x$$
$$2(C_6H_{12}O_6) - H_2O = C_{12}H_{22}O_{11},$$

which show that abstraction of water leads to the formation of compounds having the composition of starch, $C_6H_{10}O_5$, and cane-sugar, $C_{12}H_{22}O_{11}$, respectively. While this abstraction of water is difficult, it is an easy matter to cause starch or cane-sugar to take up water, with the result that sugars of the composition $C_6H_{12}O_6$ are formed.

**Properties.**—Carbohydrates are either fermentable, or can, in most cases, be converted into substances which are capable of fermentation. They are not volatile, but suffer decomposition when sufficiently heated; they have neither acid nor basic properties, but are of a neutral reaction. Oxidizing agents convert them into saccharic and mucic acids and finally into oxalic acid. (Soluble carbohydrates have generally the property of turning the plane of polarized light.)

Most carbohydrates are white, solid substances, and, with the exception of a few, soluble in water. Those carbohydrates belonging to the sugars have a more or less sweet taste. Many of them, especially glucose, are good reducing agents, as is shown by the fact that they deoxidize in alkaline solution salts (or oxides) of copper, bismuth, mercury, gold, etc., either to a lower state of oxidation or to the metallic state.

**Occurrence in Nature.**—No other organic substances are found in such immense quantities in the vegetable kingdom as the members of this group, cellulose being a chief constituent of all, starch and various kinds of sugar of most plants. Carbohydrates are also

found as products of animal life, as, for instance, the sugar in milk, in bees' honey, etc.

**Classification.**—The carbohydrates are conveniently divided into the following three groups:

1. *Monosaccharides, or simple sugars.* To this group belong the sugars which cannot be broken down into two or more simple sugars. They contain from 3 to 9 atoms of carbon, in most cases the same number of oxygen atoms, and double the number of hydrogen atoms. (Dextrose, levulose, galactose, etc.).

2. *Disaccharides, or complex sugars.* These are sugars which, on taking up 1 molecule of water, split up into two simple sugars. (Cane-sugar, maltose, lactose, etc.).

3. *Polysaccharides.* These do not resemble sugars, have no sweet taste, and form simple sugars only after repeated cleavages. (Starches, gums, cellulose, etc.).

## Monosaccharides.

The monosaccharides are white, odorless, sweet, crystallizable, neutral substances, readily soluble in water, sparingly soluble in alcohol, insoluble in ether. Like all aldehydes and ketones they are easily oxidized, acting as strong reducing agents. Trommer's, Fehling's, and Boettger's "reduction tests" depend on this property. Solutions of monosaccharides, acidified with acetic acid, give with phenyl-hydrazine crystalline precipitates of substance called *osazones*. The trioses, hexoses, and nonoses are capable of alcoholic fermentation, the others are not. Most of the monosaccharides are optically active.

According to the number of carbon atoms present, the monosaccharides are again subdivided into classes called trioses, tetroses, pentoses, hexoses, heptoses, octoses, and nonoses, having the composition $C_3H_6O_3$, $C_4H_8O_4$, $C_5H_{10}O_5$, $C_6H_{12}O_6$, $C_7H_{14}O_7$, $C_8H_{16}O_8$, and $C_9H_{18}O_9$, respectively. The hexoses are the best-known group, which is again subdivided into two groups, viz., the *aldoses*, containing the alcohol group, $CH_2OH$, and the aldehyde group, COH; and the *ketoses*, containing the alcohol group and the ketone group, CO. The constitution of these compounds is shown thus:

| | *Trioses.* | *Tetroses.* | *Pentoses.* | *Hexoses.* |
|---|---|---|---|---|
| Aldoses | COH<br>\|<br>CHOH<br>\|<br>$CH_2OH$ | COH<br>\|<br>$(CHOH)_2$<br>\|<br>$CH_2OH$ | COH<br>\|<br>$(CHOH)_3$<br>\|<br>$CH_2OH$ | COH<br>\|<br>$(CHOH)_4$<br>\|<br>$CH_2OH$. |
| Ketoses | $CH_2OH$<br>\|<br>CO<br>\|<br>$CH_2OH$ | $CH_2OH$<br>\|<br>CO<br>\|<br>CHOH<br>\|<br>$CH_2OH$ | $CH_2OH$<br>\|<br>CO<br>\|<br>$(CHOH)_2$<br>\|<br>$CH_2OH$ | $CH_2OH$<br>\|<br>CO<br>\|<br>$(CHOH)_3$<br>\|<br>$CH_2OH$. |

Glucose is an aldo-hexose, while fructose is a keto-hexose.

**Dextrose, Glucose, Grape-sugar, $C_6H_{12}O_6$.**—This substance is very abundantly diffused throughout the vegetable kingdom, and is generally accompanied by fruit-sugar. It is contained in large quantities in the juice of many fruits; the percentage of grape-sugar in the dried fig is about 65, in grape 10–20, in cherry 11, in mulberry 9, in strawberry 6, etc.

Dextrose is found also in honey and in minute quantities in the normal blood (0.1 per cent. or less), and traces occur, perhaps, in normal urine, the quantity in both liquids rising, however, during certain diseases, as high as 5 per cent. or higher.

Grape-sugar is produced in the plant from starch by the action of the vegetable acids present; it may be obtained artificially from starch (and from many other carbohydrates) by heating with dilute mineral (sulphuric) acids, which convert starch first into dextrin and then into grape-sugar. Corn-starch is now largely used for that purpose, the excess of sulphuric acid being removed by treating the solution with chalk; the filtered solution is either evaporated to a syrup and sold as "glucose," or evaporated to dryness, when the commercial "grape-sugar" is obtained.

*Experiment* 63.—Heat to boiling 100 c.c. of a 1 per cent. sulphuric acid and add to it very gradually and with constant stirring a mixture made by rubbing together 25 grams of starch and 25 grams of water. Continue to boil until iodine no longer causes a blue color (which shows complete conversion of starch into either dextrin or glucose), and until 1 c.c. of the solution is no longer precipitated on the addition of 6 c.c. of alcohol (which shows the conversion of dextrin into sugar, dextrin being precipitated by alcohol). Apply to a portion of the glucose solution thus obtained, and neutralized by sodium carbonate, the tests mentioned below. To the remaining solution add a quantity of precipitated calcium carbonate sufficient to convert all sulphuric acid into calcium sulphate. Filter, evaporate the solution to a syrup and notice its sweet taste.

Glucose is met with generally as a thick syrup which crystallizes with difficulty, combining during crystallization with one molecule of water; but anhydrous crystals, closely resembling those of cane-sugar, are also known. Glucose is soluble in its own weight of water and is less sweet than cane-sugar, the sweetness of glucose compared to that of cane-sugar being about 3 to 5; when heated to 170° C. (338° F.) it loses water, and is converted into *glucosan*, $C_6H_{10}O_5$; by stronger heating it loses more water and forms *caramel*, a mixture of various substances; it turns the plane of polarized light to the right. It is official as *glucosum*.

By gentle oxidation dextrose is first converted into monobasic *gluconic acid*, $C_6H_{12}O_7 = C_5H_6.(OH)_5.CO_2H$, and then into dibasic *saccharic acid*, $C_6H_{10}O_8 = C_4H_4.(OH)_4.(CO_2H)_2$. Further oxidation results in the formation of acids of lower molecular weight, due to splitting up of the molecules. (Saccharic acid is soluble in less than its own weight of water.)

Dextrose combines with various metallic oxides (alkalies, alkaline

earths, etc.), and also with a number of other substances, forming a series of compounds known as glucosides.

*Dextrose may be recognized analytically:*

1. By causing a bright red precipitate of cuprous oxide, when boiled with a solution of cupric sulphate in sodium hydroxide, to which tartaric acid has been added. (A solution containing these three substances in definite proportions is known as Fehling's solution. (See Index.)

2. By precipitating metallic silver, bismuth, and mercury, when compounds of these metals are heated with it in the presence of caustic alkalies.

3. By easily fermenting when yeast is added to the solution, alcohol and carbon dioxide being formed:

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2.$$

4. By forming with an excess of phenyl-hydrazine, in a solution acidified with acetic acid, a yellow crystalline precipitate of phenyl-dextrosazone.

**Levulose, Fructose, $C_6H_{12}O_6$** (*Fruit-sugar*).—Levulose occurs with glucose in sweet fruits and honey; it resembles glucose in most chemical and physical properties, but does not crystallize from an aqueous solution; it may, however, be obtained in white silky needles from an alcoholic solution; it is met with generally as a thick syrup, is about as sweet as cane-sugar, and turns the plane of polarized light to the left; it is formed by the action of dilute mineral acids or ferments on cane-sugar, which latter takes up water and breaks up thus:

$$\underset{\text{Cane-sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Fructose.}}{C_6H_{12}O_6}.$$

Levulose has been made by the polymerization of formic aldehyde, $CH_2O$, and also by several other reactions.

*Mannose*, $C_6H_{12}O_6$. Obtained by the oxidation of mannite; it does not crystallize and resembles grape-sugar.

**Galactose, $C_6H_{12}O_6$,** is formed together with dextrose when either milk-sugar or gum-arabic is boiled with dilute sulphuric acid. Galactose crystallizes, reduces an alkaline copper solution, and ferments with yeast.

When oxidized by heating with nitric acid, galactose forms *galactonic acid* and *mucic acids*, which are isomeric with the above-mentioned gluconic and saccharic acids. Mucic acid is easily distinguished from saccharic acid by being almost insoluble in water.

**Inosite, $C_6H_{12}O_6$** (*Muscle-sugar*).—This compound was classed with the carbohydrates on account of its sweet taste; its readiness to undergo lactic and butyric fermentation; and the identity of its molecular formula with that of the hexoses. It has, however, been

shown that inosite has an entirely different constitution, being a hexahydroxyl derivative of hexahydrobenzene, $C_6H_6(OH)_6$.

Inosite occurs somewhat abundantly in unripe beans and peas, and sparingly in the liquid of muscular tissue; traces are found in urine, the quantity increasing in certain diseases. It does not ferment with yeast, does not reduce alkaline copper solution, and is optically inactive.

## Disaccharides.

The general physical properties and the solubility of disaccharides are identical with those of the monosaccharides. They differ from them by not fermenting *directly*. One member of the group, cane-sugar, neither reduces metallic salts nor forms an osazone. The empirical formula is $C_{12}H_{22}O_{11}$. By treatment with dilute mineral acids or by the action of certain enzymes they undergo hydrolysis, *i. e.*, take up a molecule of water and are resolved into two hexose molecules. Thus, cane-sugar splits up into dextrose and levulose; lactose into dextrose and galactose; maltose into two molecules of dextrose.

Cane-sugar is dextrorotatory, but the mixture obtained by the hydrolysis of cane-sugar is lævorotatory, because levulose turns the plane of polarization more to the left than dextrose does to the right. For this reason the mixture is called inverted sugar and the hydrolysis, inversion. The term *inversion* is therefore used to designate the splitting of disaccharides into simpler sugars. The building up of complex sugars from simple sugars is called *reversion*.

Lactose and maltose reduce alkaline copper solution; cane-sugar does not.

**Cane-sugar** (*Saccharum*), $\mathbf{C_{12}H_{22}O_{11}}$ **= 342.17** (*Saccharose, Common sugar, Beet-sugar*).—Cane-sugar is found in the juices of many plants, especially in that of the different grasses (sugar-cane), and also in the sap of several forest trees (maple), in the roots, stems, and other parts of various plants (sugar-beet), etc. Plants containing cane-sugar do not contain free organic acids, which latter would convert it into grape-sugar.

Cane-sugar is manufactured from various plants containing it by crushing them between rollers, expressing the juice, heating and adding to it milk of lime, which precipitates vegetable albuminous matter. The clear liquid is evaporated to the consistency of a syrup, which is further purified (refined) by filtering it through bone-black and evaporating the solution in "vacuum pans" to the crystallizing-point; the mother-liquors are further evaporated, and yield lower grades of sugar; finally a syrup is left which is known as *molasses*.

Cane-sugar forms white, hard, distinctly crystalline granules, but may be obtained also in well-formed, large, monoclinic prisms. It dissolves in 0.2 part of boiling, in 0.5 part of cold water, and in 175 parts of alcohol; when heated to 160° C. (320° F.) it fuses, and the

liquid, on cooling, forms an amorphous, transparent mass, known as *barley sugar;* at a higher temperature cane-sugar is decomposed, water is evolved, and a brown, almost tasteless substance is formed, which is known as *caramel* or burnt sugar. When greater heat is applied, numerous products of decomposition are given off and finally a residue of pure carbon is left. The following substances have been identified among the products of decomposition: carbon monoxide and dioxide, methane, ethylene, acetylene, acetone, formic and acetic acids, aldehyde, acrolein, and water. Oxidizing agents act energetically upon cane-sugar, which is a strong reducing agent. A mixture of cane-sugar and potassium chlorate will deflagrate when moistened with sulphuric acid; potassium permanganate is readily deoxidized in acid solution; cane-sugar, however, does not affect an alkaline copper solution, and does not itself ferment; but when heated with dilute acids or left in contact with yeast in the presence of various bacteria it is decomposed into dextrose and levulose, both of which are fermentable. Like dextrose, cane-sugar forms compounds with metals, metallic oxides, and salts, which compounds are known as *sucrates.*

*Experiment* 64.—Make a 1 per cent. cane-sugar solution; test it with Fehling's solution and notice that no cuprous oxide is precipitated. Add to 50 c.c. of the cane-sugar solution 5 drops of hydrochloric acid and heat on a water-bath for half an hour. Again examine the liquid with Fehling's solution; a precipitate of cuprous oxide is now formed, proving the conversion of cane-sugar into dextrose (grape-sugar) and levulose.

**Maltose, $C_{12}H_{22}O_{11}$.**—Maltose is obtained by the action of *diastase* on starch. Diastase is a substance formed during the germination of various seeds (rye, wheat, barley, etc.), and it is for this reason that grain used for alcoholic liquors is converted into *malt, i. e.,* is allowed to germinate, during which process diastase is formed, which, acting upon the starch present, converts it into maltose and dextrin:

$$\underset{\text{Starch.}}{3(C_6H_{10}O_5)} + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin.}}{C_6H_{10}O_5}.$$

Maltose is also formed by the action of dilute sulphuric acid upon starch, and is hence often present in commercial glucose; by further treatment with sulphuric acid it is converted into dextrose. Maltose crystallizes, reduces alkaline copper solutions, and ferments with yeast.

*Melitose,* $C_{12}H_{22}O_{11}$, is the chief constituent of Australian manna.

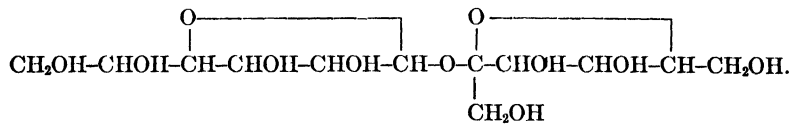
**Sugar of Milk** (*Saccharum Lactis*), $C_{12}H_{22}O_{11} + H_2O = 360.19$ (*Lactose*).—Found almost exclusively in the milk of the mammalia. Obtained by freeing milk from casein and fat and evaporating the remaining liquid (whey) to a small bulk, when the milk-sugar crystallizes on cooling.

It forms white, hard, crystalline masses; it is soluble in about 6 parts of water (at 15° C., 59° F.) and in 1 part of boiling water,

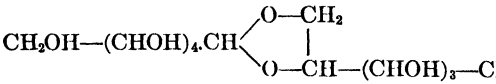
insoluble in alcohol and ether; it is much harder than cane-sugar, and but faintly sweet; it is not easily brought into alcoholic fermentation by the action of yeast, but easily undergoes "lactic fermentation" when cheese is added. During this process milk-sugar is converted into lactic acid. By hydrolysis, lactose is split into dextrose and galactose.

Milk-sugar resembles dextrose in its action on alkaline solution of copper, from which it precipitates cuprous oxide; it differs from it by not fermenting with yeast, and in forming mucic acid when heated with nitric acid.

**Structure of Disaccharides.**—These sugars are evidently the result of a combination of two molecules of simple hexose sugars with elimination of a molecule of water. The fact that they are hydrolyzed so easily indicates that the two hexose molecules are united through the medium of oxygen rather than by carbon. Milk-sugar and maltose represent one type of disaccharide. They reduce Fehling's solution and combine with phenyl-hydrazine, which facts point to the presence of an aldehyde or ketone group in their molecules. Cane-sugar represents another type of disaccharide. It does not reduce Fehling's solution nor does it combine with phenyl-hydrazine, which behavior points to the absence of an aldehyde or ketone group in its molecule. It forms acetyl derivatives, the highest one containing eight acetyl radicals in the molecule, showing the presence of eight (OH) groups in the cane-sugar molecule. From these and other considerations, it is probable that the structure of cane-sugar is



The structure of milk-sugar and maltose is probably,



**Raffinose, $C_{18}H_{32}O_{16}.5H_2O$.**—Raffinose is the principal trisaccharide. It can be obtained from beet-sugar molasses, cottonseed, barley, etc. It is crystalline, dextrorotatory, does not reduce Fehling's solution, and by hydrolysis yields dextrose, levulose, and galactose.

## Polysaccharides.

To the polysaccharides belong the starches, gums, cellulose, glycogen, etc. They differ from the two previous groups by being insoluble in water or soluble with difficulty; by not crystallizing and not being diffusible. These latter properties are generally characteristic of substances of high molecular weight. By hydrolysis polysaccharides split, forming dextrins, disaccharides, and monosaccharides; their general composition is indicated by $(C_6H_{10}O_5)_x$, which means that the molecules are made up of an unknown multiple of $C_6H_{10}O_5$. The constitution is unknown.

**Starch** (*Amylum*) $(C_6H_{10}O_5)_x$. Starch is very widely distributed in the vegetable kingdom, and is found chiefly in the seeds of cereals and leguminosæ, but also in the roots, stems, and seeds of nearly all plants.

It is prepared from wheat, potatoes, rice, beans, sago, arrow-root, etc., by a mechanical operation. The vegetable matter containing the starch is comminuted by rasping or grinding, in order to open the cells in which it is deposited, and then steeped in water; the softened mass is then rubbed on a sieve under a current of water which washes out the starch, while cellular fibrous matter remains on the sieve; the starch deposits slowly from the washings, and is further purified by treating it with water.

Starch forms white, amorphous, tasteless masses which are peculiarly slippery to the touch, and easily converted into a powder; it is insoluble in cold water, alcohol, and ether; when boiled with water, it yields a white jelly (mucilage of starch, starch-paste) which cannot be looked upon as a true solution, but is a suspension of the swollen starch particles in water; by continued boiling with much water some starch passes into solution.

Starch, when examined under the microscope, is seen to consist of granules differing in size, shape, and appearance, according to the plant from which the starch was obtained. Concentric layers, which are more or less characteristic of starch-granules, show that they are formed in the plant by a gradual deposition of starch matter.

The most characteristic test for starch is the dark blue color which iodine imparts to it (or better to the mucilage). This color is due to the formation of *iodized starch*, an unstable dark blue compound of the doubtful composition $C_6H_9IO_5I$.

Starch is an important article of food, especially when associated, as in ordinary flour, with albuminous substances. In the body starch, as well as other carbohydrates, must be converted into monosaccharides before being absorbed. This hydrolysis of starch may be made outside the body acting on starch paste with some diastatic enzyme, or by prolonged boiling with very dilute (1 per cent.) mineral acid. The intermediate products of the hydrolysis are the same in either case. Starch is first converted into *soluble starch* or *amylo-dextrin*, which gives a *blue* color with iodine; the soluble starch next passes into *malto-dextrin* and *erythro-dextrin*, giving a *red* color with iodine; erythro-dextrin passes into malto-dextrin and *achroö-dextrin*, giving *no* color with iodine, but forming a white precipitate with alcohol. Achroö-dextrin passes into *maltose*, and maltose into *dextrose*. The hydrolysis is a progressive reaction, all these compounds being present in the solution at one time.

**Dextrin, $C_6H_{10}O_5$** (*British Gum*).—This name is given to a mixture of the dextrins just mentioned, and formed by hydrolysis of starch by means of diluted acids, or by subjecting starch to a dry heat of 175° C. (347° F.), or by the action of diastase (infusion of malt) upon starch. Malt is made by steeping barley in water until it germinates, and then drying it.

Dextrin is a colorless or slightly yellowish, amorphous powder, resembling gum-arabic in some respects; it is soluble in water, does not reduce alkaline copper solution, and is colored light wine-red by iodine. It is extensively used in mucilage as a substitute for gum-arabic.

**Inulin** ($C_6H_{10}O_5)_x$.—Inulin, which is similar to starch, occurs in the roots of elecampane, chicory, dandelion, tubers of dahlia, etc. It is a white powder, slightly soluble in cold water but readily in hot water, and does not form a jelly as starch does. It is not fermentable or acted on by diastase, and is not colored by iodine. When boiled with dilute acid it forms levulose.

**Gums.**—These are amorphous substances of vegetable origin, soluble in water or swelling up in it, forming thick, sticky masses; they are insoluble in alcohol, and are converted into glucose by boiling with dilute sulphuric acid. Some gums belong to the saccharoses, others to the amyloses.

*Acacia, Gum-arabic* is a gummy exudation from Acacia Senegal; it consists chiefly of the calcium salt of *arabic acid*, $C_{12}H_{22}O_{11}$. Other gums occur in the cherry tree, in linseed or flaxseed, in Irish moss, in marsh-mallow root, etc.

Gum-arabic dissolves slowly in 2 parts of water; this solution shows an acid reaction with litmus, and yields precipitates with lead acetate or ferric chloride.

**Cellulose** ($C_6H_{10}O_5)_x$, perhaps $C_{18}H_{30}O_{15}$ (*Plant fibre, Lignin*).—Cellulose constitutes the fundamental material of which the cellular membrane of vegetables is built up, and forms, therefore, the largest portion of the solid parts of every plant; it is well adapted to this purpose on account of its insolubility in water and most other solvents, its resistance to either alkaline or acid liquids, and its tough and flexible nature. Some parts of vegetables (cotton, hemp, and flax, for instance) are nearly pure cellulose.

Pure cellulose is a white, translucent mass, insoluble in all the common solvents. It is not colored blue by iodine.

The best solvent for cellulose is an ammoniacal solution of copper hydroxide, known as Schweitzer's reagent, a very efficient preparation of which is obtained as follows: 2 grams of pure crystallized copper sulphate are dissolved in 100 c.c. of water to which a few drops of a concentrated solution of ammonium chloride have been added; 1 gram of potassium hydroxide is dissolved in 100 c.c. of water and a little of a solution of barium hydroxide added to precipitate any carbonate in the alkali. The two solutions are mixed and the precipitate thoroughly washed by decantation and on the filter-paper. The moist copper hydroxide is finally covered in a beaker with just enough concentrated ammonia water to dissolve it. The clear solution is decanted or filtered through glass wool. It must be preserved in a dark place.

Cellulose is precipitated from its solution in Schweitzer's reagent by acids as a gelatinous mass which forms a grayish powder when dried.

Treated with concentrated sulphuric acid it swells up and gradually dissolves; water precipitates from such solutions a substance

known as *amyloid*, which is an altered cellulose giving a blue color with iodine. Upon diluting the sulphuric acid solution with water and boiling it, the cellulose is gradually converted into dextrin and dextrose.

Unsized paper (which is chiefly cellulose), dipped into a mixture of two volumes of sulphuric acid and one volume of water, forms, after being washed and dried, the so-called "parchment paper," which possesses all the valuable properties of parchment.

Official purified cotton, known commercially as absorbent cotton, is prepared from raw cotton by boiling it in a weak solution of alkali to remove fatty matter, then treating it with a weak solution of chlorinated lime to bleach it. It is then washed and dried.

Medicated cotton is usually prepared by impregnating absorbent cotton with a solution of the medicinal agent in alcohol and glycerin, and drying. The glycerin is not volatilized and serves as an adhesive agent for retaining the active ingredient on the fiber of the cotton. Benzoated, borated, carbolated, iodized, salicylated, and other medicated cotton is prepared in this or a similar manner. The percentage of medicinal agent present must be calculated on the basis of finished product; thus, 25 grams of 10 per cent. borated cotton should contain 2.5 grams of boric acid, or 10 grams of 5 per cent. carbolated cotton should contain 0.5 gram of pure carbolic acid.

When cellulose is treated with about a 23 per cent. solution of sodium hydroxide (sp. gr. 1.25), it forms a compound with the alkali, which is decomposed by water into a hydrate of cellulose. Cotton fibres, treated thus, swell, become rounded, shrink, assume a lustre and appearance like silk, have their cell cavities almost obliterated, increase in weight, and hold dyes better. This product is known as "mercerized cotton." To prevent shrinkage, cotton fabrics are stretched on frames while being mercerized, washed, and dried.

When cellulose is treated with sodium hydroxide and carbon disulphide, a compound of the three substances is formed, known as cellulose xanthate, which is a salt of thiocarbonic acid, $CS{<}^{OH}_{SH}$. With a little water, cellulose xanthate forms a thick solution called *viscose*. When this is forced through a capillary opening into a solution of certain salts, it is decomposed and cellulose is reformed. The threads have a silky sheen and are used in the manufacture of artificial silk.

Cellulose triacetate is manufactured for producing thin, tough films, which are used to cover stoppers in bottles, for insulating copper wire, etc.

**Pyroxylin** (*Pyroxylinum*), chiefly *cellulose tetra-nitrate*, $\mathbf{C_{12}H_{16}O_6(NO_3)_4}$. (*Soluble gun-cotton, Nitro-cellulose.*)—Cellulose has the power to unite with acids to form ethereal salts (esters), thus exhibiting alcoholic character. When immersed in varying mixtures of concentrated nitric and sulphuric acids, and for different lengths of time, di-, tri-, tetra-, penta-, and hexa-nitrate are formed, thus:

$$C_{12}H_{20}O_{10} + 2HNO_3 = 2H_2O + C_{12}H_{18}O_8(NO_3)_2.$$
$$C_{12}H_{20}O_{10} + 4HNO_3 = 4H_2O + C_{12}H_{16}O_6(NO_3)_4.$$
$$C_{12}H_{20}O_{10} + 6HNO_3 = 6H_2O + C_{12}H_{14}O_4(NO_3)_6.$$

The sulphuric acid used takes no part in the reaction, but facilitates the same by absorbing the water which is eliminated.

The di-, tri-, and tetra-nitrate are soluble in a mixture of alcohol and ether, which solution is known as *collodion*. These lower soluble nitrates, better known as collodion cotton, are official in the U. S. and British Pharmacopœias as pyroxylin; colloxylin is also used as a synonym in this country. In Europe pyroxylin is applied to the higher (penta- and hexa-) nitrates, which are insoluble in a mixture of alcohol and ether, while colloxylin is applied to the soluble collodion cotton. The penta- and hexa-nitrates form the highly explosive *gun-cotton*. A solution of collodion cotton in molten camphor hardens upon cooling and is then known as *celluloid*. When warmed it becomes plastic and can be molded into various shapes.

*Flexible collodion* is a mixture of collodion, castor oil, and Canada balsam, which is much less constringent than official collodion. *Cantharidal (blistering) collodion* contains extract of cantharides and has blistering properties. For medication, any substance, soluble *in ether*, may be added to collodion, such as iodine, iodoform, salicylic acid, croton oil, extract of Indian cannabis, mercuric chloride, resorcinol, pyrogallol, atropine, etc.

*Smokeless gunpowder* is gun-cotton, first made gelatinous by acetone, acetic ether, or like substances, then dried and granulated. Smokeless powder occupies less space and burns more slowly than gun-cotton.

*Experiment* 65.—Immerse 2 grams of dry cotton for ten hours in a previously cooled mixture of 28 c.c. of nitric acid and 44 c.c. of sulphuric acid. Wash the pyroxylin thus obtained with cold water until the washings have no longer an acid reaction. Dissolve 1 gram of the dry pyroxylin in a mixture of 25 c.c. of ether and 8 c.c. of alcohol. The solution obtained is collodion.

Pyroxylin in well-closed bottles exposed to light decomposes with evolution of nitrous vapors and a carbonaceous mass is left. It should be kept dry and in a carton. The compound ether nature of all cellulose nitrates is shown by the fact that the nitric acid is eliminated and cellulose reformed by the action of alkalies, of concentrated sulphuric acid, and by reducing agents. Treated with a solution of a ferrous salt in hydrochloric acid, they decompose just as any nitrate, liberating nitric oxide gas.

**Glycogen** ($C_6H_{10}O_5)_x$.—Found in animals and many fungi; it occurs in the liver, the white blood corpuscles, in many embryonic tissues, and in muscular tissue. Pure glycogen is a white, starch-like, amorphous substance, insoluble in alcohol. It forms an opalescent solution with water, gives a red color with iodine, and by hydrolysis is converted into glucose. It does not reduce Fehling's solution or ferment.

**Glucosides.**—This term is applied to a group of substances (chiefly of vegetable origin) which, by the action of dilute acids or enzymes, are decomposed with the production of a sugar, and one or two other substances not carbohydrates. To this class of bodies belong amyg-

dalin, digitalin, indican, myronic acid, salicin, etc. Some of these compounds will be considered later on.

## 49. COMPOUNDS CONTAINING NITROGEN.

Organic compounds may contain nitrogen in three forms, viz., as nitric (or nitrous) acid, ammonia, cyanogen, or derivatives of these compounds.

### Derivatives of Nitric Acid.

Organic compounds containing nitrogen in the nitric acid form do not occur in nature, but are obtained exclusively by artificial means, often by treatment of the organic substance with concentrated nitric acid. Many of these compounds are highly combustible or more or less explosive, as, for instance, cellulose trinitrate, mercuric fulminate, and others.

Nitric or nitrous acid may combine with organic bases, forming salts, such as strychnine nitrate, urea nitrate, etc.; or with alcohols when esters result, such as glyceryl nitrate, ethyl nitrite, etc. Some of these compounds have been considered before.

**Nitro compounds.** These consist of radicals in combination with the nitric acid residue $NO_2$; thus, $R.NO_2$. They are isomeric with the esters of nitrous acid, but behave quite differently from these; for instance, they yield no alkali nitrite when treated with alkalies, as is the case when esters are thus treated. The difference in structure is represented thus:

$R—O—NO$, Nitrite. $\qquad$ $R—NO_2$, Nitro compound.

The highly important nitro compounds of the benzene series can be obtained by treating the hydrocarbons directly with nitric acid; thus:

$$C_6H_6 + HONO_2 = C_6H_5NO_2 + H_2O.$$

Nitric acid does not react with fatty hydrocarbons, but their nitro deriva-

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QUESTIONS.—To which group of substances is the term "carbohydrates" applied? State the general properties of carbohydrates. Mention the three groups of carbohydrates, and the composition and characteristics of the members of each group. Mention some fruits in which grape-sugar, and some plants in which cane-sugar is found. What is the difference between grape-sugar and cane-sugar, and by what tests can they be distinguished? From what source, and by what process, is milk-sugar obtained? What is starch, what are its properties, by what tests can it be recognized, and what substance is formed when diastase or dilute acids act upon it? Where is cellulose found in nature, and what are its properties? What compounds may be obtained by the action of nitric acid upon cellulose, and what are they used for? What substances are termed glucosides? Mention some of the more important glucosides.

tives can be obtained by indirect processes, for instance, by treating the halogen derivatives with silver nitrite:

$$\underset{\text{Methyl chloride.}}{CH_3Cl} + AgNO_2 = \underset{\text{Nitro-methane.}}{CH_3NO_2} + AgCl$$

This reaction is anomalous, since we would expect to obtain a true ester of nitrous acid, corresponding to silver nitrite, whereas the resulting product is not an ester, but a nitro compound. A rearrangement takes place during the reaction of the two substances on each other. Other cases of this kind are known, for example, the formation of organic isocyanides (which see) from silver cyanide.

**Nitroso and isonitroso compounds.** While compounds containing the group $-NO_2$ are called nitro compounds, those containing the group $-NO$ are termed nitroso derivatives, and those containing $=N-OH$ are known as isonitroso derivatives.

When a compound containing the group $=CH-$ is treated with nitrous acid a reaction takes place which results in the formation of a nitroso compound, thus:

$$R_3.CH + HNO_2 = \underset{\text{Nitroso compound.}}{R_3.C.NO} + H_2O.$$

Isonitroso compounds are formed by the action of hydroxylamine on aldehydes or ketones:

$$\underset{\text{Hydroxylamine.}}{H_2NOH} + \underset{\text{Ketone.}}{\begin{matrix}R\\R\end{matrix}>CO} = \underset{\text{Isonitroso compound.}}{\begin{matrix}R\\R\end{matrix}>C=N-OH} + H_2O.$$

Isonitroso compounds are isomeric with nitroso compounds; the different linkage of carbon and nitrogen in the two classes of compounds is indicated in the two equations given above.

Both nitro and nitroso compounds, when treated with nascent hydrogen, yield ammonia derivatives, as will be shown later. Isonitroso compounds are also termed *oximes;* those obtained from aldehydes are designated as *aldoximes;* those derived from ketones as *acetoximes*, or *ketoximes.*

**Fulminic acid,** $C_2N_2O_2H_2$, $\begin{matrix}C=N-OH\\ \|\\ C=N-OH\end{matrix}$, seems to be an isonitroso compound. The free acid is extremely unstable, but some of its metallic salts are well known, especially *mercuric fulminate*, which is used as an explosive in percussion caps, etc. It is made by adding alcohol to a solution of mercury in nitric acid. *Silver fulminate* can be obtained by a similar process.

## Ammonia Derivatives.

Several groups of organic compounds are known, which are formed by replacement of hydrogen in ammonia by different radicals. According to the nature of the latter the compounds are known as *amines*, *amides*, or *amino-acids*, respectively. There are, however, other compounds, such as the proteins, containing nitrogen in the ammonia form, which do not belong to either one of these three groups.

**Formation of Amines and Amides.**—These substances are found as products of animal life (urea), of vegetable life (alkaloids), of destructive distillation (aniline, pyridine), of putrefaction (ptomaines) and may also be produced synthetically—for instance, by the action of ammonia upon the chloride or iodide of an alcohol or acid radical:

$$\underset{\text{Ethyl iodide.}}{C_2H_5.I} + \underset{\text{Ammonia.}}{NH_3} = \underset{\text{Hydriodic acid.}}{HI} + \underset{\text{Ethylamine.}}{NH_2C_2H_5}.$$

$$\underset{\text{Acetyl chloride.}}{C_2H_3O.Cl} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Ammonium chloride.}}{NH_4Cl} + \underset{\text{Acetamide.}}{NH_2.C_2H_3O}.$$

By using in the above reaction two or three molecules of ethyl iodide for one molecule of ammonia, diethyl or triethyl amine is formed.

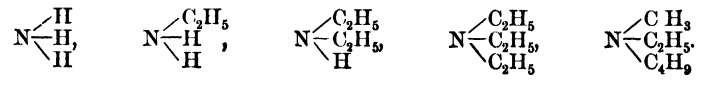
Amines may also be formed by the action of nascent hydrogen upon the cyanides of the alcohol radicals:

$$\underset{\text{Methyl cyanide.}}{CH_3CN} + 4H = \underset{\text{Ethyl amine.}}{NH_2C_2H_5}.$$

They are also formed by the action of nascent hydrogen upon nitro-compounds; the manufacture of aniline depends on this decomposition:

$$\underset{\text{Nitro-benzene.}}{C_6H_5NO_2} + \underset{\text{Hydrogen.}}{6H} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Phenylamine, or aniline.}}{NH_2C_6H_5}.$$

**Occurrence of Organic Bases in Nature.**—The various organic basic substances found in nature are either amines or amides. But a small number of organic bases are found in the animal system urea being the most important one. In plants organic bases are frequently met with, and are grouped together under the name of *alkaloids*. While the constitution of many alkaloids has not yet been sufficiently explained, we know that many of them are derivatives of aromatic compounds, for which reason the consideration of the whole group will be deferred until benzene and its derivatives are spoken of. The large number of basic substances found in putrefying matter and termed *ptomaines* will also be considered later on.



Or

$NH_3$, Ammonia. $N(C_2H_5)H_2$, Ethylamine. $N(C_2H_5)_2H$, Diethylamine. $N(C_2H_5)_3$, Triethylamine. $NCH_3.C_2H_5.C_4H_9$, Methyl-ethyl-butylamine.

The above formulas show that by replacement of either 1, 2, or 3 hydrogen atoms, *mono-*, *di-*, or *tri-amines* are obtained. These are also sometimes designated as *primary*, *secondary*, and *tertiary amines*,

respectively. Primary amines may also be considered as hydrocarbons, with one hydrogen atom replaced by the radical $NH_2$, which is called the *amine-* or *amino-group*, and compounds containing it are designated as *amino compounds*. Thus, $CH_3NH_2$ is *amino-methane*, or *methyl-amine*. The radical NH is known as the *imine-* or *imino-group*, and as this group occurs in secondary amines, these are also termed *imino compounds*.

Amines resemble ammonia in their chemical properties; they are, like ammonia, basic substances; they combine with acids, directly and without elimination of water, thus:

$$NH_3 + HCl = NH_4Cl;$$
$$N(C_2H_5)_3 + HCl = N(C_2H_5)_3HCl.$$

Triethylamine. — Triethylamine chloride.

The methyl amines are gases at ordinary temperature; the ethyl amines are liquids. Many of them are inflammable; they have a strong ammoniacal, fishy odor, are readily soluble in water, have strong basic properties (some of them more so than ammonia), and precipitate metallic salts like ammonia.

The most important reaction of primary amines is that taking place with nitrous acid, thus:

$$CH_3NH_2 + HONO = CH_3NH_3ONO = CH_3OH + H_2O + 2N.$$

Methyl amine — Nitrous acid. — Methyl alcohol.

The reaction shows the possibility of replacing the amino group, $NH_2$, by hydroxyl, which in this way may be introduced into various compounds. The reaction is analogous to the decomposition of ammonium nitrite by heat, thus:

$$NH_4ONO = HOH + H_2O + 2N.$$

Aromatic amines behave differently toward nitrous acid, as will be shown later.

Another characteristic reaction which, as in the previous case, distinguishes primary from the other amines, is that with chloroform and alkalies, giving rise to the formation of iso-nitriles, substances having a most disagreeable odor. (See tests for chloroform.) The reaction is this:

$$C_2H_5NH_2 + CHCl_3 = C_2H_5NC + 3HCl.$$

Ethyl amine. — Chloroform. — Ethyl isonitrile.

**Poly-amines.**—Whenever two or more ammonia molecules are linked together by hydrocarbon radicals, this is indicated by designating them as diamines, triamines, etc.

**Diethylene Diamine** $(C_2H_4)_2(NH)_2$, (*Piperazine*).—Diethylene diamine is a white, crystalline substance, used medicinally on account of its solvent action on uric acid.

**Hexamethylenamine** (*Hexamethylenamina*) $(CH_2)_6N_4 = 140.13$.—(*Hexamethylene tetramine, Urotropin*). This compound results from the action of ammonia on formaldehyde:

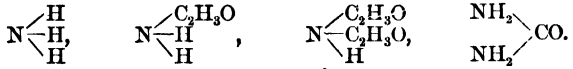
$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

It is due to this reaction that ammonia is used to remove the odor of formaldehyde after its use as a disinfectant. The compound forms colorless, odorless crystals, which are soluble in 1.5 parts of water; this solution has an alkaline reaction on red litmus. On heating it sublimes with partial decomposition. When heated with diluted sulphuric acid, it is decomposed into formaldehyde and ammonia.

This substance is sold under various trade names, such as cystogen, aminoform, formin, uritone, urotropin. These are all identical with the official hexamethylenamine.

Some derivatives of hexamethylenamine have been introduced under special names, such as salicylate (saliform), bromethylate (bromalin, bromoformin), tannate (tannopin or tannon), iodoform (iodoformin).

**Amides** are substances derived from ammonia by replacement of hydrogen atoms by acid radicals. Thus:



Ammonia. Acetamide. Diacetamide. Carbamide or urea.

Amides also resemble ammonia in their chemical properties; to a less extent, however, than amines, because the acid radicals have a tendency to neutralize the basic properties of ammonia.

The fatty acid primary amides are crystalline substances, excepting formamide which is a liquid. The lower members are readily soluble and distil undecomposed. Amides, when heated with water or, better still, with dilute alkalies, are hydrolyzed into the corresponding acids and ammonia, thus differing from amines which do not hydrolyze into alcohol and ammonia. Amides react with nitrous acid, $NH_2$ group being replaced by (OH) group just as in the case of amines. Amides, unlike amines, are neutral substances and do not combine with acids as amines do.

The introduction of an acid radical into ammonia may be accomplished by one of three generally applicable methods:

1. By heating the ammonium salt of organic acids between 200° and 250° C. in sealed tubes.

$$\underset{}{CH_3.COONH_4} = \underset{\text{Acetamide.}}{CH_3.CONH_2} + H_2O.$$

2. By the action of ammonia on ethereal salts,

$$\underset{\text{Ethyl acetate.}}{CH_3.COOC_2H_5} + NH_3 = CH_3.CONH_2 + C_2H_5OH.$$

3. By the action of ammonia on acid chlorides. This reaction is most frequently used:

$$\underset{\text{Acetyl chloride.}}{CH_3.COCl} + NH_3 = CH_3.CONH_2 + HCl.$$

*Formamide*, $H.CONH_2$, is a colorless liquid, obtained by heating ethyl formate with an alcoholic solution of ammonia. This compound is of interest because it combines with chloral, forming *Chloralformamide* (*Chloralamide*), $H.CONH_2.CCl_3CHO$, a substance used as a hypnotic. It is a colorless, odorless, crystalline substance, having a faintly bitter taste. It is soluble in about 20 parts of cold water and in 1.5 parts of alcohol. By heating the aqueous solution to 60° C. (140° F.) it is decomposed into chloral and formamide.

**Amino-acids.**—Amino-acids are acids in which hydrogen has been replaced by the amino-group, $NH_2$. Consequently, amino-acids bear the same relation to acids that amines bear to hydrocarbons. Amino-acids have both acid and basic properties, *i. e.*, they unite with bases to form salts by replacement of the carboxyl hydrogen; and they combine with acids to form weak salts; they also combine with other salts to form double salts. The $(NH_2)$ group in these acids is replaced by the (OH) group by treatment with nitrous acid, just as in the case of simple amines. Amino-acids decompose when heated, but their esters can be distilled under reduced pressure.

Amino-acids may be obtained by the action of ammonia on a halogen derivative of an acid:

$$\underset{\text{Monochloracetic acid}}{CH_2Cl.CO_2H} + 2NH_3 = \underset{\text{Amino-acetic acid}}{CH_2.NH_2.CO_2H} + NH_4Cl.$$

**Amino-acetic Acid.**—Amino-acetic acid, obtained as above, is also known as *glycocoll* or *glycine*. It is a product of the decomposition of either glycocholic or hippuric acid by hydrochloric acid. By oxidation amino-acetic acid splits up thus:

$$CH_2NH_2CO_2H + 3O = 2CO_2 + NH_3 + H_2O.$$

Amino-acids occur in the animal system, and by oxidation suffer the change indicated above. Ammonia and carbon dioxide unite to form ammonium carbamate:

$$2NH_3 + CO_2 = NH_4.NH_2.CO_2.$$

By removal of water this salt is converted into urea:

$$NH_4.NH_2.CO_2 = (NH_2)_2CO + H_2O.$$

**Amino-formic Acid or Carbamic Acid, $NH_2.COOH$.**—Amino-formic acid is the acid which, in the form of the ammonium salt, is a constituent of the commercial ammonium carbonate. It is formed by the direct action of carbon dioxide upon ammonia, as shown above.

**Urethanes.**—Urethanes are ethereal salts of carbamic acid, a class of compounds having hypnotic properties. The class name is derived from one member, which is official and generally known as "Urethane." It is ethyl urethane, or

**Ethyl Carbamate** (*Æthylis Carbamas*), **$CO.OC_2H_5.NH_2$ = 89.06.**—Obtained by the action of alcohol on urea or on one of its salts:

$$CO<\begin{matrix}NH_2\\NH_2\end{matrix} + HOC_2H_5 = CO<\begin{matrix}OC_2H_5\\NH_2\end{matrix} + NH_3.$$

It is a white crystalline powder, readily soluble in water, alcohol, or ether. Heated with solution of potassium hydroxide, ammonia is liberated, while the addition of sodium carbonate and iodine causes, on warming, the precipitation of iodoform.

Several similar compounds have been introduced under specific names, thus: *Euphorin*, or phenyl-urethane, $C_6H_5NH.COOC_2H_5$, a crystalline powder, sparingly soluble in cold water; *neurodin*, or acetyloxyphenyl-urethane, $C_6H_4<\begin{matrix}CO_2CH_3\\NH.COOC_2H_5\end{matrix}$, colorless, sparingly soluble crystals; *thermodin*, or phenacetin-urethane, $C_6H_4<\begin{matrix}OC_2H_5\\N<\begin{matrix}COCH_3\\COOC_2H_5\end{matrix}\end{matrix}$, colorless, very sparingly soluble needles; *hedonal*, or methylpropylcarbinol-urethane, $NH_2.COOCH<\begin{matrix}CH_3\\C_3H_7\end{matrix}$, a difficultly soluble white powder.

The amino-acids and acid-amides are of considerable interest because many products of animal and plant life belong to these classes of compounds. Some of these may be briefly mentioned.

**Sarcosine, Methyl-glycocoll, $CH_3NH.CH_2CO_2H$.**—Sarcosine is a product of the decomposition of creatine, which is found in flesh, and of caffeine, and may be obtained by boiling these compounds with a solution of barium hydroxide. It is much like glycocoll in properties.

**Cystine, $(SC(CH_3)NH_2CO_2H.)_2$.**—Cystine is a derivative of α-amino-propionic acid, sometimes found in the sediment of urine.

**Leucine, α-amino-isocaproic acid $(CH_3)_2.CH.CH_2.CHNH_2.COOH$,** is widely distributed in small quantity in glands of animals and in the sprouts of plants. It is one of the products of the decomposition of albumins and gelatin.

**Taurine, Amino-ethyl-sulphonic acid, $NH_2.CH_2.CH_2.SO_3H$,** is combined with cholic acid to form taurocholic acid, which is one of the constituents of bile. It forms very stable monoclinic prisms (see Index).

**Aspartic acid, Amino-succinic acid, $C_2H_3(NH_2).(CO_2H)_2$,** occurs in pumpkin seeds, and is often formed when natural compounds are boiled with dilute acids. In this manner it may be obtained from casein and albumin. It forms prisms difficultly soluble in water. When treated with nitrous acid, it yields malic acid.

**Asparagine, Amino-succinamic acid, $\begin{matrix}CH_2.CONH_2\\|\\CH(NH_2).CO_2H,\end{matrix}$** occurs in asparagus, liquorice, vetches, beans, beets, peas, and in wheat. It forms large crystals, difficultly soluble in cold water. Boiling with acids or alkalies converts it into aspartic acid and ammonia.

**Guanidine, $(NH)C(NH_2)_2$,** is obtained by the oxidation of guanine which occurs in guano. Guanine, $C_5H_3(NH_2)N_4O$, is the amino derivative of xanthine (see Index), which is closely related to uric acid, and which is found in all the tissues of the body and in the urine. Guanidine is an imide of urea, $OC(NH_2)_2$, is strongly alkaline, and when boiled with dilute sulphuric acid or barium hydroxide solution yields urea and ammonia.

**Creatine, Methyl-guanidine-acetic acid,** $(HN)C\overset{NH_2}{\underset{NCH_3.CH_2.CO_2H}{}}$, is found in the muscles of all vertebrates, and is closely related to guanidine and to sarcosine. It forms colorless, transparent prisms, soluble in 75 parts of cold water. When evaporated in dilute acid solution, it loses water to form the anhydride,

**Creatinine,** $(HN)C\overset{NH—CO}{\underset{NCH_3—CH_2}{}}$, which forms prisms, readily soluble in water. It is a strong base. It is a constant constituent of urine.

**Urea, Carbamide,** $CO(NH_2)_2$, is the amide of carbonic acid. It occurs in the urine and blood of all mammals, particularly of carnivorous animals. It has been made by various synthetic methods, but was formerly obtained exclusively from urine. Now it can be obtained in any quantity from calcium cyanamide (which see). It crystallizes in rhombic prisms, melting at 132° C., easily soluble in water and alcohol. When boiled with dilute acids or alkalies, it yields carbon dioxide and ammonia, thus:

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3.$$

Urea unites with acids, thus: urea hydrochloride, $CO(NH_2)_2.HCl$; urea nitrate, $CO(NH_2)_2HNO_3$, which is difficultly soluble in nitric acid; urea phosphate, $CO(NH_2)_2.H_3PO_4$. It also unites with metallic oxides, thus: $CO(NH_2)_2.HgO$, and also with salts, of which $HgCl_2.CO(NH_2)_2$ and $HgO.CO(NH_2)_2.HNO_3$ are examples.

Urea, the most important constituent of urine, is the chief nitrogenous end-product of the metabolism of proteins in the body, and carries off by far the largest quantity of all nitrogen ingested with the food. From 85 to 86 per cent. of the total nitrogen of the urine is found in urea, of which 25 to 35 grams are eliminated from the body in twenty-four hours. A pure solution of urea does not decompose at ordinary temperature, but on boiling, and especially under pressure, it takes up water, and is decomposed into ammonia and carbon dioxide, or into ammonium carbonate. The same decomposition takes place in urine under the influence of a bacterial enzyme, if the temperature be not too low.

A solution of urea is decomposed by the action of chlorine or bromine with generation of hydrochloric (or hydrobromic) acid, carbon dioxide, and nitrogen:

$$CO(NH_2)_2 + 6Cl + H_2O = 6HCl + CO_2 + 2N.$$

Alkali hypochlorites or hypobromites cause a similar decomposition, upon which is based the quantitative estimation of urea:

$$CO(NH_2)_2 + 3(NaBrO) = 3NaBr + CO_2 + 2H_2O + 2N$$

The liberated nitrogen is collected, and from its volume the weight of the urea is calculated. The carbon dioxide is absorbed by the excess of alkali present. The hypobromite solution must be freshly prepared.

**Ureids.** Urea contains ammonia residues and, therefore, acts in many respects like ammonia. Thus, one or more hydrogen atoms of the $NH_2$ groups can be replaced by acid radicals, forming compounds analogous to the acid amides. These are known as ureids. The following ureids are of interest.

**Oxalyl urea, Parabanic acid,** $\overset{CO—NH}{\underset{CO—NH}{}}\!\!>\!CO$, is formed when uric acid is boiled with concentrated nitric acid, and also when a mixture of urea

and oxalic acid is treated with phosphorus oxychloride, $POCl_3$, which abstracts the elements of water. It acts as an acid, since the hydrogen of the NH group can be replaced by metals.

**Malonyl urea, Barbituric acid,** $CH_2<\begin{matrix}CO—NH\\CO—NH\end{matrix}>CO$, like the previous compound, can also be obtained from uric acid, and synthetically by treating a mixture of urea and malonic acid with phosphorus oxychloride. It breaks up into urea and malonic acid when treated with an alkali. Closely related to it is

**Veronal, Diethyl-malonyl urea,** $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>C<\begin{matrix}CO—NH\\CO—NH\end{matrix}>CO$, which occurs as a white, faintly bitter, crystalline powder, melting at 191° C., and sublimable without residue. It is soluble in about 145 parts of water at 20° C., in about 12 parts of boiling water, and readily in warm alcohol. Veronal is one of the most valuable hypnotics, being prompt and relatively innocuous in small doses (8 grains), and dangerous only in large doses.

Uric acid, $C_5H_4N_4O_3$, xanthine, $C_5H_4N_4O_2$, theobromine (dimethyl-xanthine), $C_5H_2(CH_3)_2N_4O_2$, and caffeine (theine, trimethyl-xanthine), $C_5H(CH_3)_3N_4O_2 + H_2O$, are all interesting and important compounds, but rather complex, for a discussion of which see Index.

## Cyanogen Compounds.

Cyanogen itself does not occur in nature, but compounds containing it are found in a few plants (amygdalin), and also in some animal fluids (saliva contains sodium sulphocyanate). Gases issuing from volcanoes (or from iron furnaces) sometimes contain cyanogen compounds. Their formation from inorganic matter can be shown by the action of ammonia on red-hot charcoal, when ammonium cyanide and methane are generated:

$$4NH_3 + 3C = 2(NH_4CN) + CH_4.$$

The univalent radical cyanogen, $—C \equiv N$, or CN was the first compound radical distinctly proved to exist by Gay-Lussac in 1814. The name cyanogen signifies "generating blue," in allusion to the various blue colors (Prussian and Turnbull's blue) containing it.

Cyanogen and its compounds show much resemblance to the halogens and their compounds, as indicated by the composition of the following substances:

| | | | |
|---|---|---|---|
| ClCl, Chlorine, | HCl, Hydrochloric acid. | KI, Potassium iodide. | HClO, Hypochlorous acid. |
| CNCN, Cyanogen. | HBr, Hydrobromic acid. | KCN, Potassium cyanide. | HCNO, Cyanic acid. |
| CNCl, Cyanogen chloride. | HCN, Hydrocyanic acid. | AgCN, Silver cyanide. | HCNS, Sulphocyanic acid. |

**Dicyanogen, $(CN)_2$.**—The unsaturated radical CN does not exist as such in a free state, but combines whenever liberated with another CN, forming dicyanogen. It may be obtained by heating mercuric cyanide:

$$Hg(CN)_2 = Hg + (CN)_2.$$

It is a colorless gas, having an odor of bitter almonds, and burning with a purple flame, forming carbon dioxide and nitrogen; it is soluble in water, and may be converted into a colorless liquid by pressure; it acts as a poison, both to animal and vegetable life, even when present in but small proportions in the air.

**Hydrocyanic Acid, HCN = 27.02** (*Prussic acid*).—This compound is found in the water distilled from the disintegrated seeds or leaves of amygdalus, prunus, laurus, etc. It is also found among the products of the destructive distillation of coal, and is formed by a great number of chemical decompositions. For instance:

By the action of ammonia on chloroform:

$$\underset{\text{Chloroform.}}{CHCl_3} + NH_3 = \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{HCN} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{3HCl}.$$

By heating ammonium formate to 200° C. (392° F.):

$$\underset{\substack{\text{Ammonium}\\\text{formate.}}}{NH_4CHO_2} = \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{HCN} + \underset{\text{Water.}}{2H_2O}.$$

By the action of hydrogen sulphide upon mercuric cyanide:

$$Hg(CN)_2 + H_2S = HgS + 2HCN.$$

By the decomposition of alkali cyanides by diluted acids:

$$KCN + HCl = KCl + HCN.$$

By the action of hydrochloric acid upon silver cyanide:

$$AgCN + HCl = AgCl + HCN.$$

By distilling potassium ferrocyanide with diluted sulphuric acid:

$$\underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{2K_4Fe(CN)_6} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{6(H_2SO_4)} = \underset{\substack{\text{Potassium ferrous}\\\text{ferrocyanide.}}}{K_2Fe_2(CN)_6} + \underset{\substack{\text{Potassium acid}\\\text{sulphate.}}}{6KHSO_4} + \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{6HCN}.$$

*Experiment* 66.—Place 20 grams of potassium ferrocyanide and 40 c.c. of water into a boiling-flask of about 200 c.c. capacity; provide the flask with a funnel-tube and connect it with a suitable condenser, the exit of which should dip into 60 c.c. of diluted alcohol, contained in a receiver, which latter should be kept cold by ice during the operation. After having ascertained that all the joints are tight, add through the funnel-tube a previously prepared mixture of 15 grams of sulphuric acid and 20 c.c. of water. Apply heat and slowly distil until there is little liquid left with the salts remaining in the flask.

Determine the strength of the alcoholic solution of hydrocyanic acid thus

prepared volumetrically and dilute it with water until it contains exactly 2 per cent. of HCN.

Pure hydrocyanic acid is, at a temperature below 26° C. (78.8° F.), a colorless, mobile liquid, of a penetrating, characteristic odor resembling that of bitter almonds; it boils at 26.5° C. (80° F.) and crystallizes at —15° C. (5° F.). It is readily soluble in water, and a 2 per cent. solution is the *diluted hydrocyanic acid, Acidum hydrocyanicum dilutum.*

According to the U. S. P., this diluted acid is made by the decomposition of 6 grams of silver cyanide by 15.54 c.c. of diluted hydrochloric acid, mixed with 44.1 c.c. of water, allowing the silver chloride to subside and pouring off the clear liquid.

The diluted acid has the characteristic odor of bitter almonds, a slightly acid reaction, and is completely volatilized by heating. Pure absolute hydrocyanic acid may be kept unchanged, but when water or ammonia is present, the acid decomposes comparatively rapidly, giving ammonia, formic acid, oxalic acid, and other products. The official 2 per cent. acid deteriorates appreciably within several weeks, and therefore should not be kept in stock for a long time, but should be prepared as it is needed.

The salts of hydrocyanic acid are called *cyanides*, and are nearly all insoluble in water. The cyanides of the alkali metals, the alkaline-earth metals, and of mercury are soluble.

**Dissociation of Cyanogen Compounds.**—Hydrocyanic acid is an extremely weak acid, and its aqueous solution conducts electricity very badly, that is, it has a very low conductivity, due to its extremely small degree of dissociation. In a tenth-normal solution at 18° C., only 0.01 per cent. of the acid molecules are dissociated, thus:

$$HCN \rightleftarrows H^{\cdot} + CN'.$$

As in the case of the mercury salts, the poisonous character of hydrocyanic acid and its salts depends upon the degree of dissociation into $CN'$ ions. A number of complex cyanides are known, in which the cyanogen groups are combined with metals to form complex radicals, in which both the cyanogen and the metals are masked, and do not respond to the usual analytical reagents. The best examples of such compounds are the ferrocyanide and ferricyanide of potassium, $K_4FeCN_6$ and $K_3Fe(CN)_6$, respectively. These compounds are not poisonous because they do not form $CN'$ ions, being dissociated in solution according to the following equations:

$$K_4Fe(CN)_6 \rightleftarrows 4K^{\cdot} + \underset{\text{Ferrocyanogen ion.}}{Fe(CN)_6''''}$$

$$K_3Fe(CN)_6 \rightleftarrows 3K^{\cdot} + \underset{\text{Ferricyanogen ion.}}{Fe(CN)_6'''}$$

The alkali cyanides are decomposed by such a weak acid as carbonic acid, hence they have the odor of hydrocyanic acid, due to the action of the carbonic acid of the atmosphere. In aqueous solution they have a strong alkaline reaction, due to hydrolysis:

$$\left.\begin{array}{l} KCN \rightleftarrows K^{\cdot} + CN' \\ HOH \rightleftarrows (OH)' + H^{\cdot} \end{array}\right\} \rightleftarrows HCN.$$

The action is due to the extremely weak dissociating power of hydrocyanic acid (see chapter 13).

For peculiarities of mercury cyanide see chapter on Mercury.

**Potassium Cyanide, KCN = 65.11.**—The pure salt may be obtained by passing hydrocyanic acid into an alcoholic solution of potassium hydroxide. The commercial article, however, is a mixture of potassium cyanide with potassium cyanate. It is obtained by fusing potassium ferrocyanide with potassium carbonate in a crucible, when potassium cyanide and cyanate are formed, while carbon dioxide escapes, and metallic iron is set free and collects on the bottom of the crucible. The decomposition is as follows:

$$\underset{\text{Potassium ferrocyanide}}{K_4Fe(CN)_6} + \underset{\text{Potassium carbonate}}{K_2CO_3} = \underset{\text{Potassium cyanide}}{5KCN} + \underset{\text{Potassium cyanate.}}{KCNO} + \underset{\text{Iron}}{Fe} + \underset{\text{Carbon dioxide}}{CO_2}.$$

A mixture of pure potassium and sodium cyanides, free from cyanate, is now manufactured on a large scale by heating together anhydrous potassium ferrocyanide and metallic sodium:

$$K_4Fe(CN)_6 + 2Na = 2NaCN + 4KCN + Fe.$$

Potassium cyanide is a white, deliquescent substance, odorless when perfectly dry, but emitting the odor of hydrocyanic acid when moist; it is soluble in about 2 parts of water; this solution has an alkaline reaction and is unstable, decomposition soon taking place with the formation of potassium formate and ammonia, along with other products:

$$KCN + 2H_2O = HCO_2K + NH_3.$$

A solution of potassium cyanate decomposes slowly in the cold, but rapidly on heating, with the formation of potassium and ammonium carbonates:

$$2KCNO + 4H_2O = K_2CO_3 + (NH_4)_2CO_3.$$

Potassium cyanide and other alkali cyanides show a tendency to combine with the cyanides of heavy metals, forming a number of double cyanides, such as the cyanide of sodium and silver, NaCN. AgCN, etc., which are soluble in water. Hence, precipitates formed by addition of alkali cyanides to solutions of metallic salts, are dissolved in excess of the reagent. Double cyanides of silver and gold are used in commercial electroplating. A large proportion of the alkali cyanides manufactured is used in extracting gold from its ores, especially in Transvaal. In 1889 not more than 50 tons of cyanide per annum were consumed, while in 1905 the consumption was about 10,000 tons, one-third of which was used in Transvaal.

**Sodium Cyanide** (*Sodii Cyanidum*), **NaCN = 49.01.**—This salt may be made by neutralizing an alcoholic solution of sodium hydroxide with hydrocyanic acid, as described under Potassium

Cyanide, but on the large scale it is obtained by fusing calcium cyanamide with sodium carbonate.

Sodium cyanide, U. S. P., should contain at least 95 per cent. of pure salt. It occurs as white, opaque pieces or as a granular powder, deliquescent in the air and giving off the odor of hydrocyanic acid. It is freely soluble in water and very alkaline to litmus. It acts exactly like potassium cyanide in all respects.

**Mercuric Cyanide, $Hg(CN)_2$.**—A white crystalline salt, obtained by dissolving mercuric oxide in hydrocyanic acid; it is soluble in water and alcohol and evolves cyanogen when heated.

**Mercuric Oxycyanide,** $Hg(CN)_2.HgO$.—(*Basic Mercuric Cyanide*).—This is obtained by triturating mercuric oxide, dilute sodium hydroxide solution, and mercuric cyanide until the mixture becomes colorless. The salt is purified by washing with cold water, or recrystallizing from hot water. It occurs as a white, crystalline powder, soluble in 17 parts of water, and turns red litmus blue. It is recommended as a substitute for mercuric chloride, as it is claimed to have greater antiseptic power, to be less irritating, and to have no corroding action on steel instruments.

**Analytical Reactions for Hydrocyanic Acid.** (*Potassium cyanide,* KCN, may be used.)—1. Hydrocyanic acid, or soluble cyanides, give with silver nitrate a white precipitate of silver cyanide, which is sparingly soluble in ammonia, soluble in alkali cyanides or thiosulphates, but insoluble in diluted nitric acid.

$$HCN + AgNO_3 = AgCN + HNO_3.$$

2. Hydrocyanic acid, mixed with yellow ammonium sulphide and evaporated to dryness, forms sulphocyanic acid, which, upon being slightly acidulated with hydrochloric acid, gives with ferric chloride a blood-red color of ferric sulphocyanate. (Excess of ammonium sulphide must be avoided.)

3. Hydrocyanic acid, or soluble cyanides, give, when mixed with ferrous and ferric salts and potassium hydroxide, a greenish precipitate, which, upon being dissolved in hydrochloric acid, forms a precipitate of Prussian blue, $Fe_4(FeC_6N_6)_3$. This reaction depends on the formation of potassium ferrocyanide by the action of the cyanogen upon both the potassium of the potassium hydroxide and the iron of the ferrous salt. In alkaline solutions, the blue precipitate does not form, for which reason hydrochloric acid is added.

4. Hydrocyanic acid heated with dilute solution of picric acid gives a deep red color on cooling.

In cases of poisoning, the matter under examination is distilled (if necessary after the addition of water) from a retort connected with a cooler. To the distilled liquid the above tests are applied. If the substance under examination should have an alkaline or neutral reaction, the addition of some sulphuric acid may be necessary in order to liberate the hydrocyanic acid. The objectionable feature to this acidifying is the fact that non-poisonous potassium ferrocyanide might be present, which upon the addition of sulphuric

acid would liberate hydrocyanic acid. In cases where the addition of an acid becomes necessary, a preliminary examination should, therefore, decide whether or not ferro- or ferricyanides are present.

**Antidotes.** Hydrocyanic acid is a powerful poison both when inhaled or swallowed in the form of the acid or of soluble cyanides. As an antidote is recommended a mixture of ferrous sulphate and ferric chloride with either sodium carbonate or magnesia. The action of this mixture is explained in the above reaction 3, the object being to convert the soluble cyanide into an insoluble ferrocyanide of iron. In most cases of poisoning by hydrocyanic acid there is, however, no time for the action of such an antidote, in consequence of the rapidity of the action of the poison, and the treatment is chiefly directed to the maintenance of respiration by artificial means.

About fifteen years ago, hydrogen dioxide was proposed as an antidote, by which hydrocyanic acid is converted into the harmless oxamide, $CONH_2$—$CONH_2$. A solution of hydrogen dioxide is introduced into the stomach and then siphoned out. It is also used subcutaneously. In case a cyanide is the poison, vinegar may be mixed with the hydrogen dioxide solution given internally in order to liberate the hydrocyanic acid.

**Cyanogen derivatives obtained directly from nitrogen of the atmosphere.** When calcium carbide is heated to redness in contact with nitrogen, *calcium cyanamide* is formed, thus:

$$CaC_2 + 2N = CN.NCa + C.$$

This substance is an excellent fertilizer, and is manufactured in large quantities and sold under the name of nitrolim or lime-nitrogen (Kalkstickstoff). It is slowly decomposed in the soil by moisture and carbon dioxide into calcium carbonate and cyanamide:

$$CN.NCa + H_2O + CO_2 = CaCO_3 + CN.NH_2.$$

The cyanamide is further decomposed probably into urea:

$$CN.NH_2 + H_2O = CO(NH_2)_2.$$

Steam under high pressure converts all of the nitrogen of calcium cyanamide into ammonia, which thus furnishes a method of obtaining ammonia from atmospheric nitrogen.

When mixed with sodium carbonate and fused, calcium cyanamide forms sodium cyanide. By the action of acids on the calcium compound, *cyanamide*, $CN.NH_2$, is formed, which easily polymerizes to the beautifully crystallized *dicyandiamide*, $C_2N_2.N_2H_4$, which is now made by the ton and used for various purposes. It can very easily be made to unite with water to form urea, which is manufactured thus in great quantities.

Barium carbide, when heated in nitrogen, acts differently from calcium carbide, forming barium cyanide, thus:

$$BaC_2 + 2N = Ba(CN)_2.$$

**Cyanic Acid, HCNO,** and **Sulphocyanic Acid, HCNS,** are both colorless acid liquids, the salts of which are known as *cyanates* and *sulphocyanates*. These salts are obtained from alkali cyanides by treating them with oxidizing agents or by boiling their solutions

with sulphur, when either oxygen or sulphur is taken up by the alkali cyanide:

$$KCN + O = KCNO = \text{Potassium cyanate.}$$
$$KCN + S = KCNS = \text{Potassium sulphocyanate.}$$

The acids themselves are obtained by indirect processes, as they decompose when the salts are treated with mineral acids. Sulphocyanates give with ferric salts a deep red color, which is not affected by hydrochloric acid, but disappears on the addition of mercuric chloride.

**Metallocyanides.**—Cyanogen not only combines with metals to form true cyanides, which may be looked upon as derivatives of hydrocyanic acid, but cyanogen also enters into combination with certain metals (chiefly iron), forming a number of complex radicals, which upon combining with hydrogen form acids, or with basic elements form salts. It is a characteristic feature of the compound cyanogen radicals, thus formed, that the analytical characters of the metals (iron, etc.), entering into the radical are completely hidden. Thus, the iron in ferro- or ferricyanides is not precipitated by either alkalies, soluble carbonates, ammonium sulphide, or any of the common reagents for iron, and its presence can only be demonstrated by these reagents after the organic nature of the compound has been destroyed by burning it (or otherwise), when ferric oxide is left, which may be dissolved in hydrochloric acid and tested for in the usual manner.

The principal iron-cyanogen radicals are *ferrocyanogen* $[Fe^{ii}(CN)_6{}^{i}]^{iv}$, and *ferricyanogen* $[Fe^{iii}(CN)_6{}^{i}]^{iii}$. These two radicals contain iron in the ferrous and ferric state respectively, and form, upon combining with hydrogen, acids which are known as *hydroferrocyanic acid*, $H_4Fe(CN)_6$ (tetrabasic), and *hydroferricyanic acid*, $H_3Fe(CN)_6$ (tribasic); the salts of these acids are termed ferrocyanides and ferricyanides. (For dissociation of these, see p. 523.)

**Potassium Ferrocyanide, $K_4Fe(CN)_6.3H_2O$** (*Yellow Prussiate of Potash*).—This salt is manufactured on a large scale by heating refuse animal matter (waste leather, horns, hoofs, etc.), with potassium carbonate and iron (filings, etc.). The fused mass is boiled with water, and from the solution thus formed the crystals separate on cooling.

The nitrogen and carbon of the organic matter (heated as above stated) combine, forming cyanogen, which enters into combination first with potassium and afterward with iron.

The above method has been largely displaced by another in which the source of the cyanogen is the hydrocyanic acid present in illuminating gas. To purify the gas, it is passed over moist precipitated ferric hydroxide, which absorbs the hydrocyanic acid and ultimately forms a ferrocyanide. The spent iron hydroxide is treated with milk of lime, forming soluble calcium ferrocyanide. The hot filtrate is

treated with potassium chloride, to form the difficultly soluble double salt of potassium calcium ferrocyanide, which is separated and decomposed with a solution of potassium hydroxide, by which soluble potassium ferrocyanide is formed,

$$K_2CaFe(CN)_6 + 2KOH = K_4Fe(CN)_6 + Ca(OH)_2.$$

In the laboratory the salt may be made by dissolving ferrous hydroxide in potassium cyanide solution:

$$Fe(OH)_2 + 2KCN = Fe(CN)_2 + 2KOH.$$
$$Fe(CN)_2 + 4KCN = K_4Fe(CN)_6.$$

Potassium ferrocyanide forms large, translucent, pale lemon-yellow, soft, odorless, non-poisonous, neutral crystals, easily dissolving in water, but insoluble in alcohol.

*Analytical reactions:*

1. Ferrocyanides heated on platinum foil burn and leave a residue of (or containing) ferric oxide.

2. Ferrocyanides heated with concentrated sulphuric acid evolve carbonic oxide; with dilute sulphuric acid liberate hydrocyanic acid; with concentrated hydrochloric acid liberate hydroferrocyanic acid.

3. Soluble ferrocyanides give a blue precipitate with ferric salts (Plate I, 5):

| $3K_4Fe(CN)_6$ | + | $4FeCl_3$ | = | $12KCl$ | + | $Fe_4(FeC_6N_6)_3$. |
|---|---|---|---|---|---|---|
| Potassium ferrocyanide. | | Ferric chloride | | Potassium chloride | | Ferric ferrocyanide. |

The blue precipitate of ferric ferrocyanide, or *Prussian blue,* is insoluble in water and diluted acids, soluble in oxalic acid (blue ink), and is decomposed by alkalies with separation of brown ferric hydroxide and formation of potassium ferrocyanide. The addition of an acid restores the blue precipitate.

4. Soluble ferrocyanides give, with cupric solutions, a brownish-red precipitate of cupric ferrocyanide. (Plate III, 5.)

5. Soluble ferrocyanides produce, with solutions of silver, lead, and zinc, white precipitates of the respective ferrocyanides.

6. Ferrocyanides give with ferrous salts a white precipitate of ferrous ferrocyanide, soon turning blue by absorption of oxygen. (Plate I, 4.)

**Potassium Ferricyanide, $K_3Fe(CN)_6$** (*Red Prussiate of Potash*).—Obtained by passing chlorine through solution of potassium ferrocyanide:

| $K_4Fe(CN)_6$ | + | $Cl$ | = | $KCl$ | + | $K_3Fe(CN)_6$. |
|---|---|---|---|---|---|---|
| Potassium ferrocyanide. | | Chlorine. | | Potassium chloride | | Potassium ferricyanide |

While apparently this decomposition consists merely in a removal of one atom of potassium from one molecule of potassium ferrocyanide, the change is actually more complete, as the atoms arrange themselves differently, the iron passing also from the ferrous to the ferric state.

Potassium ferricyanide crystallizes in red prisms, soluble in water. It forms, with ferrous solutions, a blue precipitate of ferrous ferricyanide, or *Turnbull's blue:*

$$2K_3Fe(CN)_6 + 3FeSO_4 = 3K_2SO_4 + Fe_3Fe_2(CN)_{12}.$$

With ferric solutions no precipitate is produced by potassium ferricyanide, but the color is changed to a deep brown.

**Sodium nitroferricyanide,** $Na_2Fe(CN)_5NO.2H_2O$. (*Sodium nitroprusside.*) This is a salt of nitroferricyanic acid, which is obtained by the action of nitric acid on potassium ferrocyanide. Potassium nitrate is crystallized out by concentrating and cooling the solution, which is then neutralized by sodium carbonate, and the sodium salt crystallized. Addition of alcohol increases the separation of potassium nitrate. The salt forms large ruby-red crystals, soluble in 2.5 parts of water and in alcohol. The aqueous solution decomposes on standing. It serves as a delicate test for soluble sulphides (but not free $H_2S$), giving a purple color which quickly passes into violet. It is also used as a test for acetone (Legal's test).

**Cyanides and isocyanides of organic radicals.** Only one form of hydrocyanic acid and of metallic cyanides is known, but among organic cyanides two isomeric forms exist, known respectively as *cyanides* or *nitriles*, and *isocyanides* or *carbylamines*. Experiments show that the constitution of these compounds is represented by the formulas:

$$\underset{\text{Cyanide.}}{R{-}C{\equiv}N}, \qquad \underset{\text{Isocyanide.}}{R{-}N{\equiv}C},$$

In one case the organic radical is in combination with carbon; in the other, with nitrogen. These compounds are apparently esters of hydrocyanic acid, but they behave quite differently from esters, as they do not yield alcohols or metallic cyanides on treatment with alkalies.

**Cyanides or nitriles.** These may be formed by heating together iodides of hydrocarbon radicals with potassium cyanide:

$$CH_3I + KCN = CH_3CN + KI.$$

The cyanides are volatile liquids or solids. When heated with water in presence of mineral acids or alkalies, they yield organic acids, thus:

$$\underset{\substack{\text{Methyl}\\\text{cyanide.}}}{CH_3.CN} + 2H_2O = \underset{\text{Acetic acid.}}{CH_3.CO_2H} + NH_3.$$

This is an important reaction, as it furnishes a simple means of introducing carboxyl into compounds, thus forming organic acids. For this reason the cyanides are called nitriles of the acids, just as the acid oxides are called anhydrides of the corresponding acids. Thus, methyl cyanide is called acetonitrile, because it yields acetic acid. In fact, the ammonium salts of organic acids, by abstraction of water, yield cyanides:

$$CH_3.CO_2NH_4 = CH_3.CN + 2H_2O.$$

**Isocyanides or carbylamines.** These compounds are distinguished by a

disgusting odor. They are formed by heating silver cyanide, instead of potassium cyanide, with iodides of hydrocarbon radicals, thus:

$$CH_3I + AgCN = CH_3NC + AgI.$$

It is strange, and as yet not explained, why hydrocarbon iodides produce cyanides with potassium cyanide, and isocyanides with silver cyanide.

Isocyanides are also formed by heating together chloroform, primary amines, and an alkali, as shown above in the paragraph on amines.

The isocyanides behave differently from the cyanides when heated with water and acids, thus:

$$\underset{\text{Methyl isocyanide.}}{CH_3NC} + 2H_2O = \underset{\text{Methyl amine.}}{CH_3NH_2} + \underset{\text{Formic acid.}}{HCO_2H}.$$

**Isosulphocyanates or mustard oils.** The difference in structure between sulpho- and iso-sulphocyanates is expressed in the following formulas:

R—S—C≡N, sulphocyanate. R—N=C=S, isosulphocyanate.

The organic sulphocyanates are of no importance here. The principal member of the mustard oils is allyl-isosulphocyanate, $C_3H_5NCS$, one of the decomposition products of myronic acid.

Treated with water and alkali, mustard oils break down, thus:

$$C_3H_5NCS + 2H_2O = C_3H_5NH_2 + H_2S + CO_2.$$

This reaction is similar to that which takes place in case of isocyanides. (See above.)

**Myronic acid, $C_{10}H_{19}NS_2O_{10}$,** is found as the potassium salt, which is known as *sinigrin*, in black mustard seed. When treated with solution of *myrosin*, a substance also contained in mustard seed and acting as a ferment upon myronic acid or its salts, potassium myronate is converted into dextrose, allyl mustard oil, and potassium bisulphate.

$$\underset{\text{Potassium myronate.}}{KC_{10}H_{18}NS_2O_{10}} = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Allyl mustard oil.}}{C_3H_5NCS} + \underset{\text{Potassium bisulphate.}}{KHSO_4}.$$

**Allyl mustard oil, $C_3H_5NCS$.** Mustard oils are esters of isosulphocyanic acid, HNCS. Ordinary mustard oil, obtained from sinigrin, as stated above, contains the radical allyl, derived from the unsaturated hydrocarbon propylene, $C_3H_6$. The univalent radical allyl is isomeric, but not identical, with the trivalent radical glyceryl, $C_3H_5$, derived from propane, $C_3H_8$. The difference may be seen from the structural formulas:

$-CH_2-CH=CH_2$, allyl. $-CH_2-\underset{|}{CH}-CH_2-$, glyceryl.

The triatomic alcohol glycerin, $C_3H_5(OH)_3$, may be converted into the monatomic allyl alcohol, $C_3H_5OH$, by various processes. From allyl alcohol an artificial allyl mustard oil is manufactured.

Mustard oil is a colorless or pale yellow liquid, which has a very pungent and acrid odor and taste. When brought together with ammonia, direct combination takes place and crystals of thiosinamine (allyl-thio-urea), $CS.N_2H_3.C_3H_5$, are formed.

$$C_3H_5NCS + NH_3 = CS.N_2H_3.C_3H_5.$$

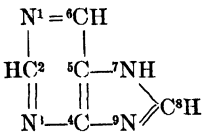
*Allyl sulphide*, $(C_3H_5)_2S$, is the chief constituent of the oil of garlic.

## 50. PURINE DERIVATIVES.

Uric acid and substances formed from it by decomposition, as well as other related nitrogen compounds were known for a long time. Many researches were carried out with the object of determining the constitutional formula of uric acid, but this problem and that of the relationship between uric acid and other purine derivatives were successfully solved by Emil Fischer.

### Purine.

As a result of Fischer's researches, it is certain that uric acid and its related compounds are derivatives of a nucleus which has been named purine and has the formula:



Purine.

For purposes of reference, the carbon atoms are numbered. In some of the derivatives of purine, the positions of the double bonds are shifted.

**Uric Acid, $H_2.C_5H_2N_4O_3$, 2, 6, 8-Oxypurine.**—Uric acid is found in small quantities in human urine, chiefly in combination with sodium, potassium, and ammonium, but also with calcium and magnesium. In larger proportions, uric acid is found in the excrement of birds, mollusks, insects, and chiefly of serpents, the solid urine of the latter consisting almost entirely of uric acid and urates. It is also found

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QUESTIONS.—What are the three chief forms in which nitrogen enters into organic compounds? What are amines and amides; in what respects do they resemble ammonia compounds? What is cyanogen, what is dicyanogen, and how is the latter obtained? How does cyanogen occur in nature, and which non-metallic elements does it resemble in the constitution of various compounds? Mention some reactions by which hydrocyanic acid is formed, and state the two processes by which the official diluted acid is obtained. What strength and what properties has this acid? State the composition of pure potassium cyanide and of the commercial article. How is the latter made? Give reactions for hydrocyanic acid and cyanides. Explain the constitution and give the composition of ferro- and ferricyanides. Give composition, mode of manufacture, and tests of potassium ferrocyanide. What is red prussiate of potash, how is it obtained, and by what reactions can it be distinguished from the yellow prussiate?

in Peruvian guano. The proportion of uric acid to urea in human urine is normally between 1 : 50 and 1 : 70. The normal amount for twenty-four hours is about 0.7 gram.

Pure uric acid is a white, crystalline, tasteless, and odorless substance, almost insoluble in water, requiring 1900 parts of boiling and 15,000 parts of cold water for its solution; it is also insoluble, or nearly so, in alcohol and ether. The great insolubility of uric acid causes its separation in the solid state, both in the bladder and in the tissues.

It is a weak dibasic acid, forming normal and acid salts. Normal sodium urate is soluble in 62 parts, the acid salt in 1100 parts of water at ordinary temperature.

Uric acid may be gotten from urine thus: Add 100 c.c. of hydrochloric acid to 1 liter of urine and set aside for a day. Collect the highly colored crystals of uric acid, wash with water, transfer them to a beaker with a little water, heat, and add enough sodium hydroxide to dissolve the crystals. Decolorize the solution of sodium urate with bone-black, filter while hot, acidify with hydrochloric acid, and allow to crystallize. Examine the crystals microscopically and chemically.

**Tests for Uric Acid.**—1. *Murexide Test.*—Place a few fragments of uric acid in a porcelain dish, add a drop of nitric acid, and carefully evaporate over a flame. To the dry residue add a drop of ammonia-water, which produces a beautiful purplish-red color.

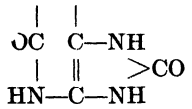
To distinguish from xanthine and guanine, add a drop of caustic soda, when the red changes to a deep blue color. Moisten with water and evaporate to dryness, when the color disappears. With xanthine or guanine the color persists.

For the following tests use solution of sodium urate prepared by dissolving uric acid in warm water with the aid of sodium carbonate.

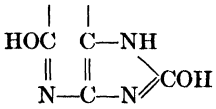
2. *Schiff's Reaction.*—Place a drop of the solution on a piece of filter-paper previously moistened with silver nitrate. A dark stain is formed, due to the reduction of the silver salt.

3. Add magnesia-mixture and then silver nitrate. Uric acid is precipitated as a gelatinous magnesia-silver salt. (This reaction may be used to precipitate uric acid from urine, especially in those cases in which hydrochloric acid fails to precipitate the acid.)

**Structure of Uric Acid.**— From a study of the decomposition products of uric acid, the methods of building it up synthetically, and the derivatives of uric acid, the conclusion has been drawn that in certain cases it acts as if it had the first formula, in other cases, as if it had the second formula, given below:



Uric acid I.



Uric acid II.

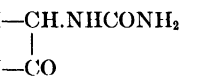
There is no doubt that the structure of the uric acid molecule changes from that shown in formula I to that shown in formula II,

or *vice versa*, according to the kind of chemical action to which the acid is subjected. A number of such cases are known, and this kind of isomerism or change in constitution is known as *tautomerism*. A compound, like uric acid, is said to exist in tautomeric forms.

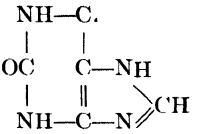
The formula of uric acid is in keeping with products obtained by oxidation or reduction of the acid. In the previous chapter, it was stated that *parabanic acid* (oxalyl urea) and *barbituric acid* (malonyl urea) can be obtained by oxidation of uric acid. These substances are ureids of oxalic and malonic acid respectively.

**Alloxan, $C_4H_2N_2O_4$.**—This is obtained by moderated oxidation of uric acid with nitric acid, chlorine or bromine. It has been shown by synthesis to be the ureid of mesoxalic acid, $CO<^{COOH}_{COOH}$.

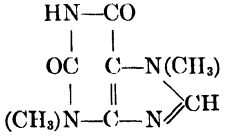
**Allantoin, $C_4H_6O_3N_4$.**—This is formed when uric acid is oxidized with permanganate. It is the ureid of glyoxylic acid $\left(\begin{matrix}HO\\HO\end{matrix}>CH.COOH\right)$ and has the formula,



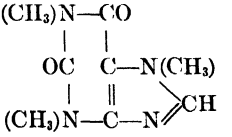
**Xanthine, 2, 6-Dioxypurine.**—This compound is closely related to uric acid. It occurs in small quantity in many animal secretions, in urine, blood, the liver, and certain urinary calculi. It is obtained by the action of nitrous acid on guanine, which occurs in guano. By this action an imido group is displaced by oxygen. Xanthine is a white amorphous solid, slightly soluble in boiling water, but easily soluble in boiling ammonia-water. It forms salts with acids and bases, but those with the latter are decomposed by carbonic acid. Xanthine has the constitution shown by the formula:



**Theobromine,** 3, 7-dimethyl-2, 6-dioxypurine, is a dimethyl derivative of xanthine and *caffeine* or *theine*, 1, 3, 7-trimethyl-2, 6-dioxypurine, is a trimethyl derivative of xanthine. They have the following formulas:



Theobromine



Caffeine.

These interesting and important compounds will be described more in detail under Alkaloids.

## 51. BENZENE SERIES. AROMATIC COMPOUNDS.

**General Remarks.**—It has been stated before that most organic compounds may be looked upon as derivatives of either methane, $CH_4$, or benzene, $C_6H_6$, these derivatives being often spoken of as fatty and aromatic compounds respectively. The term aromatic

compounds was given to these substances on account of the peculiar and fragrant odor possessed by many, though not by all of them. Benzene and methane derivatives differ considerably in many respects and, as a general rule, aromatic compounds cannot be converted into fatty compounds, or the latter into aromatic compounds, without suffering the most vital decomposition of the molecule, and in many cases this transformation cannot be accomplished at all.

On the average, aromatic compounds are richer in carbon than fatty compounds, containing of this element at least 6 atoms; when decomposed by various methods, aromatic compounds, in many cases, yield benzene as one of the products; most aromatic substances have antiseptic properties, and none of them serves as animal food, although quite a number are taken into the system in small quantities, as, for instance, some essential oils, caffeine, etc.

While some aromatic compounds are products of vegetable life, many of them (like benzene itself) are obtained by destructive distillation, and are therefore contained in coal-tar, from which quite a number are separated by fractional distillation.

**Constitution.**—There is not known any benzene compound which has less than six atoms of carbon. In all of the various decompositions and replacements which occur in the formation of benzene derivatives, the six carbon atoms persist, like a unit. These conditions have led chemists to look upon the six carbon atoms as being joined together, forming a nucleus to which other atoms or groups are attached, in all of the known aromatic compounds. Thus, in benzene, $C_6H_6$, which is the fundamental or mother-substance of these compounds, the six carbon atoms are joined to six atoms of hydrogen.

If benzene were of the nature of a fatty compound, we should expect to find its structure to correspond to a formula of this kind:

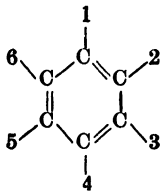
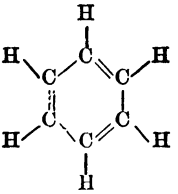
$$\begin{matrix} H \\ H \end{matrix}\!\!>\!C=C=C\!\!<\!\!\begin{matrix} H \\ H \end{matrix} \qquad \begin{matrix} H & H \\ | & | \\ -C=C- \end{matrix}$$

This representation would indicate that benzene ought to behave like a highly unsaturated compound. Moreover, we should expect to obtain two isomeric compounds by replacing either a centrally located hydrogen atom or one occupying a terminal position.

As a matter of fact, benzene does not behave like an unsaturated chain compound (although it can be caused to unite directly with some elements), and by replacement of a hydrogen atom but one kind of substitution product has ever been obtained. These facts lead us to believe that benzene is not an unsaturated chain compound, and that all the hydrogen atoms are equivalent; in other words, *the molecule $C_6H_6$ is perfectly symmetrical.*

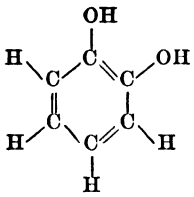
In view of these and many other facts the conclusion is that the six carbon atoms in benzene are united in a cycle or ring, and that each carbon atom is in combination with one hydrogen atom. This view was first put forth by August Kekulé in 1865. Graphically,

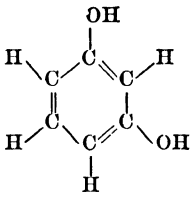
the closed carbon chain and also benzene (usually referred to as Kekulé's benzene hexagon) are represented thus:

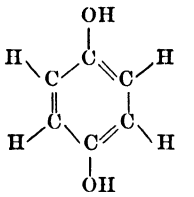



This formula for benzene accounts for the facts mentioned above. Moreover, if two hydrogen atoms are replaced by substituting atoms or radicals, three isomeric products are obtained.

For instance, we know three different substances which have been obtained by replacement of two hydrogen atoms in benzene by two hydroxyl groups. This would indicate that it makes a difference, as far as the properties of a compound are concerned, in which relative position the introduced radicals stand to one another, and as a result of a great deal of investigation it was found that the following formulas represent the three relative positions which the two replacing groups may occupy in a benzene molecule:


Ortho-position.
1 : 2.


Meta-position.
1 : 3.


Para-position.
1 : 4

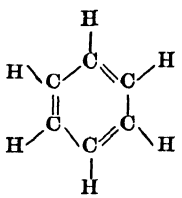
Designating the hydrogen atoms in benzene with numbers, thus:
$C_6\ \overset{1}{H}\ \overset{2}{H}\ \overset{3}{H}\ \overset{4}{H}\ \overset{5}{H}\ \overset{6}{H}$, the above 3 compounds show that in one case the hydrogen atoms 1 and 2, in the second 1 and 3, in the third 1 and 4 have been replaced by OH. The compounds formed in this way are distinguished as ortho-, meta-, and para-compounds.

The molecular formula of the above three compounds is $C_6H_6O_2$, apparently indicating benzene in combination with two atoms of oxygen or dioxy benzene; actually they are dihydroxy benzene. *Ortho*-dihydroxy benzene, $C_6H_4\overset{1}{O}H\overset{2}{O}H$, or $C_6H_4(OH)_2$ 1 : 2, is known as pyrocatechin. *meta*-dihydroxy benzene, $C_6H_4\overset{1}{O}H\overset{3}{O}H$, or $C_6H_4(OH)_2$ 1 : 3, as resorcin, and *para*-dihydroxy benzene, $C_6H_4\overset{1}{O}H\overset{4}{O}H$, or $C_6H_4(OH)_2$ 1 : 4, as hydroquinone.

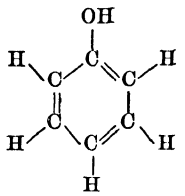
**Benzene Derivatives.**—The analogy existing between methane- and benzene derivatives may be shown by comparing the composition of a few derivatives:

| | | | |
|---|---|---|---|
| Methane, | $CH_4$ | Benzene, | $C_6H_6$ |
| Methyl, | $CH_3$ | Benzyl, Phenyl, | $C_6H_5$ |
| Ethane, Methyl-methane, | $CH_3.CH_3$ | Toluene, Methyl-benzene, | $C_6H_5.CH_3$ |
| Methyl-hydroxide, Methyl-alcohol, | $CH_3OH$ | Phenyl-hydroxide, Phenol, | $C_6H_5.OH$ |
| Glycerin, | $C_3H_5(OH)_3$ | Pyrogallol, | $C_6H_3(OH)_3$ |
| Acetic acid, | $CH_3.CO_2H$ | Benzoic acid, | $C_6H_5.CO_2H$ |
| Acetic aldehyde, | $CH_3.COH$ | Benzoic aldehyde, | $C_6H_5.COH$ |
| Ethyl-sulphonic acid, | $SO_2(C_2H_5)(OH)$ | Benzene-sulphonic acid, | $SO_2(C_6H_5)(OH)$ |
| Malonic acid, | $CH_2(CO_2H)_2$ | Phthalic acid, | $C_6H_4(CO_2H)_2$ |
| Tartaric acid, | $C_2H_2(OH)_2(CO_2H)_2$ | Salicylic acid, | $C_6H_4(OH)(CO_2H)$ |
| Ethyl ether, | $(C_2H_5)_2O$ | Phenyl-ether, | $(C_6H_5)_2O$ |
| Methyl-ethyl ether, | $(CH_3)(C_2H_5)O$ | Methyl-phenyl ether, anisol, | $(CH_3)(C_6H_5)O$ |

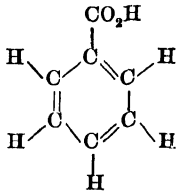
The following graphic formulas may serve to illustrate the constitution of some aromatic compounds:



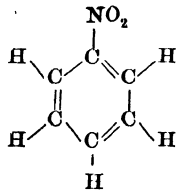
Benzene, $C_6H_6$.



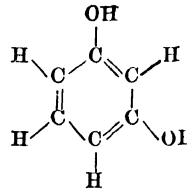
Phenol or carbolic acid, $C_6H_5.OH$.



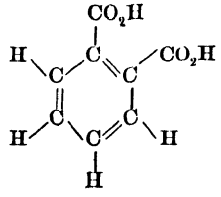
Benzoic acid, $C_6H_5.CO_2H$.



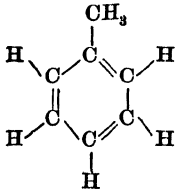
Nitro-benzene, $C_6H_5NO_2$.



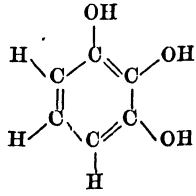
Resorcin, $C_6H_4(OH)_2$.



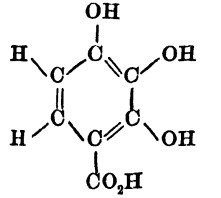
Phthalic acid, $C_6H_4(CO_2H)_2$.



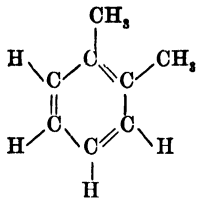
Toluene, methyl-benzene, $C_6H_5.CH_3$.



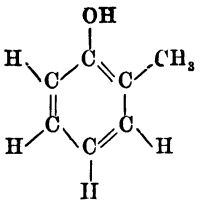
Pyrogallol, $C_6H_3(OH)_3$.



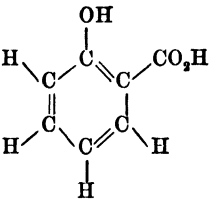
Gallic acid, $C_6H_2.CO_2H.(OH)_3$.



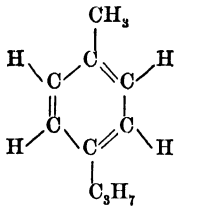
Xylene, di-methyl-benzene, $C_6H_4.(CH_3)_2$.



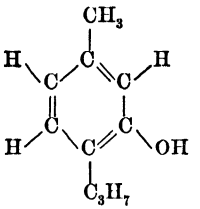
Cresol, $C_6H_4.CH_3.OH$.



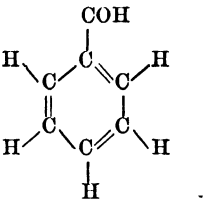
Salicylic acid, $C_6H_4.CO_2H.OH$.



Cymene, methyl-propyl benzene, $C_6H_4\,CH_3\,C_3H_7$.



Thymol, $C_6H_3CH_3.C_3H_7.OH$.



Benzaldehyde, oil of bitter almond, $C_6H_5.COH$.

The preceding graphic formulas show in the first column (besides nitro-benzene) a number of hydrocarbons, in the second column phenols, obtained by introducing hydroxyl into the hydrocarbon molecule, and in the third column chiefly aromatic acids, formed by introducing carboxyl, $CO_2H$, or carboxyl and hydroxyl.

**Differences between Aromatic and Fatty Compounds.**—Substitution products with nitric acid, sulphuric acid, bromine, hydrocarbon radicals, etc., are much more easily formed and held much more strongly in aromatic compounds than in fatty ones. The phenols, which in composition correspond to alcohols, are more acid than the fatty alcohols; aromatic amines are less alkaline than in the fatty series. The phenols do not readily form esters like the alcohols.

Fatty amines with nitrous acid yield alcoholic compounds; aromatic amines behave quite differently, viz., a new series of bodies, known as diazo compounds, is formed. Fatty compounds are easily oxidized, while benzene is very stable in the presence of oxidizing agents.

## Benzene Series of Hydrocarbons.

By replacing the hydrogen atoms in benzene by methyl, $CH_3$, a series of hydrocarbons is formed having the general composition $C_nH_{2n-6}$. To this benzene series belong:

| | | | |
|---|---|---|---|
| Benzene . . . | $C_6H_6$ | ..... | B. P. 80.5° C. |
| Toluene . . . | $C_7H_8$ | $C_6H_5CH_3$ | 110 |
| Xylene . . . | $C_8H_{10}$ | $C_6H_4(CH_3)_2$ | 141 |
| Cumene . . . | $C_9H_{12}$ | $C_6H_3(CH_3)_3$ | 169 |
| Tetra-methyl-benzene | $C_{10}H_{14}$ | $C_6H_2(CH_3)_4$ | 190 |
| Penta-methyl-benzene | $C_{11}H_{16}$ | $C_6H(CH_3)_5$ | 231 |
| Hexa-methyl-benzene | $C_{12}H_{18}$ | $C_6(CH_3)_6$ | 264 |

The first four members of this series are found in coal-tar; the last three have been obtained by synthetical processes. While but one toluene is known, the higher members form quite a number of isomeric compounds. Instead of adding two or more methyl groups it is possible to add an ethyl group, $C_2H_5$, or even higher homologous groups, thus producing a great many isomeric compounds. Thus, cymene, $C_{10}H_{14}$, found in the oil of thyme, is not tetra-methyl-benzene, but para-methyl-isopropyl-benzene, $C_6H_4CH_3.C_3H_7$. This compound is of interest on account of its close relation to the terpenes and camphors, which will be spoken of later.

**Benzene, $C_6H_6$** (*Benzol*).—When coal-tar is distilled, products are obtained which are either lighter or heavier than water, and by collecting the distillate in water a separation into so-called *light oil* (floating on the water) and *heavy oil* (sinking beneath the water) is accomplished. Benzene is found in the light oil and obtained from it by distillation after phenol has been removed by treatment with caustic soda and some basic substances by means of sulphuric acid. Pure benzene may be obtained by heating benzoic acid with calcium hydroxide:

$$C_6H_5CO_2H + Ca(OH)_2 = CaCO_3 + H_2O + C_6H_6.$$

*Experiment* 67.—Mix 25 grams of benzoic acid with 40 grams of slaked lime and distil from a dry flask, connected with a condenser. Add to the distilled fluid a little calcium chloride and redistil from a small flask. The product obtained is pure benzene. Notice that it solidifies when placed in a freezing mixture of ice and common salt. Observe the analogy between Experiments 67 and 51. In one case a fatty acid is decomposed by an alkali with liberation of methane, in the other an aromatic acid with liberation of benzene, the carbonate of the decomposing hydroxide being formed in both cases.

Pure benzene is a colorless, highly volatile liquid, having a peculiar, aromatic odor and a specific gravity of 0.884; it boils at 80.5° C. (177° F.) and solidifies at 0° C. (32° F.); it is an excellent solvent for fats, oils, resins, and many other organic substances.

**Toluene, $C_6H_5CH_3$** (*Methyl Benzene*).—This was first obtained by dry distillation of balsam of tolu, whence its name. It occurs in coal-tar, from which it can be separated, but may also be made from benzene by using a reaction generally employed for the introduction of the methyl groups, thus:

$$C_6H_5Br + CH_3Br + 2Na = C_6H_5CH_3 + 2NaBr.$$

This is known as the *Fittig synthesis*. Another synthesis of general application is that devised by Friedel and Crafts. This consists in the action of alkyl halogen compounds on benzene hydrocarbons in the presence of anhydrous aluminum chloride, thus:

$$C_6H_6 + CH_3Cl = C_6H_5.CH_3 + HCl.$$

Toluene boils at 111° C. and has the sp. gr. 0.865. It has a pleasant aromatic odor and is an excellent solvent.

Toluene, as well as the other hydrocarbon derivatives of benzene, possess properties of the fatty hydrocarbons as well as benzene properties. This is quite natural, because of the fatty radicals present in the molecule. Thus, when oxidized, toluene yields benzoic acid, $C_6H_5CO_2H$, the methyl being oxidized while the benzene ring is unchanged. When chlorine is passed into toluene in the sunlight or while boiling, substitution in the methyl radical takes place, forming benzyl chloride, $C_6H_5CH_2Cl$, benzal chloride, $C_6H_5.CHCl_2$, and benzotrichloride, $C_6H_5.CCl_3$. In the presence of certain substances called carriers, such as iodine, powdered iron or aluminum, in small quantity, chlorine acts on toluene to produce products in which hydrogen in the benzene radical is substituted by chlorine, mono-, di-, and even trichlor-toluene being formed. Bromine acts similarly to chlorine.

**Xylenes, $C_6H_4(CH_3)_2$** (*Dimethyl Benzenes*).—Three xylenes are found in coal-tar, and are distinguished as ortho-, meta-, and para-xylene. They can be made synthetically from toluene in the same manner as toluene is made from benzene. When oxidized they yield ortho-, meta-, and para-phthalic acids, of the composition $C_6H_4(CO_2H)_2$.

**Cymene, $C_{10}H_{14}$ or $C_6H_4.CH_3.C_3H_7$** (*para-methyl-isopropyl-benzene*).—This hydrocarbon occurs in the oil of thyme and in the volatile oils of a few other plants; it has also been made synthetically; it is a liquid of a pleasant odor, boiling at 175° C. (347° F.).

Cymene is of special interest, because it is closely related to the terpenes and camphors, from all of which it may be obtained by comparatively simple processes. The easiest way to prepare it is to heat camphor with phosphorus pentoxide, which removes a molecule of water from a molecule of camphor.

$$C_{10}H_{16}O = C_{10}H_{14} + H_2O.$$

**Positions taken by Substituting Atoms or Radicals in the Benzene Hydrocarbons.**—Although a number of chemicals, such as nitric and sulphuric acids, chlorine and bromine, act more or less readily on benzene hydrocarbons, and alkyl and acyl radicals can be made to replace hydrogen by the Friedel and Crafts reaction, the number of substitution products formed in any reaction is limited, and also some regularity is noted in regard to the positions occupied by atoms or radicals that are substituted for hydrogen in the hydrocarbons. As has been stated, only one kind of mono-substitution product is known, but di-substitution products always exist in three varieties, known as ortho, meta, and para. The character of an atom or radical present in a mono-substitution product has a decided directing influence on the position taken by a second atom or radical to form a di-substitution product. As a rule not all three di-substitution products are formed at the same time but either ortho or para, or a mixture of these with para usually predominating and very little meta compound, or the meta compound with very little ortho and para, are formed.

If the mono-substitution product contains the atom or group Cl, Br, I, $NH_2$, OH, or R (hydrocarbon radical), and the second

atom or group to be introduced is Cl, Br, I, $SO_3H$, $NO_2$, alkyl ($CH_3$, $C_2H_5$, etc.), or RCO (acyl radical), ortho or para compound is formed, or a mixture of these.

If the mono-substitution product contains the group $NO_2$, $SO_3H$, CN, CHO, COOH, or COR, a second atom or group introduced results in the formation of a meta-compound, together with a little ortho and para.

## Nitro Compounds.

These compounds and their difference from nitrates have been referred to in chapter 49. They are of very little importance in the chemistry of fatty hydrocarbons, but are of great value in benzene chemistry. Nitric acid has practically no action on fatty hydrocarbons, but acts more or less readily on aromatic compounds, according to the nature of atoms or radicals already present in the benzene ring. The nitro compounds are not ethereal salts, as they cannot be saponified. They contain the group, $-NO_2$, which results from the combination of hydroxyl of nitric acid with hydrogen of the benzene compound, to form water, thus:

$$C_6H_5.H + HO.NO_2 = \underset{\text{Nitro-benzene}}{C_6H_5.NO_2} + H_2O.$$

The nitrogen is in direct union with carbon, which gives rise to a much more stable compound than is an ethereal salt of nitric acid, in which nitrogen is connected with carbon through the medium of oxygen.

The nitro compounds of the benzene hydrocarbons are either pale yellow liquids, or yellow or colorless crystalline solids, soluble in alcohol and ether, but not in water.

The nitro group is readily reduced to the amine group, $NH_2$. In this manner certain aromatic amine compounds are made which are indispensable in the manufacture of dyes.

**Nitro-benzene, $C_6H_5.NO_2$.**—When benzene is treated with concentrated nitric acid, or with a mixture of nitric and sulphuric acids, nitro-benzene is formed.

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O.$$

*Experiment* 68.—Mix 50 c.c. of sulphuric acid with 25 c.c. nitric acid; allow to cool, place the vessel containing the mixture in water, and add gradually 5 c.c. of benzene, waiting after the addition of a few drops each time until the reaction is over. Shake well until all benzene is dissolved and pour the liquid into 300 c.c. of water. The yellow oil which sinks to the bottom is nitro-benzene. It may be purified by washing with water and redistilling, after removal of water and shaking with calcium chloride.

Nitro-benzene is an almost colorless or yellowish oily liquid, which is insoluble in water, has a specific gravity of 1.2, a boiling-point of 210° C. (410° F.), a sweetish taste, highly poisonous properties, even when inhaled, and an odor resembling that of oil of bitter almond,

for which it is substituted under the name of *essence of mirbane*. It is manufactured on a large scale, and is used chiefly in the preparation of aniline.

**Dinitro-benzene, $C_6H_4(NO_2)_2$.**—Dinitro-benzene is formed as described above but with the application of heat. The meta is the main product, but small quantities of ortho and para compound are also formed. Meta-dinitro-benzene forms colorless needles from alcohol, melting at 91° C. and boiling at 297° C. Either one or both of the $NO_2$ groups of the dinitro-benzenes, can be reduced to $NH_2$ groups, forming nitro-anilines or phenylene-diamines.

**Nitro-toluene, $C_6H_4(CH_3)NO_2$.**—When toluene is nitrated, the chief products are ortho and para compounds, with a small amount of the meta. The relative proportions of each depends on the temperature during nitration. Orthonitro-toluene melts at 10.5° C. and boils at 218° C.; the meta compound melts at 16° C. and boils at 230° C., the para compound melts at 54° C. and boils at 234° C.

## Sulphonic Acids.

The action of sulphuric acid on hydrocarbons is similar to that of nitric acid. It does not act on fatty hydrocarbons, but acts more or less readily on aromatic hydrocarbons, forming sulphonic acids, in which an (OH) group of the acid has been replaced by hydrocarbon radical, thus,

$$C_6H_5H + \begin{matrix}HO\\HO\end{matrix}\!\!>SO_2 = \underset{\text{Benzene sulphonic acid}}{\begin{matrix}C_6H_5\\HO\end{matrix}\!\!>SO_2} + H_2O.$$

The sulphonic acids are not ethereal salts and cannot be saponified. The sulphur is united directly with carbon as is shown by the fact that sulphonic acids are converted into mercaptans by strong reducing agents. They are strong acids, crystallizable, and for the most part soluble in water. The barium salts of sulphonic acids are soluble in water, whereas barium sulphate is highly insoluble. Use is made of this fact for separating sulphonic acids from excess of sulphuric acid, by digesting the diluted mixture with barium carbonate and filtering.

Sulphonic acids, heated with water under pressure, revert to the hydrocarbons by replacement of the $SO_3H$ group by hydrogen. When sulphonates are fused with caustic alkalies, hydroxyl (OH) is substituted for the $SO_3H$ group. This furnishes a convenient method for making phenols synthetically.

$$C_6H_5SO_3Na + 2NaOH = \underset{\text{Sodium phenolate}}{C_6H_5ONa} + Na_2SO_3 + H_2O.$$

The phenols are liberated by treating the alkali compounds formed with an acid, thus:

$$C_6H_5ONa + HCl = \underset{\text{Phenol.}}{C_6H_5OH} + NaCl.$$

Sulphonates, distilled with an alkali cyanide, form nitriles (cyanides), which by hydrolysis are converted into carboxyl acids, thus:

$$C_6H_5SO_3Na + NaCN = \underset{\text{Benzonitrile.}}{C_6H_5CN} + Na_2SO_3.$$

$$C_6H_5CN + 2H_2O = \underset{\text{Benzoic acid.}}{C_6H_5COOH} + NH_3.$$

**Benzenesulphonic Acid, $C_6H_5SO_3H.1\frac{1}{2}H_2O$.**—When benzene is shaken constantly with warm concentrated sulphuric acid, combination takes place slowly. The barium salt can be obtained as described above, and from it the acid is liberated by exact precipitation of the barium with sulphuric acid. Crystals of benzenesulphonic acid can be obtained, which are deliquescent, very soluble in water, and melt at 42° C.

**Toluenesulphonic Acids, $CH_3.C_6H_4.SO_3H$.**—When toluene is shaken constantly with concentrated sulphuric acid at ordinary temperature, it combines gradually with the acid, forming a mixture of ortho- and para-sulphonic acid. When, however, the action takes place on a boiling water-bath, the para-sulphonic acid is the chief product.

## Aromatic Amines.

From benzene, only one variety of amine can be derived, namely, amines in which the nitrogen is united with carbon in the benzene ring. The homologues of benzene, containing fatty hydrocarbon radicals as side-chains, can give rise to two varieties of amines, namely, a variety in which the nitrogen is attached to a carbon atom in the benzene ring, and a variety in which nitrogen is attached to carbon in the fatty hydrocarbon side-chain. The latter class of amines have practically the same properties as the simple fatty amines, and should be considered as substituted fatty amines. The amines of the other class are the aromatic amines proper. These have many properties like those of fatty amines but differ in some respects from the latter. For example, they are less basic, do not act on litmus, their salts undergo hydrolysis in water, show an acid reaction to litmus, and are decomposed by alkali carbonates. A sharp contrast is shown between the fatty amines and aromatic amines in their behavior toward nitrous acid. The former are converted directly into hydroxyl compounds (see chapter 49), whereas the latter are converted first into the very important class of diazonium compounds, thus:

$$\underset{\text{Aniline hydrochloride.}}{C_6H_5NH_2.HCl} + HONO = \underset{\substack{\text{Diazonium}\\\text{chloride.}}}{C_6H_5.N_2.Cl} + 2H_2O.$$

These diazonium compounds are very important in the manufacture of dyes and other compounds. When they are heated with

water, nitrogen is given off, and a hydroxyl compound is formed, as in the case of fatty amines.

$$C_6H_5.N_2.Cl + H_2O = \underset{\text{Phenol.}}{C_6H_5OH} + N_2 + HCl.$$

Aromatic amines are usually prepared by reduction of the nitro compounds, which may be accomplished by various reducing agents, such as tin and hydrochloric acid, iron or zinc and hydrochloric or acetic acid, stannous chloride and hydrochloric acid, and alcoholic ammonium sulphide.

Aromatic amines containing one $NH_2$ group are liquids or crystallizable solids, which gradually turn brown when in contact with the air, have a peculiar odor, and are only slightly soluble in water.

**Aniline, Phenyl-amine, $C_6H_5NH_2$.**—Aniline is found in coal-tar and in bone-oil; it is manufactured on a large scale by the action of nascent hydrogen upon nitro-benzene, iron and hydrochloric acid being generally used for generating the hydrogen.

*Experiment* 69. Dissolve 20 c.c. of nitro-benzene (this may be obtained according to the directions given in Experiment 68, using larger quantities of the material) in alcoholic ammonia and pass through this solution hydrogen sulphide as long as a precipitate of sulphur is produced; the reaction takes place thus:

$$C_6H_5NO_2 + 3H_2S = C_6H_5NH_2 + 2H_2O + 3S.$$

Evaporate on a water-bath to expel ammonium sulphide and alcohol; add to the residue dilute hydrochloric acid, which dissolves the aniline, but leaves any unchanged nitro-benzene undissolved. Separate the nitro-benzene from the aniline chloride solution, evaporate this to dryness, mix with some lime, in order to liberate the aniline, which may be obtained by distillation from a dry flask.

Pure aniline is a colorless, slightly alkaline liquid, having a peculiar, aromatic odor, a bitter taste, and strongly poisonous properties. It boils at 184.5° C. (364° F.). Like all true amines, it combine with acids to form well-defined salts. It is soluble in about 30 parts of water, and the solution becomes violet when treated with a solution of bleaching-powder, or blue with a solution of dichromate. In the presence of an acid, dichromate gives a green color with aniline. Aniline is more sensitive to the halogen elements than benzene. Its aqueous solution gives a precipitate of tribrom-aniline with bromine water.

**Acetanilide** (*Acetanilidum*), **$C_6H_5.NH.(CH_3CO)$ = 135.08,** (*Antifebrine, Phenylacetamide*). The term anilide is used for derivatives of aniline obtained from this compound by replacement of the ammonia hydrogen (or amino hydrogen) by acid radicals. If the radical introduced is acetyl, $C_2H_3O$, the resulting compound is acetanilide, the constitution of which is represented in the formula $NH < \begin{matrix} C_6H_5 \\ C_2H_3O \end{matrix}$.

It is obtained by boiling together for one or two days equal weights of pure aniline and glacial acetic acid, distilling and collecting the portion which passes over at a temperature of about 295° C. (563° F.). The distillate solidifies on cooling and may be purified by recrystallization from solution in water. The chemical change taking place is this:

$$C_6H_5NH_2 + C_2H_4O_2 = C_6H_5.NH.C_2H_3O + H_2O.$$

Pure acetanilide forms white odorless crystals of a silky lustre and a greasy feeling to the touch. It fuses at 113° C. (235° F.) and boils at 295° C. (563° F.); it is but slightly soluble in cold, much more soluble in hot water, readily soluble in alcohol and ether; the solutions have a neutral reaction and are not colored by either concentrated sulphuric acid or by ferric chloride.

*Analytical reactions:*

1. When 0.1 gram of acetanilide is boiled for several minutes with 2 c.c. of hydrochloric acid, and to this solution are added 3 c.c. of an aqueous solution of phenol (1 in 20) and 5 c.c. of a filtered, saturated solution of bleaching powder, a brownish-red liquid is obtained which turns deep blue upon supersaturation with ammonia water.

2. On heating 0.1 gram of acetanilide, with a few c.c. of concentrated solution (1 in 4) of potassium hydroxide, the odor of aniline becomes noticeable; on now adding chloroform, and again heating, the disagreeable odor of the poisonous phenyl-isocyanide, $C_6H_5NC$, is evolved (distinction from antipyrine).

3. A mixture of equal parts of acetanilide and sodium nitrite sprinkled upon concentrated sulphuric acid produces a bright red color.

The presence of the acetyl radical renders acetanilide less sensitive to halogen elements and nitric acid than free aniline. With bromine, acetanilide forms monobrom-acetanilide, whereas aniline forms a tribrom-derivative. Monobrom-acetanilide, when hydrolyzed, yields monobrom-aniline.

**Methyl Aniline, $C_6H_5.NHCH_3$.**—This is made commercially by heating together aniline hydrochloride and methyl alcohol. It is an oil lighter than water, boiling at about 190° C., and used in dye industries.

**Methyl Acetanilide, $C_6H_5.N.CH_3.C_2H_3O$** (*Exalgin*), may be made by the acetylating of monomethyl-aniline. It occurs as a crystalline powder or in large crystalline needles; it is tasteless and almost insoluble in water.

**Sulphanilic Acid, Aniline-para-sulphonic Acid, $C_6H_4.NH_2.SO_3H$.**—Obtained by heating 1 part of pure aniline oil with 2 parts of fuming sulphuric acid, and purifying the product by crystallization.

$$C_6H_5.NH_2 + H_2SO_4 = C_6H_4.NH_2.SO_3H + H_2O.$$

It is a colorless crystalline substance, soluble in 182 parts of cold water. When sulphanilic acid is acted upon by nitrous acid, it is converted into *diazo-benzene-sulphonic acid*, $C_6H_4N.N.SO_3$, which is of interest because it is used as a reagent in Ehrlich's diazo-reaction in urinary analysis, and in the preparation of dyes.

**Toluidines, $CH_3.C_6H_4.NH_2$.**—Three isomeric compounds of this composition exist. They are obtained by reduction of the corresponding nitrotoluenes, just as

in the case of nitrobenzene. The boiling-points of the toluidines are almost identical, lying between 198° C. and 200° C. The melting-points of the acetyl derivatives of ortho-, meta, and para-toluidine, respectively, are 107°, 65°, and 147° C.

**Aniline Dyes.**—The crude benzene used in the manufacture of aniline dyes is generally a mixture of benzene, $C_6H_6$, and toluene, $C_7H_8$. This mixture is first converted into nitro-benzene, $C_6H_5NO_2$, and nitro-toluene, $C_7H_7NO_2$, and then into aniline, $C_6H_5NH_2$, and toluidine, $C_7H_7NH_2$. When these substances are treated with oxidizing agents, such as arsenic oxide, hypochlorites, chromic or nitric acid, etc., various substances are obtained which are either themselves distinguished by beautiful colors or may be converted into numerous derivatives showing all the various shades of red, blue, violet, green, etc.

As an instance of the formation of an aniline dye may be mentioned that of *rosaniline*, which takes place thus:

$$\underset{\text{Aniline}}{C_6H_7N} + 2\underset{\text{Toluidine.}}{C_7H_9N} + 3O = \underset{\text{Rosaniline}}{C_{20}H_{19}N_3} + 3H_2O.$$

*Experiment* 70.—To some of the aniline obtained by performing Experiment 69 add a little solution of bleaching powder: a beautiful purple color is obtained. Treat another portion with sulphuric acid to which an aqueous solution of potassium dichromate has been added: a green color is produced. A third quantity treat with solution of cupric sulphate and potassium chlorate: a dark color is the result.

**Diphenyl-amine, $(C_6H_5)_2NH$,** is obtained by the destructive distillation of triphenyl-rosaniline (aniline-blue) as a grayish crystalline substance, slightly soluble in water, more soluble in acids. A 0.2 per cent. solution in diluted sulphuric acid (forming diphenylamine sulphuric acid) is colored intensely blue by nitric acid; also, temporarily by nitrous acid and, somewhat less intensely, by hypochlorous, bromic, and iodic acids, and a number of other oxidizing agents.

**Diamino-benzene, Meta-phenylene-diamine, $C_6H_4(NH_2)_2$,** is obtained by the reduction of meta-dinitro-benzene as a grayish crystalline powder. It has strongly basic properties, is somewhat soluble in water, readily soluble in alcohol or ether. It is a valuable reagent for nitrites, as it forms, with even traces of nitrous acid, an intense yellow color.

**Methylthionine Chloride** (*Methylthioninæ Chloridum*) **$C_{16}H_{18}N_3SCl$ = 319.7** (*Methylene Blue*).—This is a very complex dye obtained by treating dimethyl-paraphenylene-diamine, $C_6H_4.(NH_2)N(CH_3)_2$, in hydrochloric acid solution with hydrogen sulphide and subsequently with ferric chloride. It occurs as a dark green powder or in prismatic crystals having a bronze-like lustre, readily soluble in water and somewhat less so in alcohol, giving solutions of a deep blue color. Alkalies change the color of the aqueous solution to a purplish shade, and in excess cause a precipitate of a dull violet color. It is incompatible with potassium iodide, and reducing agents decolorize it.

Methylene blue should not be confounded with the commercial article, which is often the zinc chloride double salt of methylthionine, is employed as a dye or stain, and is unfit for medicinal purposes. The presence of zinc can be told by incinerating 2 grams of the substance and testing the ash in the usual way for zinc. Methylene blue should also not be confounded with methyl blue, which

is the sodium salt of triphenyl-pararosaniline-trisulphonic acid. A solution of the latter with alkalies changes to reddish brown.

*Methylene azure*, $C_{16}H_{18}N_3SO_2Cl$, is derived from methylene blue by the addition of oxygen. It is present in "ripened" methylene blue and almost always in even the best specimens of the medicinal article. It may be detected by adding ammonia to a solution of methylene blue and then shaking with ether; the methylene azure passes into the ether, which is colored red.

## Diazo (diazonium) Compounds of Benzene.

When fatty amines are treated with nitrous acid the amino group is replaced by hydroxyl, thus:

$$C_2H_5.NH_2 + HONO = C_2H_5OH + 2N + H_2O.$$

When, however, an aromatic amine is treated with nitrous acid, in acid solution, a new class of compounds is formed, known as diazo-compounds, thus:

$$\underset{\text{Aniline hydrochloride.}}{C_6H_5.NH_2HCl} + HONO = \underset{\text{Diazo-benzene chloride.}}{C_6H_5.N_2.Cl} + 2H_2O.$$

The characteristic diazo grouping is expressed thus: R—$N_2$—, and this group combines with acid residues to form diazo-salts, such as diazo-benzene nitrate, $C_6H_5.N_2.NO_3$, sulphate, $C_6H_5.N_2.SO_4H$, etc.

The diazo-compounds are colorless, crystalline, unstable, and even explosive substances; soluble in water, insoluble in ether. They are of great scientific and technical importance, as they form the starting-point for a large class of dyes. Diazo-compounds are decomposed by water, either in the cold or upon heating, the $N_2$ group being usually replaced by the (OH) group, thus:

$$C_6H_5.N_2.NO_3 + H_2O = C_6H_5OH + N_2 + HNO_3.$$

It is thus possible to introduce hydroxyl into the benzene nucleus through the medium of nitro-compounds, and obtain substances belonging to the class of phenols.

These compounds were originally called "diazo" because they contained two nitrogen atoms in the molecule, the word azote being the French for nitrogen. By a careful study of their properties, it became evident that diazo-salts were in many respects similar to ammonium salts and that the formula which best explains their behavior is R—N=N—X, in which X represents acid residues. Because of

their similarity to ammonium salts, the diazo-salts are now called *diazonium* salts. It is certain, however, that in some of the reactions of diazonium salts, a molecular rearrangement takes place to produce the grouping R—N=N—X, which is now known as the *diazo grouping*.

Diazo-compounds have a marked tendency to react with other substances, especially amino-compounds and phenols, to form a class known as *azo*-compounds, which are characterized by having the group —N=N— in combination with two residues. Azobenzene, $C_6H_5$—N=N—$C_6H_5$, is the mother-

substance of all azo-compounds, most of which are highly colored, and many are used as dyes. The formation of colored azo-compounds is involved in the test for nitrites in drinking-water by meta-phenylene-diamine (chapter 38), which gives triamino-azobenzene, $NH_2.C_6H_4—N=N—C_6H_3(NH_2)_2$, a dye which has been on the market since 1866 and known as Bismarck brown; also the test in which sulphanilic acid and alpha-naphthylamine are used. In Ehrlich's Diazo-reaction for typhoid fever, it is believed that some unknown phenolic or amino compound in the urine unites with the diazo-sulphanilic acid reagent, and forms an azo-dye. Some of the indicators used in volumetric analysis are azo-dyes, for example, methyl-orange (chapter 38). Dimethyl-amino-azobenzol, $C_6H_5 - N = N - C_6H_4.N(CH_3)_2$, is used to detect hydrochloric acid in stomach contents.

**Phenyl hydrazine, $C_6H_5.NH.NH_2$.** When diazo-compounds are reduced, they yield derivatives of the mother-substance, $H_2N—NH_2$, known as hydrazine, or diamine. Thus, diazo-benzene yields phenyl hydrazine. It is a strongly basic substance and unites readily with acids to form salts; it is a colorless crystalline substance, sparingly soluble in water, but soluble in acids. Phenylhydrazine is of interest because it is used in the manufacture of antipyrine, and as a valuable reagent for the detection of aldehydes and sugars. It combines with both classes of compounds, forming with aldehydes bodies known as *hydrazones*, with sugars, *osazones*. Most of these compounds are solid and crystalline; the crystalline structure often serves for identification.

**Arsenic and phosphorus derivatives.** A number of compounds of aromatic hydrocarbons containing arsenic and phosphorus, and having compositions similar to nitro-, azo-, and amino-compounds, are known. The similarities are shown in the following table:

| | | |
|---|---|---|
| $C_6H_5.NO_2$ | $C_6H_5.N_2.C_6H_5$ | $C_6H_5NH_2$ |
| Nitrobenzene. | Azobenzene. | Phenylamine. |
| $C_6H_5.PO_2$ | $C_6H_5P_2.C_6H_5$ | $C_6H_5.PH_2$ |
| Phosphinobenzene | Phosphobenzene. | Phenylphosphine. |
| $C_6H_5AsO_2$ | $C_6H_5.As_2.C_6H_5$ | |
| Arsinobenzene. | Arsenobenzene. | |

*Arsenobenzene*, $C_6H_5.As : As.C_6H_5$, is obtained by the reduction of phenyl-arsine oxide, $C_6H_5.AsO$, by phosphorous acid, as yellow needles. By oxidation it is converted into phenylarsonic acid, $C_6H_5.AsO(OH)_2$.

*Sodium para-aminophenyl arsonate*, $NH_2.C_6H_4.AsO(OH).ONa.3H_2O$ (*sodium arsanilate, sodium aniline arsonate, atoxyl*), is a white, odorless, crystalline salt, soluble in about 6 parts of water, and having a faint salty taste. The aqueous solution on standing assumes a yellowish tint. It is used in sleeping sickness (trypanosomiasis), syphilis, malaria, etc. It should be given hypodermically, and not by the mouth. Atoxyl is made by heating aniline arsenate to about 200° C. for several hours, when a reaction takes place analogous to that by which para-amino-benzene sulphonic acid (sulphanilic acid) is formed by heating aniline sulphate:

| | | | | |
|---|---|---|---|---|
| $C_6H_5NH_2.(HO)_3AsO$ | = | $NH_2.C_6H_4.AsO(OH)_2$ | + | $H_2O$ |
| Aniline arsenate. | | Para-aminophenyl arsonic acid. | | |

The sodium salt of this acid is atoxyl.

*Dioxydiaminoarsenobenzene*, $\begin{matrix}(HO)\\NH_2\end{matrix}\diagdown\!\!\diagup C_6H_3.As : As.C_6H_3\diagup\!\!\diagdown\begin{matrix}(OH)\\NH_2\end{matrix}\ \begin{matrix}(1)\\(2)\end{matrix}$. The

dihydrochloride ("bichloride," as it is called in the market) of this diamine compound was prepared by Ehrlich and Bertheim, and was the 606th compound made in a search for a specific remedy for germ diseases. It is known as "606," or *salvarsan*. The arsenic occupies the para position in the benzene nucleus. This substance has basic properties due to the $NH_2$ groups, and therefore unites with acids; it also has acid properties due to the (OH) groups, and forms salts with alkalies just as phenol does.

Salvarsan is a lemon-yellow powder, which comes in sealed tubes. It is soluble in water with a decided acid reaction, due to hydrolysis and liberation of hydrochloric acid. The sodium salt gives an alkaline reaction in solution, due to hydrolysis and liberation of sodium hydroxide. The free base is insoluble in water and is precipitated by the cautious addition of alkali to the solution of the hydrochloride, or of acid to the solution of the sodium compound. For injections, either a suspension of the free base or a solution of the mono- or di-sodium salt is prepared from salvarsan.

## Hydroxyl Derivatives of the Benzene Series.

Two classes of hydroxyl derivatives of the aromatic hydrocarbons exist. In one, called the *aromatic alcohols*, the hydroxyl group replaces hydrogen in the fatty side-chain hydrocarbon. These compounds are true alcohols, being aromatic substitution products of the fatty alcohols. Accordingly, they closely resemble alcohols in properties; they combine with acids to form esters, and when oxidized, form aldehydes and acids. In the other class of hydroxyl derivatives, the hydroxyl radical is united with a carbon atom of the benzene ring. These compounds, called *phenols*, show acid characteristics, owing to the negative character of the aromatic radicals. They differ from alcohols in not yielding aldehydes or acids by oxidation, and in combining readily with dilute alkalies to form soluble compounds. Phenols may contain one, two, or more hydroxyl groups, just as alcohols do.

## Phenols.

Phenols are either liquid or solid, and often have a peculiar odor. Most of them can be distilled without decomposition, and are readily soluble in alcohol and ether; some are readily soluble in water. Many are antiseptic, for example, phenol, cresol, resorcin, thymol, etc. Many individual phenols are found in the vegetable and animal kingdoms. Destructive distillation of complex carbon compounds usually results in the formation of phenols among the products; thus, wood-tar and coal-tar are rich in phenols.

Phenols act like weak acids, forming salts with caustic alkalies, which are soluble in water and far more stable than the alcoholates. But they do not decompose carbonates.

Phenols can be obtained readily by first preparing sulphonic acids, and fusing the alkali salts of these with caustic soda or potash. The actions are shown in the following equations, which relate to synthetic phenol:

$$C_6H_6 + H_2SO_4 = \underset{\text{Benzene sulphonic acid.}}{C_6H_5SO_3H} + H_2O.$$

$$C_6H_5SO_3Na + NaOH = \underset{\text{Phenol.}}{C_6H_5OH.} + Na_2SO_3.$$

The phenol is liberated from its alkali salt by an acid, and is purified by further appropriate treatment.

Phenols can also be prepared from primary amines through the diazo-reaction. They cannot be obtained easily by the action of caustic alkalies on halogen substitution products of benzene hydrocarbons.

**Phenol, $C_6H_5OH$ = 94.05** (*Carbolic Acid, Phenyl Hydroxide*).—Crude carbolic acid is a liquid obtained during the distillation of coal-tar between the temperatures of 170°–190° C. (338°–374° F.), and containing chiefly phenol, besides cresol, $C_7H_7OH$, and other substances. It is a reddish-brown liquid of a strongly empyreumatic and disagreeable odor.

By fractional distillation of the crude carbolic acid, the pure acid is obtained, which forms colorless, interlaced, needle-shaped crystals, sometimes acquiring a pinkish tint; it has a characteristic, slightly aromatic odor, is deliquescent in moist air, soluble in from 15 to 20 parts of water, and very soluble in alcohol, ether, chloroform, glycerin, fat and volatile oils, etc.; it has, when diluted, a sweetish and afterward burning, caustic taste; it produces a benumbing and caustic effect, and even blisters on the skin; it is strongly poisonous, and a powerful disinfectant, preventing fermentation and putrefaction to a marked degree; fusing-point of the official article not less than 40° C. (104° F.); boiling-point 188° C. (370° F.).

Phenol, though generally called carbolic acid, has a neutral or but faintly acid reaction, and the constitution of a tertiary alcohol, but it readily combines with strong bases, for instance, with sodium hydroxide, forming sodium phenoxide or sodium phenolate:

$$C_6H_5OH + NaOH = C_6H_5ONa + H_2O.$$

Phenol obtained by synthetical processes is now sold in a state of great purity; it has comparatively little odor.

Phenol is readily liquefied by a small amount of water and is usually dispensed in this form. The *Liquefied phenol* of the U. S. P. contains about 13.6 per cent. of water.

Phenol often becomes colored when exposed to air and light. This is due to oxidation. When pure it remains colorless even in sunlight if it is kept in an atmosphere of inert gases, as hydrogen, nitrogen, or carbon dioxide. The rate of oxidation varies with the temperature, being rapid at the boiling-point of phenol. The products of oxidation are quinol, quinone, and catechol, and the principal colored compounds are probably quinone condensation products. The formation of the intensely red substance called phenoquinone is probable.

Glass which most completely absorbs ultra-violet light retards the action of oxygen on phenol in the greatest degree.

**Phenol or Carbolic Acid Coefficient** (*Rideal-Walker coefficient*).—Bacteriological standardization of disinfectants was proposed in 1896 by C. G. Moor. In 1903 Samuel Rideal and Ainslie Walker developed the method now in use, which, with later improvements, is the best available in spite of some defects. In this method carbolic acid is taken as the standard of comparison for other disinfectants. The *phenol or carbolic acid coefficient* is the ratio of the strength in which a given disinfectant kills a given organism to that of carbolic acid which effects the same sterilization in the same time. The colon or typhoid bacillus is employed in the experiments of comparison.

The meaning of the coefficient will appear clear from the following example, which refers to a culture of bacillus pestis. A 1 in 40 formaldehyde solution was equivalent to a 1 in 110 solution of carbolic acid, both sterilizing in ten minutes, but not in seven and a half minutes. Hence, carbolic acid coefficient of the formaldehyde in this instance was $\frac{40}{110}$, or 0.36.

The laws of some states require the labels of substances sold as disinfectants to state the carbolic acid coefficient. The following table shows the coefficients and the relative money values of various disinfectants in the market:

| Disinfectant. | Carbolic acid coefficient. | Cost of the quantity of disinfectant equivalent to 1 English gallon of 98 per cent. carbolic acid. |
|---|---|---|
| Carbolic acid, 98 per cent. | 1.00 | $ 0.25 |
| Chinosol | 0.30 | 127.87 |
| Condy's fluid | 0.90 | 2.00 |
| Cyllin (a cresol) | 11.00 | 0.08 |
| Formaldehyde | 0.30 | 4.40 |
| Izal | 8.00 | 0 12 |
| Listerine | 0.03 | 324.62 |
| Lysoform | 0.10 | 36.49 |
| Lysol | 2.50 | 0.76 |
| Pearson's antiseptic | 1.40 | 0.42 |
| Sanitas | 0.02 | 42.56 |

The coefficients of some other disinfectants are: sulphonaphthol, 2.2; zenoleum, 2.49; kreso, 2.5; chloronaphtholeum, 5.4; hyco, 19; Platt's chlorides, 3.

*Antidotes.* Alcohol is the best antidote; it prevents the corrosive action of phenol. But the stomach should be at once emptied and washed out, else the phenol will be absorbed and then alcohol would prove worse than no antidote. Soluble sulphates have been recommended on the supposition that harmless phenolsulphonates are formed, but recent experimenters have asserted that they are useless as an antidote. Hot applications to the extremities, hypodermic injection of cardiac and respiratory stimulants, intravenous injection of normal saline solution, and morphine to relieve pain, are valuable aids in phenol poisoning.

**Tests for Phenol.** (Use an aqueous solution.)—1. It coagulates albumin and collodion.

2. It colors solutions of neutral ferric chloride intensely and permanently violet blue.

3. Bromine water, added in excess, produces, even in dilute solutions, a white precipitate of tribrom-phenol, $C_6H_2Br_3OH$, which has been used medicinally under the name of *Bromol.*

4. Millon's reagent (see Index), heated to boiling with phenol solution, gives an intense red color on addition of a few drops of nitric acid.

5. On heating with nitric acid it turns yellow, nitro-phenols being formed.

**Bismuth Tribrom-phenolate, $Bi_2O_2.OH.(OC_6H_2Br_3)$** (*Xeroform*).—Bismuth tribrom-phenolate is a fine yellow, nearly odorless and tasteless powder, insoluble in water or alcohol, but soluble in 2 per cent. hydrochloric acid in the proportion of 30 : 100. It is incompatible with alkaline media and should not be heated above 120° C. It is a non-irritant and non-toxic antiseptic, recommended as a substitute for iodoform.

**Cresol, $C_7H_7OH$ = 108.06.**—The official cresol is a mixture of the three isomeric cresols, $(C_6H_4.CH_3.OH)$, or hydroxyl derivatives of toluene, the ortho-, para-, and meta-cresol. The cresols bear the same relation to toluene that phenol bears to benzene, and they resemble phenol very closely in their properties. Cresol is a colorless or straw-colored refractive liquid having a phenol-like odor. It is soluble in 60 parts of water, miscible with alcohol, ether, and glycerin in all proportions. It boils at about 200° C. (392° F.). The individual cresols cannot easily be separated from a mixture of the three cresols. If a pure cresol is wanted, it is prepared either by fusing the corresponding toluene sulphonic acid with an alkali, or by converting a toluidine into a diazonium compound and decomposing the latter by heating with water.

Cresol is slightly soluble in water, hence it is often used in the form of emulsions, or dissolved with the aid of salts or of soap. *Compound solution of cresol, Liquor cresolis compositus,* is a linseed-oil-soap solution of cresol, of 50 per cent. strength. It is of much more definite composition than many commercial preparations of similar nature. *Lysol* is about the same as the official solution. The mixtures known as *creolins* usually contain impure cresol dissolved with the aid of rosin soap. They usually form emulsions when diluted with water. *Solveol* and *solutol* are solutions of cresol made with the aid of salts. *Tri-cresol* (*enterol*) is said to contain 35 per cent. of ortho-cresol, 40 per cent. of meta-cresol, and 25 per cent. of para-cresol, and is soluble to the extent of 2.2 to 2.55 per cent. in water. A vast number of other similar solutions are on the market. It is generally held that cresol is more toxic to bacteria than phenol is. *Losophan* and *europhen* are iodine compounds of cresol.

**Creosote** (*Cresotum*).—Two different preparations of this name are sold in the market. One is coal-tar creosote and is chiefly an impure carbolic acid. The official creosote is a liquid product of the distillation of wood-tar, especially of beechwood-tar, which contains

sometimes as much as 25 per cent. of creosote; it resembles carbolic acid in many respects, especially in its antiseptic properties and its action on the skin. It is a mixture of substances, but consists chiefly of guaiacol, $C_6H_4.OCH_3.OH$, and creosol, $C_6H_3.CH_3.OCH_3.OH$.

Beechwood creosote may be distinguished from carbolic acid by requiring as much as 150 parts of water for solution; by being miscible with the official collodion in equal volumes without forming a coagulum; by not being solidified on cooling; by not coloring ferric chloride permanently; and by its boiling-point, which rises from 205° to 215° C. (401° to 419° F.).

**Creosote Carbonate** (*Creosoti Carbonas, Creosotal*).—This is a mixture of carbonic acid esters, analogous to guaiacol carbonate, prepared from creosote by passing a current of carbonyl chloride into a solution of creosote in sodium hydroxide. It is a yellowish, thick, clear, and transparent liquid, odorless, and has a bland, oily taste. It is insoluble in water, but soluble in alcohol and in fixed oils. It is non-toxic and non-irritant and is used as a substitute for creosote.

**Thymol, $C_{10}H_{14}O$ or $C_6H_3.CH_3.C_3H_7.OH$ = 150.11** (*Methyl-isopropylphenol*).—Thymol is found in small quantities as a constituent of the volatile oils of wild thyme, horse-mint, and a few other plants.

Thymol crystallizes in large translucent plates, has a mild odor, a warm, pungent taste, melts at 50° C. (122° F.) and boils at 230° C. (446° F.). It is now largely used as an excellent and very valuable antiseptic, preference being given to it on account of its comparative harmlessness when compared with the strongly poisonous carbolic acid.

Thymol dissolved in moderately concentrated warm solution of potassium hydroxide, gives on the addition of a few drops of chloroform a violet color, which on heating soon changes into a beautiful violet red.

**Thymol Iodide** (*Thymolis Iodidum*) **($C_6H_2.CH_3.C_3H_7.OI)_2$ = 550.03** (*Dithymol-diiodide, Aristol, Annudalin*).—Obtained by the action of a solution of iodine in potassium iodide upon an alkaline solution of thymol. Condensation of two molecules of thymol takes place with the introduction of two atoms of iodine into its phenolic group. It is a bright, chocolate-colored, or reddish-yellow, bulky powder, with a very slight aromatic odor; it contains 46.14 per cent. of iodine and is used as a substitute for iodoform.

**Pyrocatechol, $C_6H_4(OH)_2$, 1 : 2** (*Catechol, Pyrocatechin, Ortho-dihydroxy-benzene*).—This is made by heating ortho-phenolsulphonic acid with caustic potash at 350° C., by which the $SO_3H$ group is replaced by the (OH) radical. It occurs in colorless needles, which melt at 104° C., and are easily soluble in water. An alkaline solution of pyrocatechol absorbs oxygen. It turns green and finally black. Pyrocatechol is a good reducing agent, for which reason it is sometimes used in photography as a developer. Ferric chloride colors an aqueous solution green.

**Guaiacol, $C_6H_4.OH.OCH_3$ = 124.06,** found in beechwood creosote to the extent of from 60 to 90 per cent., is a derivative of pyrocatechol and obtained from it by replacing a hydroxyl hydrogen atom by methyl, $CH_3$. Guaiacol is consequently monomethyl pyrocatechol. It is a colorless, crystalline solid, melting at 28.5° C. (83.5° F.), or a colorless refractive liquid, boiling at 205° C. (401° F.), and possessing a strong aromatic odor. It is difficultly soluble in water, easily

soluble in alcohol and ether. In alcoholic solution ferric chloride produces an immediate blue color, changing to emerald green, later to yellowish. It is obtained either synthetically or from creosote.

**Veratrol, $C_6H_4(OCH_3)_2$,** the dimethyl ether of pyrocatechol, is a colorless, aromatic, oily liquid, having the same boiling-point as guaiacol.

A number of derivatives of guaiacol are on the market, being chiefly compounds with acid radicals, such as the camphorate (*guaiacamphol*), carbonate, benzoate (*benzosol*), cinnamate (*styracol*), phosphate, phosphite, salicylate (*guaiacol-salol*), valerate (*geosote*), etc., one of which is official, namely,

*Guaiacol carbonate, Guaiacolis carbonas,* $(C_7H_7O)_2CO_3$, is prepared by saturating guaiacol with sodium hydroxide, and treating this compound with carbonyl chloride, $COCl_2$. It is a white crystalline powder, insoluble in water, sparingly soluble in alcohol, soluble in ether and chloroform.

*Creosol,* $C_6H_3.CH_3.OH.OCH_3$, the second constituent of creosote, is the next homologue to guaiacol, *i. e.*, the methyl-ether of dioxytoluene.

**Eugenol, $C_6H_3(OH)(OCH_3).C_3H_5$, 4 : 3 : 1 = 164.10,** is an unsaturated aromatic phenol obtained from oil of cloves and other sources. It is a colorless, or a pale yellow liquid, having a strongly aromatic odor of cloves.

**Safrol, $C_6H_3.C_3H_5.OOCH_2$, 1 : 3 : 4** (*Shikimol, Allylpyrocatechol methylene ether*), is found in oil of sassafras, oil of camphor, and other volatile oils. It is a colorless liquid with a sassafras-like odor.

**Resorcinol, $C_6H_4(OH)_2$, 1 : 3 = 110.04** (*Resorcin, Meta-dihydroxybenzene.*—It is formed by fusing different resins, such as galbanum, asafœtida, etc., with caustic alkalies, but it is now made almost altogether from benzene by heating the latter with fuming sulphuric acid to 257° C., whereby benzene-meta-disulphonic acid, $C_6H_4(SO_3H)_2$, is produced. The sodium salt of this acid is fused with sodium hydroxide for several hours, forming sodium resorcin, $C_6H_4(ONa)_2$. The mass is dissolved in water, acidified, and extracted with ether, which dissolves out the resorcin. This is further purified by sublimation and recrystallization.

Resorcinol is a white, or faintly-reddish, crystalline powder, having a somewhat sweetish taste and a slightly aromatic odor; it fuses at 119° C. (246° F.), boils at 276° C. (529° F.), and is soluble in less than its own weight of water. A dilute solution gives with ferrric chloride a bluish-violet color. Resorcinol, when heated for a few minutes with phthalic acid in a test-tube, forms a yellowish-red mass, which, when added to a dilute solution of caustic soda, forms a highly fluorescent solution. Other fluorescent compounds are obtained by heating resorcinol with very little sulphuric and either citric, oxalic, or tartaric acid, dissolving in a mixture of water and alcohol and supersaturating the solution with ammonia. Resorcinol is largely used in the manufacture of certain dyes. It must not be confused with the proprietary preparation of the same name, composed of equal parts of resorcin and iodoform fused together.

**Quinol, $C_6H_4(OH)_2$, 1 : 4** (*Hydroquinone, Para-dihydroxy-benzene*), is formed by dry distillation of quinic acid (from Peruvian bark), by reduction of quinone, and by fusing para-iodophenol with sodium hydroxide. It occurs combined with sugar as the glucoside *arbutin*, in uva ursi (Bear-berry) leaves. It forms small plates or hexagonal prisms, melting at 169° C., easily soluble in

hot water, alcohol, and ether. Oxidizing agents, such as ferric chloride, chlorine, etc., convert it into quinone, $C_6H_4O_2$. It is used as a developer in photography.

Solution of lead acetate gives a white precipitate with pyrocatechol, none with resorcinol, and a precipitate only in the presence of ammonia with hydroquinone.

**Pyrogallol, Pyrogallic Acid, $C_6H_3.(OH)_3$.**—When gallic acid is heated to 200° C. (392° F.) it is decomposed into carbon dioxide and pyrogallol, a substance which is not a true acid, but a trihydroxybenzene, *i. e.*, a phenol. Pyrogallol crystallizes in colorless needles, melts at 131° C. (268° F.), is easily soluble in water, ether, and alcohol. In alkaline solution it absorbs oxygen rapidly, assuming a red, then reddish-brown and dark brown color. Nitric acid also colors it yellow, then brown, and this property is made use of in testing for traces of nitric acid. Solutions of silver, gold, and mercury are reduced by pyrogallol even in the cold.

**Gallacetophenone or Gallactophenone, $C_6H_2<\begin{matrix}CO.CH_3\\(OH)_3,\end{matrix}$** obtained by heating a mixture of pyrogallol, zinc chloride, and glacial acetic acid to 148° C. It is a crystalline powder of dirty flesh-color, soluble in water, introduced to replace pyrogallol, which is poisonous.

**Phloroglucinol, $C_6H_3(OH)_3$. 1 : 3 : 5** (*Phloroglucin, Symmetrical trihydroxy-benzene*), results when resorcin and several resins, as gamboge, dragon's blood, etc., are fused with potassium hydroxide. It forms colorless prisms, melting at 218° C., very soluble in water and alcohol, and of a sweet taste. It stains lignin red and, together with vanillin, is used to detect hydrochloric acid in stomach contents.

**Hydroxy-hydroquinone, $C_6H_3(OH)_3$. 1 : 2 : 4,** is the third trihydroxybenzene. It is an interesting fact that according to the theory as to the structure of the benzene molecule, three isomeric dihydroxy-benzenes and trihydroxy-benzenes should exist, and in each case three actually do exist.

Most of the phenols give colors with ferric chloride solution, and are acted on by the oxygen of the air with formation of colored bodies. They are unstable toward oxidizing agents, forming in many cases carbon dioxide. The di- and trihydroxyl derivatives are less stable than the simple phenols. The same is true also of hydroxy acids of benzene, for example, salicylic and gallic acids.

## Ethers of Phenols.

Two kinds of ethers are possible, namely, one kind in which a fatty hydrocarbon radical is present, and these compounds have a close resemblance to the fatty ethers; and a second kind in which only aromatic hydrocarbon radicals are present. Ethers of the first kind can readily be made by the action of an alkyl halide on the alkali salt of a phenol, thus,

$$C_6H_5ONa + RX = C_6H_5.O.R + NaX.$$

With the reverse compounds, namely, an aromatic halogen derivative and sodium or potassium alcoholate, action does not take place readily, but requires heating under pressure,

$$C_6H_5X + NaOR = C_6H_5.O.R + NaX.$$

In the above reactions R stands for an alkyl radical and X for halogen.

Ethers are often formed when a diazonium salt is decomposed by heating with an alcohol, thus,

$$C_6H_5.N_2.Cl + HOR = C_6H_5O.R + N_2 + HCl.$$

Halogen derivatives of aromatic hydrocarbons do not react with alkali salts of phenols.

**Anisol, $C_6H_5OCH_3$.**—This compound, phenyl methyl ether, can be made by the action of methyl iodide on phenol in a solution of alkali. Also by boiling anisic acid, $C_6H_4<\begin{matrix}OCH_3\\COOH\end{matrix}$, with a solution of barium hydroxide, whereby carbon dioxide is split off. Anisic acid is formed by oxidation of anethol, $C_6H_4<\begin{matrix}OCH_3\\C_3H_5\end{matrix}$, which occurs in oil of anise. Anisol also results when benzene diazonium chloride is boiled with methyl alcohol. The ether is a liquid of pleasant odor and boils at 155° C.

**Phenetol, $C_6H_5OC_2H_5$.**—Phenyl ethyl ether is a liquid, boiling at 172° C. It is similar to anisol in properties.

Guaiacol, veratrol, creosol, eugenol and safrol, mentioned above, are also ethers.

## Nitro-phenols.

Phenols are much more readily nitrated than are the aromatic hydrocarbons, resembling in this respect the alcohols which are much more reactive to reagents than are the fatty hydrocarbons. Dilute nitric acid at low temperatures acts on phenols to produce the lower nitro compounds, while concentrated acid produces di- or trinitro compounds. As more and more negative $NO_2$ radicals are introduced into the phenols, the more acid do the phenols become. The student will note that there are other types of organic acids besides the carboxyl acids.

**Nitro-phenol $HO.C_6H_4.NO_2$.**—When phenol is added to a mixture consisting of one volume of concentrated nitric acid and two volumes of water at ordinary temperature, nitration takes place with formation of the ortho and para compound. They are separated by first washing with water, and then distilling with steam, by which the ortho product is volatilized.

Ortho-nitro-phenol melts at 45° C. and para-nitro-phenol at 114° C. The latter is of interest because it is used in the preparation of acetphenetidin.

Meta-nitro-phenol is made by diazotizing meta-nitro-aniline, and decomposing the product with water.

**Trinitro-phenol, $C_6H_2(NO_2)_3OH$** (*Picric Acid, Carbazotic Acid*).—This substance is formed by the action of nitric acid on various matters (silk, wool, indigo, Peruvian balsam, etc.), and is manufactured on a large scale by slowly dropping phenol into fuming nitric acid. Picric acid forms yellow crystals which are sparingly soluble in water; it has a very bitter taste, strongly poisonous properties, and is used as a yellow dye for silk and wool and as a reagent for albumin. While phenol has but slight acid properties, picric acid behaves like a strong acid, forming salts known as picrates, most of which are explosives. Picric acid decomposes carbonates but phenol does not. Potassium picrate is an orange-colored salt, difficultly soluble in water. Picric acid is stronger than acetic acid.

## Amino-phenols.

These are readily obtained by reduction of nitro-phenols. Like phenols, they are soluble in alkalies, and, like amines, they unite with strong acids to form salts.

**Amino-phenol, $HO.C_6H_4.NH_2$.**—Each of the three varieties of amino-phenol is formed by reduction of the corresponding nitro-phenol. They are colorless crystalline bodies which oxidize when exposed to the air and turn brown.

Certain amino-phenols are used as developers in photography. *Rodinal* is the hydrochloric acid salt of para-amino-phenol; *amidol* is a salt of diamino-phenol; *metol* is the sulphate of methyl amino-cresol; *eikonogen* is amino-naphtholsulphonic acid.

**Acetphenetidin** (*Acetphenetidinum*), $C_6H_4.O(C_2H_5).NH(C_2H_3O)$ = **179.11** (*Phenacetin*).—The ethyl ether of para-amino-phenol can readily be prepared. It has the composition $NH_2.C_6H_4OC_2H_5$ and is called *para-phenetidin* in allusion to the fact that it is an amino derivative of phenetol or phenylethyl ether. By the action of glacial acetic acid upon paraphenetidin, one hydrogen atom in $NH_2$ is replaced by acetyl, $C_2H_3O$, when para-acetphenetidin is formed. The compound is used as an antipyretic under the name of phenacetin.

It is a colorless, odorless, tasteless powder, sparingly soluble in water, readily soluble in alcohol; it fuses at 135° C. (275° F.). Fresh chlorine water colors a hot aqueous solution first violet, then ruby-red. The same color is obtained by boiling 0.1 gram of phenacetin with 1 c.c. of hydrochloric acid for one minute, diluting with 10 c.c. of water, filtering when cold, and adding 3 drops of solution of chromic acid.

Acetphenetidin is the best-known one of a large number of derivatives of para-amino-phenol, known as the phenetidin series. These derivatives, as well as acetphenetidin itself, are contained in many migraine and headache powders. *Lactophenin* is lactyl-para-phenetidin, $C_2H_5OC_6H_4NH.COCH(OH)CH_3$, a diffi-

cultly soluble white powder. *Salophen, saliphen, phenocoll, salocoll,* etc., are similar derivatives.

**Phenolsulphonic Acid, $C_6H_4(OH)SO_3H$** (*Sulphocarbolic acid*).—There are three varieties of this acid, namely, ortho, meta, and para. The ortho and para acid are most easily obtained. When pure phenol is mixed with an equal weight of sulphuric acid in the cold, the ortho acid is the chief product formed:

$$C_6H_5OH + H_2SO_4 = C_6H_4(OH)SO_3H + H_2O.$$

At 100° C. (212° F.) only the para acid results. Both varieties form clear solutions with water, but differ from each other in the character of their salts, both as regards solubility and form of the crystals. They are monobasic acids. The ortho acid is converted into the para acid by boiling with water.

*Ortho-phenolsulphonic acid* (*Sozolic acid, Aseptol*) occurs on the market as a 33 per cent. solution. It is a syrupy liquid, having a reddish color and a feeble odor. It is used as an antiseptic.

*Sodium phenolsulphonate, Sodii phenolsulphonas* (*Sodium sulphocarbolate*), $C_6H_4(OH)SO_3Na + 2H_2O$, and *Zinc phenolsulphonate, Zinci phenolsulphonas* (*Zinc sulphocarbolate*), $(C_6H_4(OH)SO_3)_2Zn + 8H_2O$, are official salts of para-phenolsulphonic acid. They are obtained by precipitating a solution of barium para-phenolsulphonate by sodium carbonate and zinc sulphate respectively, filtering off the precipitate of barium carbonate or sulphate, and evaporating the filtrate to crystallization. Both salts are readily soluble and have antiseptic and astringent properties.

*Ichthyol, Sodium ichthyo-sulphonate,* $C_{26}H_{36}S_3Na_2O_6$.—Ichthyol is the sodium or ammonium salt of a complex sulphonic acid, obtained by the dry distillation of a bituminous mineral found in Tyrol. It is a brown, tar-like liquid, having a disagreeable odor.

## Aromatic Alcohols and Aldehydes.

**Aromatic Alcohols.**—These are aromatic derivatives of the fatty alcohols, *i. e.*, alcohols in which hydrogen of the fatty hydrocarbon residue is replaced by a benzene derivative. The aromatic alcohols have the properties of true fatty alcohols.

*Benzyl alcohol,* $C_6H_5.CH_2.OH$, is the simplest member of the class; it is isomeric with *cresol,* $C_6H_4{<}^{CH_3}_{OH}$, but has entirely different properties. Benzyl alcohol is found in balsam of Peru and Tolu, mostly in combination with benzoic or cinnamic acid.

**Aromatic Aldehydes.**—These are aromatic derivatives of the fatty aldehydes and behave in some respects like the latter; thus they combine readily with oxygen to form acids and behave generally like unsaturated compounds. There are some marked differences in behavior which may be illustrated in the case of benzaldehyde.

**Benzaldehyde** (*Benzaldehydum*) $C_6H_5.COH$ = **106.05.**—This is the simplest one of the aromatic aldehydes, and is produced artificially or obtained from natural oil of bitter almonds or other oils. It is a colorless, strongly refractive liquid, having a bitter-almond-like odor. It is easily converted into benzoic acid by oxidation. It boils at 179° C. and has the sp. gr. 1.05. It enters into a number of condensation reactions which are of great value.

Benzaldehyde is made commercially by heating benzal chloride, $C_6H_5.CHCl_2$, with milk of lime, or by oxidizing benzyl chloride, $C_6H_5.CH_2Cl$, with lead nitrate solution. These chlorides are obtained by the action of chlorine on toluene in sunlight or at the boiling-point of toluene.

Benzaldehyde, like fatty aldehydes, reduces ammonio-silver nitrate, unites with sodium bisulphite and with hydrocyanic acid, and can be reduced to an alcohol. It does not form an addition product with ammonia as acetaldehyde does, nor does it polymerize to resin-like bodies when treated with alkalies, but it is converted into benzyl alcohol and benzoic acid, thus,

$$2C_6H_5CHO + KOH = C_6H_5CH_2OH + C_6H_5COOH.$$

With chlorine benzaldehyde forms benzoyl chloride, which is made commercially in this manner,

$$C_6H_5.CHO + Cl_2 = C_6H_5COCl + HCl.$$

**Oil of Bitter Almond** (*Oleum Amygdalæ Amaræ*).—Benzaldehyde does not occur in a free state in nature, but is formed by a peculiar fermentation of a glucoside, *amygdalin*, existing in bitter almonds, in cherry-laurel, and in the kernels of peaches, cherries, etc., but not in sweet almonds. The ferment causing the decomposition of amygdalin is a substance termed *emulsin*, which is found in both bitter and sweet almonds. As water is required for the decomposition, the emulsin does not act upon the amygdalin contained in the same seed until water is added, when the decomposition takes place as follows:

| $C_{20}H_{27}NO_{11}$ | + | $2H_2O$ | = | $2C_6H_{12}O_6$ | + | HCN | + | $C_7H_6O$. |
|---|---|---|---|---|---|---|---|---|
| Amygdalin. | | Water. | | Glucose. | | Hydrocyanic acid. | | Benzaldehyde. |

The oil is obtained by maceration of bitter almonds with water, and subsequent distillation when it distils over with hydrocyanic acid and steam, and separates as a heavy oil in the distillate.

It is an almost colorless, thin liquid of a characteristic aromatic odor, a bitter and burning taste, and a neutral reaction. Pure benzaldehyde is not poisonous, but the oil of bitter almond is poisonous on account of its containing hydrocyanic acid.

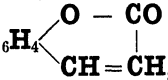
*Bitter-almond water, Aqua amygdalæ amaræ*, is made by dissolving 1 part of the oil in 999 parts of water.

**Cuminic Aldehyde, $C_3H_7.C_6H_4CHO$, 1:4.**—This is para-isopropylbenzaldehyde, and occurs in oil of caraway and other oils. It is a liquid of pleasant odor and boils at about 237° C.

**Cinnamic Aldehyde, $C_6H_5.CH : CH.COH$** (*Cinnamyl Aldehyde, Phenyl Acrolein*).—This aldehyde is prepared synthetically, or is obtained from oil of cinnamon by extracting with acid sodium sulphite. Cinnamic aldehyde is a colorless oil, having a cinnamon-like odor and a burning, aromatic taste. When exposed to the air it is oxidized to cinnamic acid. It is made by treating benzaldehyde with acetaldehyde in dilute sodium hydroxide solution:

$$C_6H_5CHO + CH_3CHO = C_6H_5CH : CH.CHO + H_2O.$$

**Vanillin** (*Vanillinum*), **$C_6H_3.OH.OCH_3.COH$, 4 : 3 : 1 = 152.06** (*Methylprotocatechuic Aldehyde*).—Vanillin is the active constituent in vanilla bean, and is made artificially in a variety of ways. One of these is the action of chloroform and caustic potash on guaiacol. Another is the oxidation of eugenol with potassium permanganate. It occurs in white, crystalline needles, having the odor and taste of vanilla, and melting at 80° to 81° C. It is soluble in 100 parts of cold, and 15 parts of warm water, easily soluble in alcohol, ether, chloroform, and dilute alkalies. It is extracted completely from its solution in ether by shaking with a saturated aqueous solution of sodium bisulphite, from which it may be precipitated by sulphuric acid; it is also extracted by ammonia water.

**Coumarin,**  the anhydride of ortho-hydroxy-cinnamic acid, is found in the Tonka bean and resembles vanillin in odor. It forms white, shining prisms, melting at 67° C., and soluble in 400 parts of cold, 45 parts of hot water, and in 7.5 parts of alcohol; easily soluble in ether.

An aqueous solution of vanillin is turned blue by a few drops of ferric chloride solution, coumarin is not. An aqueous solution of coumarin, unlike vanillin, forms a precipitate when iodine in potassium iodide is added in excess, at first brown and flocculent, and afterward, on shaking, forming a dark green, curdy clot.

"Extracts of vanilla" made, not from the vanilla bean, but consisting of alcoholic tinctures of synthetic vanillin or coumarin, can readily be detected by evaporating off the alcohol, making up the original volume with water, and acidifying with acetic acid. A reddish-brown precipitate of resin is formed in the case of a true extract, but none in the artificial. The filtrate from this resin gives a copious precipitate with basic lead acetate solution, the artificial extract gives none.

Vanillin has been found adulterated with benzoic acid, acetanilide, boric acid, terpin hydrate, and coumarin.

## Acids of the Benzene Series.

These are derivatives in which one or more carboxyl groups (COOH) have replaced hydrogen in the benzene molecule. Benzoic acid is the simplest, and bears the same relation to benzene as acetic acid bears to methane. Many of these acids are found as natural products, but the carboxyl group may be introduced by various reactions, of which the following are the principal ones:

1. Oxidation of benzene compounds containing fatty hydrocarbon radicals or substituted radicals:

$$C_6H_5CH_2OH + 2O = C_6H_5COOH + H_2O.$$

2. Hydrolysis of a cyanide by heating with dilute acid:

$$C_6H_5CN + 2H_2O = C_6H_5COOH + NH_3.$$

3. The treatment of alkali salts of phenols with carbon dioxide (see Salicylic Acid).

**Benzoic Acid** (*Acidum Benzoicum*) **$HC_7H_5O_2$ or $C_6H_5CO_2H$ = 122.05.** —Found in benzoin and some other resins also; in combination with other substances in the urine of herbivorous animals; it is obtained from benzoin by heating it carefully, when the volatile benzoic acid sublimes. It is now also manufactured from toluene, which is first converted into benzo-trichloride (trichlormethyl benzene) by passing chlorine into hot toluene:

$$C_6H_5CH_3 + 6Cl = C_6H_5CCl_3 + 3HCl.$$

Benzo-trichloride, when treated with water under pressure, yields benzoic and hydrochloric acids, thus:

$$C_6H_5CCl_3 + 2H_2O = C_6H_5CO_2H + 3HCl.$$

Benzoic acid forms white, lustrous scales or friable needles, which are but slightly soluble in cold water, but easily soluble in alcohol, ether, oils, etc. Shaken in solution with hydrogen dioxide, benzoic acid is converted into salicylic acid.

Benzoic acid, prepared by sublimation from gum benzoin, has a slight aromatic odor resembling that of benzoin; the acid obtained synthetically is odorless. It melts at 121.4° C. and boils at 250° C., and is volatile with steam.

Benzoic acid, when neutralized with an alkali, gives a flesh-colored or reddish precipitate of ferric benzoate on the addition of a neutral solution of ferric chloride.

By neutralizing benzoic acid with either ammonium hydroxide or sodium hydroxide, the official salts *ammonium benzoate*, $NH_4C_7H_5O_2$, and *sodium benzoate*, $NaC_7H_5O_2.H_2O$, are obtained. The salts are white, soluble in water, and have a slight odor of benzoin.

Benzoic acid and its derivatives, taken internally, are eliminated in the urine as hippuric acid, $C_6H_5CO.NH.CH_2COOH$ (benzoyl-amino-acetic acid), and its derivatives.

Many halogen, nitro- and amino-benzoic acids exist which are interesting in pure and technical chemistry.

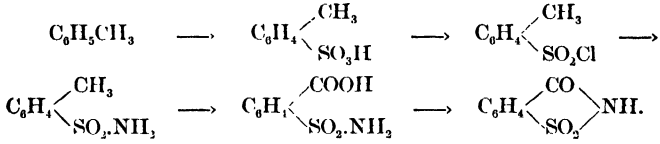
**Ethyl para-amino-benzoate, $C_6H_4(NH_2)(COOC_2H_5)$** (*Anesthesin*), is a local anesthetic, introduced as a substitute for cocaine. It is a white, odorless, tasteless powder, melting at 90° to 91° C., almost insoluble in cold and difficultly soluble in hot water. It is soluble in 6 parts of alcohol. When placed on the tongue it produces a sensation of numbness.

**Benzoyl chloride, $C_6H_5.COCl$**, is obtained by distilling benzoic acid with phosphorus pentachloride. It is a colorless, irritating oil, boiling at 200° C., slowly decomposed by cold water, but more stable than acetyl chloride. It acts on hydroxyl compounds, forming benzoic acid esters, thus:

$$C_6H_5.COCl + C_6H_5OH = \underset{\text{Phenyl benzoate.}}{C_6H_5COOC_6H_5} + HCl.$$

This process of introducing the benzoyl radical is known as "benzoylation." It is greatly facilitated when carried out in the presence of alkali.

**Benzosulphinide, Saccharin** (*Benzosulphinidum*), **$C_6H_4.CO.SO_2.NH$ = 183.12** (*Anhydro-ortho-sulphamide-benzoic Acid, Benzoyl Sulphonic-imide*).—This substance is a derivative of benzoic acid, $C_6H_5.CO_2H$, obtained by the discoverers from toluene by the transformations indicated in the following formulas:



Other methods of preparing saccharin have been devised.

Saccharin is a white, crystalline, odorless powder. It is but sparingly soluble in water, requiring about 250 parts for solution; this solution is slightly acid and has an extremely sweet taste, which is yet perceptible when saccharin is dissolved in 125,000 parts of water, which shows that it is about 500 times sweeter than cane-sugar, a solution of which in 250 parts of water is yet perceptibly sweet. Saccharin is soluble in alcohol and ether, and it is this latter property which is made use of in testing sugar (or other substances insoluble in ether) for saccharin. The substances are treated with ether, which is filtered off and evaporated, when the saccharin may be recognized by its taste in the residue.

Saccharin forms very soluble and well-crystallizing salts with the alkalies, which are also intensely sweet; they are articles of commerce. The sodium salt is known as *soluble saccharin* or *krystallose*. Saccharin is known in the British Pharmacopœia as *Glusidum* (*Gluside*), and in commerce as *glucusimide*, *saccharol*, *saccharinol*, *saccharinose*, *agucarine*, etc. A number of preparations, such as *antidiabetin*, contain saccharin. *Dulcin* or *sucrol*, another very sweet substance, is para-phenetol-carbamide.

**Sodium Benzosulphinide** (*Sodii Benzosulphinidum*), $NaC_7H_4O_3NS.2H_2O$ = 241.14.—This is the sodium salt of saccharin, and occurs in colorless prisms or as a crystalline powder. It is somewhat efflorescent, odorless, and intensely sweet. One gram dissolves in 1.2 c.c. of water and in about 50 c.c. of alcohol, the solution being neutral to litmus and phenolphthalein. The aqueous solution, acidified with hydrochloric acid, gives a crystalline precipitate of the difficultly soluble saccharin.

**Cinnamic Acid, $C_6H_5.CH = CH.COOH$.**—This is phenyl-acrylic acid and is an example of an unsaturated aromatic acid, with the COOH group in the side-chain instead of in the benzene ring. It occurs in balsams of Peru and Tolu, storax, gum-benzoin, oil of cinnamon, etc. It can be made synthetically by heating benzal chloride with sodium acetate,

$$C_6H_5.CHCl_2 + CH_3.COONa = C_6H_5.CH=CH.COOH + NaCl + HCl.$$

or by heating benzaldehyde with anhydrous sodium acetate and acetic anhydride,

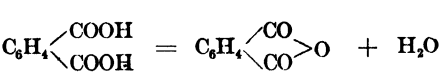
$$C_6H_5.CHO + CH_3.COONa = C_6H_5.CH=CH.COONa + H_2O.$$

By using salts of other fatty acids, corresponding unsaturated aromatic acids can be made. This method is known as the Perkin synthesis.

Cinnamic acid melts at 134° C., and boils at 300° C. with some decomposition. It can be crystallized from water.

**Phthalic Acid, $C_6H_4(COOH)_2$, 1 : 2.**—Of the aromatic polybasic acids, the dibasic acids are the most important. They are called phthalic acids in allusion to the fact that one of them can be obtained from naphthalene. Theoretically, three dibasic acids are possible and all are known. When mixed with lime and distilled they yield benzene.

Phthalic acid can be obtained by the oxidation of derivatives of benzene containing two side-chain hydrocarbons in the ortho-position, but it is manufactured by oxidizing naphthalene by hot fuming sulphuric acid with the help of a catalytic agent, as mercury. The sulphuric acid loses oxygen to the naphthalene and forms sulphur dioxide, which escapes in great quantities. Enormous quantities of phthalic acid are employed in the manufacture of synthetic indigo. It is a crystalline white substance, readily soluble in hot water, alcohol, and ether. When heated it decomposes, yielding water and phthalic anhydride, which latter sublimes in long needles, melting at 128° C.



Phthalic anhydride.

*Iso-phthalic acid* (*Meta-phthalic acid*), $C_6H_4(COOH)_2$ 1 : 3, may be obtained by oxidizing benzene derivatives containing two side-chains in the meta-position, and from rosin by oxidation with nitric acid. It is difficultly soluble in water and does not give an anhydride when heated.

*Terephthalic acid* (*Para-phthalic acid*), $C_6H_4(COOH)_2$ 1 : 4, can be formed by

oxidation of turpentine and in other ways. It is nearly insoluble in water, alcohol and ether, and does not yield an anhydride.

**Phenolphthalein** (*Phenolphthaleinum*).—When phthalic anhydride is heated with phenols and concentrated sulphuric acid, a class of substances is obtained known as *phthaleins*. The simplest of these is phenolphthalein, the composition of which is shown in the following reaction:

$$\underset{\text{Phthalic anhydride}}{C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O} + \underset{\text{Phenol.}}{2C_6H_5OH} = \underset{\text{Phenolphthalein.}}{C_6H_4{<}\begin{matrix}C(C_6H_4.OH)_2\\CO\end{matrix}{>}O}$$

It occurs as a creamy-white powder or crystals, soluble in 600 parts of water and in 10 parts of alcohol. It dissolves in alkaline solutions with a beautiful red color, and is used as a sensitive indicator in acidimetry and alkalimetry. Acids destroy the red color by reforming the colorless phenolphthalein from its salts. Taken internally, it acts as a purgative, but appears to possess no further physiological action. For adults the average dose is 0.1 to 0.2 gram, given as powder, in cachets, capsules, or pills. In obstinate cases 0.5 gram doses may be given.

*Resorcinolphthalein* or *fluorescein* is obtained by heating phthalic anhydride and resorcinol at 210° C. with zinc chloride as a dehydrating agent. It is a reddish-brown substance which exhibits an intense yellowish-green fluorescence in an alkaline solution, hence its name. By treatment with bromine it forms *tetrabromfluorescein*, the potassium salt of which is the dye known as *eosin*, $C_{20}H_6O_5Br_4K_2$. This is a valuable stain for animal and plant tissues. In dilute solution it shows a beautiful rose tint.

**Phenolsulphonephthalein**, $C_6H_4{<}\begin{matrix}C(C_6H_4OH)_2\\SO_2\end{matrix}{>}O$. This substance is analogous to phenolphthalein, and may be obtained in a similar manner by heating together phenol and the anhydride of orthosulphobenzoic acid, $C_6H_4{<}\begin{matrix}CO\\SO_2\end{matrix}{>}O$, which is analogous to the anhydride of phthalic acid. The source of the anhydride of sulphobenzoic acid is saccharin.

Phenolsulphonephthalein is a red or brownish-red powder, soluble in alcohol, but not in ether. It is slightly soluble in cold water, giving a deep yellow color to the solution, but readily soluble in alkalies, the mono-sodium salt having a bordeaux red color, while with excess of alkali the solution has a beautiful purple color similar to that of phenolphthalein in alkaline solution. It is used as a diagnostic test of renal efficiency by injecting 6 Mgm. in the form of the mono-sodium salt. The test depends upon the fact that normal kidneys excrete 40 to 60 per cent. of the dose during the first hour after its first appearance in the urine, whereas kidneys not functioning properly excrete a much smaller per cent. The readings are made by means of a colorimeter.

## Hydroxy-acids of the Benzene Series.

These derivatives, which are known also as phenol-acids, contain the (OH) and (COOH) groups in the benzene nucleus, and accordingly possess the properties of phenols and acids. The hydrogen of the (OH) group as well as that of the (COOH) group can be replaced by a metal or hydrocarbon radical. The radical introduced into the (COOH) group is easily removed by saponification, as in the case of any ethereal salt, whereas that introduced into the (OH) group is not.

The simplest hydroxy-acids are those containing one (OH) group and one (COOH) group. There are three such acids, namely, ortho-, meta-, and para-hydroxy-benzoic acid. Of these, the ortho acid, known better as salicylic acid, is the most important.

**Salicylic Acid** (*Acidum Salicylicum*) **$HC_7H_5O_3$ or $C_6H_4OH.CO_2H$ = 138.05.**—Derived from benzene by introducing one hydroxyl and one carboxyl radical. It is found in several species of violet, and in the form of methyl salicylate in the wintergreen oil (oil of Gaultheria procumbens). May be obtained by fusing potassium hydroxide with salicin.

Nearly all salicylic acid used medicinally or otherwise is obtained by synthesis. The first step is the conversion of phenol into sodium phenolate by treatment with sodium hydroxide, thus:

$$C_6H_5OH + NaOH = C_6H_5ONa + H_2O.$$

Sodium phenolate is next dried and treated with carbon dioxide, when direct combination takes place and sodium phenol carbonate is formed, thus:

$$\underset{\text{Sodium phenolate.}}{C_6H_5ONa} + CO_2 = \underset{\text{Sodium phenol carbonate.}}{NaC_6H_5CO_3}.$$

Sodium phenol carbonate is isomeric with sodium salicylate and is actually converted into the latter compound by being heated to 130° C. (266° F.), in tightly closed vessels, or in vessels through which carbon dioxide passes.

Salicylic acid is a white, solid, odorless substance, having a sweetish, slightly acrid taste, and an acid reaction; it is soluble in 308 parts of water and in 2 parts of alcohol; it fuses at about 157° C. (315° F.), and sublimes slowly at 100° C. (212° F.) and rapidly at 140° C. (281° F.). It is a valuable antiseptic.

By the action of the alkali hydroxides on salicylic acid, the various salts may be obtained, as, for instance, *sodium salicylate*, $NaC_7H_5O_3$, and *ammonium salicylate*, $NH_4C_7H_5O_3$, which are official. They are white salts, readily soluble in water. In the presence of free alkali, the solutions absorb oxygen from the air and become colored. Solutions of salicylates are incompatible with acids, salicylic acid being precipitated.

**Bismuth Subsalicylate** (*Bismuthi Subsalicylas*).—It has approximately the composition, $C_6H_4(OH)CO_2BiO$. It is a white, amorphous or crystalline, odorless and tasteless powder, permanent in the air,

and almost insoluble in water. Alcohol or ether extracts salicylic acid, with decomposition of the salt.

**Strontium Salicylate** (*Strontii Salicylas*) $(C_6H_4(OH)CO_2)_2.Sr+2H_2O$. —It is a white crystalline powder, odorless, and having a sweetish, saline taste. It is soluble in 18 parts of water and 66 parts of alcohol. It is incompatible with ferric salts, mineral acids, quinine salts in solution, spirit of nitrous ether, sulphates and carbonates, and sodium phosphate in powder.

**Mercuric Salicylate,** (*Hydrargyri Salicylas*), $C_6H_4<\overset{O}{\underset{CO_2}{}}>Hg$. —It is prepared by heating on a water-bath 21.5 parts of yellow mercuric oxide, 15 parts of salicylic acid, and a little water until the mixture is perfectly white. It occurs as a white, amorphous powder, tasteless, and neutral to litmus paper, slightly soluble in water or alcohol, but soluble in solutions of sodium hydroxide and sodium carbonate, forming a double salt. It is soluble also in warm solutions of chlorides, bromides, and iodides. It is used as a disinfectant, and as a remedy in syphilis and in certain skin diseases.

**Analytical Reactions.**—1. Add to solution of salicylic acid or its salts ferric chloride: a reddish-violet color is produced, yet noticeable in solutions containing 1 part of salicylic acid in 500,000 parts of water.

2. Add some cupric sulphate: a bright green color will result.

3. Dissolve some salicylic acid or sodium salicylate in methyl alcohol and add one-fourth the volume of sulphuric acid. Heat gently and set aside for a few minutes. On reheating, the odor of methyl salicylate is developed.

**Aspirin,** $C_6H_4.O(CH_3CO)COOH$ (*Acetyl-salicylic acid*), is obtained by the prolonged action of acetic anhydride on salicylic acid at about 150° C. It forms colorless needles, melting at 135° C., odorless, and of an acidulous taste, soluble in 100 parts of water and freely in alcohol or ether. Boiling water or alkalies decompose it, liberating acetic acid.

**Salicin,** $C_{13}H_{18}O_7$.—This glucoside is found in several species of Salix (willow), and is mentioned here because it splits into glucose and salicylic alcohol, $C_6H_4.OH.CH_2OH$, when boiled with dilute acids:

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_7H_8O_2.$$

Salicylic alcohol is converted by chromic acid into salicylic aldehyde, $C_6H_4$-OH.COH, which by further oxidation is converted into salicylic acid.

Salicin forms white, silky, shining needles, which are soluble in less than an equal weight of water, have a neutral reaction and a very bitter taste.

Salicin sprinkled upon concentrated sulphuric acid produces a red color. Boiled with very dilute hydrochloric acid for a few minutes, and this solution nearly neutralized with sodium carbonate, a violet color is produced on the addition of a drop of ferric chloride solution.

**Methyl Salicylate** (*Methylis Salicylas*), $CH_3.C_7H_5O_3$ **or** $C_6H_4(OH)COOCH_3$ **= 152.06.**—Oil of wintergreen is chiefly methyl salicylate, a nearly colorless liquid with a characteristic, strongly aromatic odor. It is made by the method so extensively used in the manufacture of esters, viz., by heating of salicylic

acid with alcohol in the presence of sulphuric acid. (See above reaction 3 of salicylic acid). It is also found in many other volatile oils, especially in oil of betula.

**Phenyl Salicylate, Salol** (*Phenylis Salicylas*), $C_6H_5.C_7H_5O_3$ **or** $C_6H_4(OH)COOC_6H_5$ **= 214.08.**—This ester is a white, crystalline, almost tasteless powder, which is nearly insoluble in water, readily soluble in alcohol, ether, and benzol, and fuses at 42° C. (107.4° F.). It is used as an antiseptic and antipyretic.

Salol heated with potassium hydroxide solution is decomposed into phenol, which can be recognized by its odor, and potassium salicylate, from which crystalline salicylic acid will separate upon supersaturating the liquid with hydrochloric acid. An excess of brominewater produces a white precipitate in an alcoholic solution of salol.

Salol is made by the action of suitable dehydrating agents upon a mixture of phenol and salicylic acid:

$$C_6H_5OH + HC_7H_5O_3 = C_6H_5.C_7H_5O_3 + H_2O.$$

A simpler method for its manufacture consists in the heating of salicylic acid between 220° and 230° C. (428° and 446° F.) in an atmosphere of carbon dioxide, in a flask with a long, narrow neck. The reaction is this:

$$2C_6H_4\begin{matrix}OH\\COOH\end{matrix} = C_6H_4\begin{matrix}OH\\COOC_6H_5\end{matrix} + H_2O + CO_2.$$

**Anisic Acid,** $C_6H_4<\begin{matrix}OCH_3\\CO_2H\end{matrix}$ (*Para-methoxy-benzoic acid*), is isomeric with methyl salicylate, but, unlike the latter, it is not saponified when heated with alkalies. This is due to the fact that the methyl group is combined as in an ether. The ether groups, as $OCH_3$, $OC_2H_5$, $OC_6H_5$, etc., are often called *methoxy, ethoxy, phenoxy*, etc. Anisic acid is formed by the oxidation of anethol, $C_6H_4<\begin{matrix}OCH_3\\C_3H_5\end{matrix}$ an ether contained in oil of anise.

**Protocatechuic Acid,** $C_6H_3(OH)_2.COOH$**, 1:2:4.**—This acid is a carboxyl derivative of ortho-dihydroxybenzene (pyrocatechol), from which it can be made by heating it with ammonium carbonate and water at 140° C. It also results when potassium hydroxide is fused with many resins, and when certain tannins are hydrolyzed.

The acid is soluble in water and reduces ammonio-silver nitrate, but not Fehling's solution. It gives a bluish-green color with ferric chloride. Heated dry it decomposes into pyrocatechol and carbon dioxide.

**Gallic Acid** (*Acidum Gallicum*) $HC_7H_5O_5 + H_2O$ **or** $C_6H_2(OH)_3.CO_2H + H_2O$ **= 188.06, 1 : 2 : 3 : 5.**—It is obtained by exposing moistened nut-galls to the air for about six weeks, when a peculiar fermentation takes place, during which tannic acid is converted into gallic acid, which is purified by crystallization. The crystals contain one molecule of water, which may be expelled at 100° C. (212° F.). It is a white, solid substance, forming long, silky needles; it has an

astringent and slightly acidulous taste and an acid reaction; it is soluble in about 100 parts of cold or in 3 parts of boiling water, also readily soluble in alcohol, but sparingly in ether and chloroform; it gives a bluish-black precipitate with ferric salts, and does not coagulate albumin, nor precipitate alkaloids, gelatin, or starch (difference from tannic acid). A piece of potassium cyanide added to solution of gallic acid produces a deep rose color. It reduces silver and gold salts and Fehling's solution.

*Bismuth subgallate*, a salt which is somewhat variable in composition, is official. It is a yellow, amorphous, insoluble powder, known as *Dermatol*.

**Tannic Acid** (*Acidum Tannicum*), $C_{13}H_9O_7.COOH$ = **322.1** (*Gallotannic Acid, Digallic Acid*).—There are a number of tannic acids, or *tannins*, found in various parts of different plants (oak-bark, nut-galls, cinchona, coffee, tea, etc.), the properties of which are not quite identical. All tannins, however, are amorphous, have a faint acid reaction and strongly astringent properties; they all precipitate albumin and most of the alkaloids; they give with ferric salts a dark-colored solution or precipitate, the color being dark green or dark blue; they form with animal substances compounds which do not putrefy. Use is made of this property in the process of tanning, *i. e.*, converting hides into leather. Tannins cannot be melted or volatilized without decomposition. They reduce Fehling's solution, and are oxidized by the air, especially in alkaline solution, to colored compounds.

The official tannic acid is obtained by extracting nut-galls with ether and alcohol, and evaporating the solution; it forms light yellowish, amorphous scales, having a faint and characteristic odor, a strongly astringent taste, and an acid reaction; it is easily soluble in water and diluted alcohol.

It begins to decompose at 215° C. into carbon dioxide and pyrogallol. It reduces salts of copper, silver, gold, and mercury.

**Analytical Reactions.**—1. To solution of tannic acid add ferric chloride: a blue-black precipitate falls, soluble in large excess of tannic acid with violet color. If ferric chloride is added in excess, the black precipitate dissolves in it with green color. Ferrous salts and tannic acid give a colorless solution, which gradually turns dark by absorption of oxygen from the air and formation of ferric tannate. This is the basis of iron writing inks. Oxalic acid decolorizes iron ink by reducing ferric to ferrous tannate.

2. Add a few drops of potassium hydroxide: a brown coloration results.

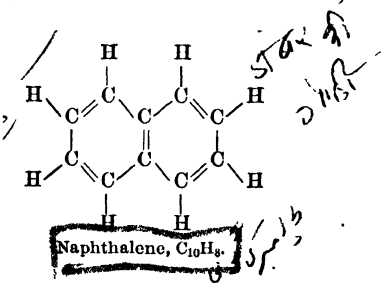
3. To a dilute solution (1 in 100) of tannic acid add a small quantity of lime-water. A pale bluish-white, flocculent precipitate is formed, which is not dissolved on shaking (difference from gallic acid), but becomes more copious and of a deeper blue than pinkish by the addition of an excess of lime-water.

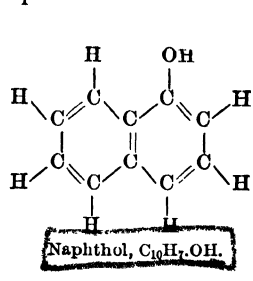
4. Tannic acid precipitates solutions of gelatin, albumin, gelatinized starch, tartar emetic, and most of the alkaloids.

Besides the type of tannins represented by the official tannic acid, there is another type which gives a green color with ferric chloride, pyrocatechol when heated, and protocatechuic acid, phloroglucinol and acetic acid when fused with caustic alkalies. This type appears to be derived from protocatechuic acid instead of gallic acid. *Caffetannic acid*, $C_{14}H_{16}O_7$, is an example of this type. It occurs in coffee beans. It does not precipitate gelatin.

## The Naphthalene Series.

**Naphthalene, $C_{10}H_8$.**—The constitution of all benzene derivatives considered so far may be explained by the introduction of radicals in benzene. Naphthalene and its derivatives must be assumed to be formed by the union of two benzene residues in such a way that they have two carbon atoms in common, as represented in these formulas:

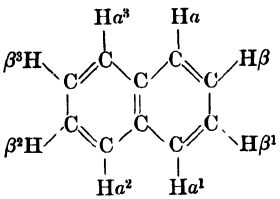

Naphthalene, $C_{10}H_8$.

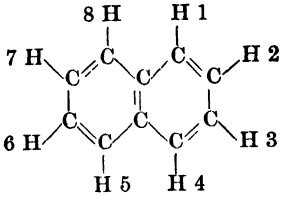

Naphthol, $C_{10}H_7.OH$.

Naphthalene has been mentioned as a product of the destructive distillation of coal, and is obtained from that portion of coal-tar which boils between 180° and 220° C. (356° and 428° F.). This distillate is treated with caustic soda and then with sulphuric acid and distilled with water vapor.

When pure, naphthalene forms colorless, lustrous crystalline plates, having a penetrating, but not unpleasant, odor and a burning, aromatic taste. It fuses at 80° C. (176° F.), and boils at 218° C. (424° F.), but volatilizes slowly at ordinary temperature, and readily with water vapor. It is only sparingly soluble in water, but easily soluble in alcohol, ether, chloroform, etc. Impure naphthalene assumes, when exposed to light, a reddish or brownish color. Naphthalene is converted into phthalic acid by oxidizing agents.

**Derivatives of Naphthalene.**—While benzene yields only one kind of mono-substitution product, naphthalene yields two varieties in every case. Thus, there are two mono-hydroxy derivatives (naphthol) two mono-amino derivatives (naphthylamine), etc. This is exactly what would be expected if the formula for naphthalene given above be true. The 8 hydrogen atoms in the molecule fall into two groups of 4 each, the atoms of each group bear the same relation to the molecule, but different from the relation that the atoms of the other group bear. This is shown in the following formulas, in which the hydrogen atoms are designated in a manner that permits of reference in the formulas for the derivatives of naphthalene:




In the first formula, hydrogen atoms $\alpha$, $\alpha^1$, $\alpha^2$, $\alpha^3$ are alike, and $\beta$, $\beta^1$, $\beta^2$, $\beta^3$, are alike, but bear a different relation from that of the $\alpha$ hydrogen atoms. In the second formula, the corresponding groups are 1, 4, 5, 8 and 2, 3, 6, 7. The mono-substitution products in which the $\alpha$ hydrogen is replaced, are known as *alpha-* or *α-derivatives*, the others are *beta-* or *β-derivatives*.

Theoretically, the number of di- and tri-substitution products of naphthalene is very large. Thus, ten di-chlor and fourteen tri-chlor derivatives are possible, and *all are known*. Such facts as these leave very little doubt as to the truth of the structural formula of naphthalene as given above.

**Naphthol, $C_{10}H_7OH$ = 144.06.**—This monatomic phenol bears to naphthalene the same relation that phenol bears to benzene, *i. e.*, hydroxyl replaces hydrogen in the respective hydrocarbons. Two isomeric naphthols, the alpha- and beta-naphthol, are known, which differ in their physical properties and in their physiological action. The naphthol which is used medicinally is *beta-naphthol*, a solid compound crystallizing in thin, shining plates, having an odor similar to phenol and a sharp, pungent taste. It fuses at 122° C. (252° F.), boils at 286° C. (547° F.), is soluble in about 1000 parts of cold, or 75 parts of boiling water; and readily soluble in alcohol, ether, chloroform, and fatty oils. The aqueous solution is colored greenish by ferric chloride. A few drops of iodine solution added to an aqueous solution of beta-naphthol, followed by an excess of alkali solution, should produce no color, but if alpha-naphthol is present, an intensely violet color is produced.

Naphthol occurs in coal-tar, but it is prepared synthetically from naphthalene in the same manner in which phenol is prepared from benzene. When concentrated sulphuric acid is heated with naphthalene for several hours at 200° C., the beta-sulphonic acid is formed, $C_{10}H_7SO_3H$; during the early stage of the process, and particularly at 80°–90° C., much alpha-sulphonic acid is formed, but at a higher temperature this is converted into the beta variety. The sodium salt of the beta acid is fused with sodium hydroxide, forming sodium naphthol and sodium sulphite. By treating the former with an acid, beta-naphthol is liberated, which must be further purified.

*Microcidine*, $C_{10}H_7.ONa$, is the name given to sodium naphthol. Its aqueous solution is used as a disinfectant for cleansing dental instruments.

**Alpha-naphthol** is obtained in the same manner as the beta product, from the sodium salt of alpha-naphthalene sulphonic acid. It forms lustrous needles, melting at 95° C. and boiling at 278°–280° C. It is more readily soluble in water than beta-naphthol, and is said by one author to be three times more powerful as an antiseptic and only one-third as poisonous as the beta compound. It is official in the French Pharmacopœia. Most authorities state, however, that it is more poisonous than beta-naphthol. It has been used as a test for sugar in urine and is employed in the preparation of certain azo dyes, as is also beta-naphthol.

The naphthols act in general like the phenols, but the (OH) group reacts more readily than in the phenols. Thus, it can easily be replaced by the amido ($NH_2$) group. Naphthols readily form sulphonic acids, of which many are known and are used in the manufacture of azo dyes. The 1, 4, naphthol-sulphonic acid is used most.

*Beta-naphthol benzoate*, $C_6H_5COOC_{10}H_7$ (*Benzoyl-naphthol*), is obtained by the action of benzoyl chloride on beta-naphthol at 170° C. It is a white crystalline powder, melting at 107° C., tasteless, odorless, and insoluble in water, but soluble in alcohol, chloroform, and hot ether. It splits into beta-naphthol and benzoic acid in the intestines.

*Beta-naphthol-bismuth*, *Bismuthi Betanaphtholas* (*Orphol*) has approximately the composition, $C_{10}H_7O.Bi_2O_2(OH)$, and is said to be formed by the action of an alkaline solution of naphthol on a solution of bismuth nitrate in dilute glycerin. It is a light brown, odorless, almost tasteless powder, insoluble in alcohol as well as water. In the intestines it splits into naphthol and bismuth hydroxide.

*Alpha-amino-naphthalene*, $C_{10}H_7.NH_2$ (*Alpha-naphthylamine*), is obtained by the reduction of the corresponding nitro-naphthalene, the chief product of the action of nitric acid on naphthalene in the cold. It is also formed by heating alpha-naphthol with the ammonia compound of zinc chloride. It melts at 50° C., has a pungent odor, and turns red in contact with air. It is easily soluble in alcohol, and forms crystalline salts with acids, the solutions of which with oxidizing agents give a blue precipitate, which soon turns red.

*Beta-amino-naphthalene*, $C_{10}H_7.NH_2$ (*Beta-naphthylamine*), is easily obtained by heating beta-naphthol with the ammonia compound of zinc chloride to 210° C. It forms pearly scales, soluble in hot water, ordorless, and melting at 112° C. It does not give a colored compound with oxidizing agents.

*Naphthionic acid*, $C_{10}H_6(NH_2)SO_3H$ (1, 4, *Naphthylamine-sulphonic acid*). A number of sulphonic acids are formed when the naphthylamines are treated with sulphuric acid, some of which are valuable in the preparation of dyes. The sodium salt of naphthionic acid is used in making congo red, which has the composition:

$$\begin{matrix} C_6H_4.N_2.C_{10}H_5(NH_2)SO_3Na. \\ | \\ C_6H_4.N_2.C_{10}H_5(NH_2)SO_3Na. \end{matrix}$$

Four mono-sulphonic acids are formed when beta-naphthylamine is treated with sulphuric acid.

**Santonin** (*Santoninum*), $C_{15}H_{18}O_3$ = **246.14,** is an anhydride of *santonic acid*, $C_{15}H_{20}O_4$. As several reactions point to a relationship between this acid and naphthalene, santonin is mentioned in this place.

Santonin is the active principle of wormseed, the unexpanded flowerheads of Artemisia, from which it is obtained by extraction

with alcohol and lime-water, and decomposition of the soluble compound of lime and santonin by an acid. Santonin crystallizes in colorless prisms, which turn yellow on exposure to light; it is but sparingly soluble in water, more soluble in alcohol and ether.

Santonin taken internally confers upon the urine a dark color resembling the color of urine containing bile; upon heating such urine it turns cherry red or crimson, the color disappearing on the addition of an acid, and reappearing on neutralization.

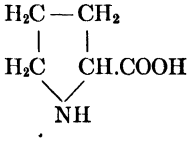
**Analytical Reactions.**—1. Santonin added to alcoholic solution of potassium hydroxide produces a bright red liquid which gradually becomes colorless.

2. To 1 c.c. of sulphuric acid add a few drops of ferric chloride solution and a crystal of santonin: on heating, a dark red color is produced, changing into violet brown.

## Aromatic Compounds Containing Nitrogen in the Cycle. (Heterocyclic Compounds.)

**Pyrrole, $C_4H_4NH$.**—During the destructive distillation of certain nitrogenous matters (chiefly bones), a liquid known as *bone-oil* is obtained, which contains a number of nitrogenous basic substances, among which pyridine and pyrrole are found. Pyrrole has but weak basic properties, is insoluble in water, has an odor like chloroform, boils at 131° C., and is lighter than water. Pine-wood dipped in a hydrochloric acid solution of pyrrole, assumes a carmine-red color. The carboxyl derivative of tetrahydro-pyrrole (pyrrolidine) is proline, which is one of the products of the hydrolysis of many proteins.

Its composition is,



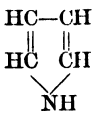
A solution of pyrrole in alcohol, treated with iodine in the presence of oxidizing agents, such as ferric chloride, deposits after some time crystals of *tetra-iodo pyrrole*. This compound is known by the name of *iodol*, $C_4I_4NH$. It is a pale-yellow crystalline powder, almost insoluble in water, soluble in 9 parts of alcohol, 1 or 2 parts of ether, and 15 parts of fatty oils; it is, when pure, tasteless and odorless, and contains 88.97 per cent. of iodine.

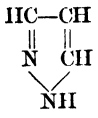
**Antipyrine** (*Antipyrina*), $C_{11}H_{12}N_2O$ = **188.1** (*Phenyl-dimethyl-isopyrazolone*).—When phenyl-hydrazine is heated with *diacetic ether*, $CH_3CO.CH_2.COOC_2H_5$, a substance is formed known as phenyl-methyl-isopyrazolone.

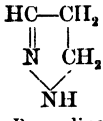
In this compound a second hydrogen atom may be replaced by methyl, when phenyl-dimethyl-isopyrazolone is formed, which is the substance to which the name antipyrine has been given.

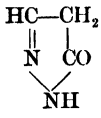
Antipyrine is a white, crystalline, odorless powder, having a slightly bitter taste; it fuses at 113° C. (235° F.), is soluble in less than its own weight of water, in 1 part of alcohol, and 1 part of chloroform, but only in 50 parts of ether.

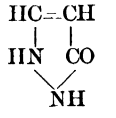
The structure of antipyrine and its relation to pyrrole and isopyrazolone may be shown by the constitutional formulas:

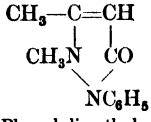

Pyrrole.


Pyrazole.


Pyrazoline.


Pyrazolone.


Isopyrazolone


Phenyl-dimethyl-isopyrazolone.

**Analytical Reactions.**—1. 0.2 gram of antipyrine dissolves in 2 c.c. of nitric acid without change of color. On heating slightly the liquid assumes a yellow, then an intense red color.

2. 12 c.c. of a 1 per cent. solution of antipyrine treated with 0.1 gram of potassium nitrite solution yield a colorless solution, which turns intensely green on the addition of 1 c.c. of dilute sulphuric acid. In a more concentrated solution green crystals of isonitroso-antipyrine form on standing.

3. The addition of ferric chloride to solution of antipyrine causes a deep red color, changing to yellow on the addition of sulphuric acid.

4. Mercuric chloride, as well as tannic acid, produces a white precipitate.

**Incompatibilities.** In addition to those indicated in the above tests, the following may be mentioned: A mixture of antipyrine and calomel produces a poisonous organic mercury compound; with phenol, even in dilute aqueous solution, an oily mass is formed; rubbed with sodium salicylate, a pasty mass is produced, in solution, however, there seems to be no effect; with beta-naphthol, a moist mixture results; rubbed with chloral hydrate, an oil is produced. On the other hand, antipyrine increases the solubility in water of caffeine and the quinine salts.

**Salipyrin** is antipyrine salicylate, obtained by direct combination of antipyrine and salicylic acid. It is a white odorless powder, with a harsh, sweetish taste, and is almost insoluble in water.

*Resopyrin* is a compound of antipyrine and resorcin. *Hypnal* is a compound of antipyrine and chloral hydrate. *Pyramidon* is a dimethyl-amido substitution product of antipyrine. *Ferripyrine* is a combination of antipyrine and ferric chloride. Many other combinations are known.

Antipyrine is a constituent of many "migraine powders."

**Pyridine, $C_5H_5N$.**—This substance has been mentioned above as being a constituent of bone-oil. Other substances have been isolated from this oil and have been found to form a homologous series:

| | |
|---|---|
| Pyridine, $C_5H_5N$ | Lutidine, $C_7H_9N$ |
| Picoline, $C_6H_7N$ | Collidine, $C_8H_{11}N$ |

Pyridine is of special interest, because it has been found that several of the alkaloids, such as quinine, cinchonine, etc., when oxidized, yield acids containing nitrogen, which bear to pyridine the same relation that benzoic acid bears to benzene, or that acetic acid bears to methane.

Thus, when nicotine is treated with oxidizing agents, nicotinic acid, $C_6H_5NO_2$, is obtained, which, when distilled with lime, breaks up into pyridine and carbon dioxide, thus:

$$C_6H_5NO_2 = C_5H_5N + CO_2.$$

The relation of nicotinic acid to pyridine, of benzoic acid to benzene, acetic acid to methane, may be shown thus:

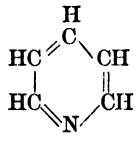
| | | |
|---|---|---|
| $CH_3.H$ | $C_6H_5.H$ | $C_5H_4.N.H$ |
| Menthane | Benzene | Pyridine. |
| $CH_3.CO_2H$ | $C_6H_5.CO_2H$ | $C_5H_4N.CO_2H.$ |
| Acetic acid. | Benzoic acid | Nicotinic acid. |

Pyridine is also obtained together with another basic substance, termed quinoline, $C_9H_7N$, by distilling quinine or cinchonine with potash. These observations, showing an intimate relationship between alkaloids and the pyridine and quinoline bases, have led to numerous experiments made with the view of either solving the problem of making alkaloids synthetically, or of obtaining substances which might have physiological actions similar to those of the alkaloids. The result of these efforts has been the introduction into the materia medica of quite a number of new remedies.

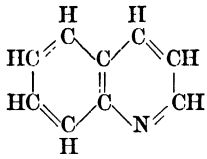
Pyridine is a colorless liquid, having a sharp, characteristic odor, strongly basic properties, and a boiling-point of 116° C. (241° F.). It is lighter than and miscible with water and the solution has an alkaline reaction and precipitates the hydroxides of metals. It is a tertiary amine of great stability, being unaffected by nitric or chromic acid even when heated with them.

**Quinoline, $C_9H_7N$** (*Chinoline*).—Quinoline has been mentioned above as a product of the distillation of quinine with potash; it may also be obtained by the action of sulphuric acid upon a mixture of aniline, nitro-benzene, and glycerin. It is, like pyridine, a colorless liquid, but its aromatic odor is less pleasant and its basic properties are less marked than those of pyridine. Boiling-point 237° C. (458° F.).

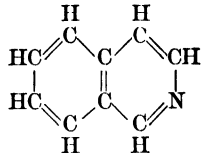
The constitution of pyridine and quinoline corresponds to that of benzene and naphthalene respectively, one of the groups CH having been replaced by an atom of nitrogen, thus:



Pyridine.



Quinoline.



Isoquinoline.

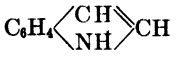
Isoquinoline is very similar to quinoline, but differs slightly in its properties. Like quinoline it is closely related to a number of alkaloids, especially those of the opium group. It is found together with quinoline among the bases of coal-tar and bone-oil. It melts at 21° C. and boils at 237° C.

**Kairine, $C_{10}H_{13}.NO.HCl$.**—The name kairine has been given to the hydrochloride of methyl-oxyquinoline hydride. It is a white, crystalline, odorless powder, soluble in 6 parts of water or in 20 parts of alcohol.

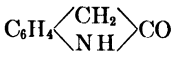
**Thalline, $C_{10}H_{11}NO$** (*Tetra-hydro-paramethyl-oxyquinoline*).—Quinoline serves in the manufacture of thalline, a white crystalline substance, which has an aromatic odor, fuses at 40° C. (104° F.) and is soluble in water, alcohol, and ether. The most characteristic feature of the substance is that it is colored intensely green by various oxidizing agents, such as ferric chloride and others. Some of the salts of thalline, chiefly the sulphate, tartrate, and tannate, have been used medicinally.

**Indole, $C_8H_7N$.**—This is an amine that contains a benzene ring and a pyrrole ring in the molecule. It bears the same relation to benzene and pyrrole that quinoline bears to benzene and pyridine. It is closely related to indigo and is formed in the decomposition of certain proteins. *Skatole* (β-methyl-indole), which has a very unpleasant odor, is present in feces.

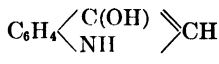
There are a number of oxygen derivatives of indole, such as oxindole, indoxyl, isatin. The relationships between these compounds and indigo is shown in the following formulas:



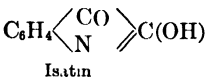
Indole.



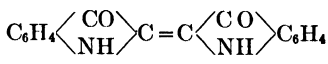
Oxindole.



Indoxyl.



Isatin



Indigo (Indigotin)

**Indigo, $C_{16}H_{10}N_2O_2$.**—This is a valuable blue dye, which formerly was derived from the glucoside indican occurring in certain plants of India, Java, etc. Now the bulk of indigo is made synthetically and the product is purer than the natural indigo. Several methods of synthetizing indigo have been devised, but the one used in its manufacture starts with naphthalene and acetic acid. Naphthalene is oxidized to phthalic acid, which by appropriate treatment is converted into ortho-amino-benzoic acid. This is combined with monochlor-acetic acid to form phenyl-glycine-carboxylic acid, $C_6H_4\begin{matrix}NH.CH_2.COOH\\COOH\end{matrix}$. When the latter is fused with caustic soda, indoxyl is formed, which in alkaline solution is oxidized by air to indigo.

Indigo is insoluble in water, alcohol, and most other solvents, readily soluble in hot aniline from which it crystallizes. It can be reduced to indigo-white, $C_{16}H_{12}N_2O_2$, which is colorless and soluble in solutions of alkalies. A fabric dipped into such an alkaline solution and subsequently exposed to the air, assumes a blue color owing to the oxidation of indigo-white to indigo.

**Sodium Indigotindisulphonate** (*Sodii Indigotindisulphonas*), $C_{16}H_8O_2N_2(SO_3Na)_2$ = **466.22** (*Indigo-carmine*).—When indigo is treated with concentrated sulphuric acid, it dissolves and forms a disulphonic acid derivative. The sodium salt occurs as a blue powder or a dark purple paste. The powder, when compressed, assumes a copper-like lustre. It is sparingly soluble in water and almost insoluble in alcohol. The blue color of the aqueous solution is discharged by oxidizing agents, such as nitric acid, bromine or chlorine, and also by reducing agents, as sodium hydroxide and zinc dust, stannous chloride, and also by alkaline hydrogen dioxide solution.

## 52. TERPENES AND THEIR DERIVATIVES.

The group of hydrocarbons of the general formula $(C_5H_8)_x$, found largely in the volatile oils, has been called by the generic word *terpenes*, but this term has been more specifically applied to the subgroup $C_{10}H_{16}$. According to the molecular complexity this group has been classified into:

| | |
|---|---|
| Hemiterpenes . . . . . | $C_5H_8$, |
| Terpenes proper . . . . . | $C_{10}H_{16}$, |
| Sesquiterpenes . . . . . | $C_{15}H_{24}$, |
| Diterpenes . . . . . | $C_{20}H_{32}$, |
| Polyterpenes . . . . . | $(C_{10}H_{16})_x$. |

Isoprene is the only representative of the hemiterpenes found in a volatile oil, and does not occur naturally, but is formed by the destructive distillation of rubber or gutta-percha. The terpenes

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QUESTIONS.—What is the difference between fatty and aromatic compounds, and from which two hydrocarbons are they derived? From what source is benzene obtained, how can it be made from benzoic acid, and what are its properties? Give the graphic formulas of benzene, nitro-benzene, phenol, thymol, benzoic acid, and salicylic acid. Mention methane derivatives which have a constitution analogous to that of the substances mentioned. Give composition, properties, and mode of manufacture of, and tests for carbolic acid. What relation exists between benzoic acid and oil of bitter almond? What is the source of amygdalin, to which class of substances does it belong, and what are the products of its decomposition under the influence of emulsin? Explain the process for the manufacture of salicylic acid, and state its properties. Give composition and properties of naphthalene and naphthol. Give tests for tannin, state the source from which it is derived and for what it is used. From what, and by what process, is aniline obtained; what is its composition and what its constitution? How are aniline dyes manufactured from aniline? State the properties and some reactions characteristic of antipyrine. What is saccharin, and what are its properties? State the composition of iodol.

proper and sesquiterpenes are among the principal constituents of the volatile oils. The diterpenes and higher polyterpenes are more rarely found and but little studied.

**Volatile or Essential Oils.**—The term essential oil is more a pharmaceutical than chemical term, and is used for a large number of liquids obtained from plants, and having in common the properties of being volatile, soluble in ether and alcohol, almost insoluble in water, and having a distinct and in most cases even highly characteristic odor. They stain paper as do fats or fat oils, from which they differ, however, by the disappearance after some time of the stain produced, while fats leave a permanent stain.

The specific gravity of volatile oils ranges generally between 0.85 and 0.99. Being nearly insoluble in, and specifically lighter than, water, they will float on it. The water, however, retains in most cases enough of the oils to assume their odor (medicated waters). Most volatile oils are optically active, turning the plane of polarized light either to the right or left. While chemically pure oils are colorless, many, even when freshly prepared, have a distinct color; some are pale yellow, dark yellow, reddish or reddish brown, while a few are green or blue. The oils generally darken with age, especially when exposed to light and air, the atmospheric oxygen acting on them and converting the oils often into a sticky and resinous mass.

Volatile oils are found in different parts of plants, and are the principles imparting to the respective plants their characteristic odor. The extraction of volatile oils from plants is accomplished generally by distilling with water the vegetable matter containing the oil, the oil passing over with the steam and floating on the surface of the condensed water. In some instances mechanical pressure is used for the separation, as in case of the oils of orange, lemon, bergamot, etc. In other cases the oils are extracted by suitable solvents, or special methods are used.

In their chemical composition essential oils differ widely; some are compound ethers (oil of wintergreen is methyl salicylate), others are aldehydes (oil of bitter almonds is benzaldehyde), but most of them are hydrocarbons of the aromatic series, or mixtures of them, often associated with oxygen derivatives, alcohols, phenols, ketones, aldehydes, esters, etc.

*Oil of Cloves.*—The principal constituent of this oil is eugenol, $C_6H_3.C_3H_5.OCH_3.OH$, a monatomic phenol; a sesquiterpene, $C_{15}H_{24}$, called caryophyllene is also present.

*Oil of cinnamon* consists chiefly of cinnamic aldehyde, $C_6H_5CH{:}CHCOH$, a compound which has been prepared synthetically. Oil of cinnamon also contains cinnamyl acetate, $C_9H_9.C_2H_3O_2$, and a small amount of cinnamic acid $C_8H_8O_2$.

*Oil of Peppermint.*—The oils found in the market differ widely from one another, and there is no other volatile oil containing so many different constituents; as many as seventeen having been found in one sample. Besides

three different terpenes and one sesquiterpene, were found acetaldehyde, acetic acid, isovalerianic acid, amyl alcohol, menthol, menthon, $C_{10}H_{18}O$, menthyl acetate, $C_{10}H_{19}O.C_2H_3O$, and others.

## Terpenes, $C_{10}H_{16}$.

The terpenes are widely distributed in the vegetable kingdom, especially in the coniferæ and varieties of citrus, etc., and are found in the volatile oils obtained from the individual plants. The terpenes are readily acted upon by many agents and hence undergo numerous changes. One of these changes is polymerization, *i. e.*, conversion into compounds of the composition $C_{15}H_{24}$ and $C_{20}H_{32}$, which may be effected by heating a terpene in a sealed tube, or by shaking it with concentrated sulphuric acid or with certain other substances. Many of them also show a great tendency to pass into more stable isomers under certain conditions, *i. e.*, when acted on by acids. Gaseous chlorine acts violently upon them, and bromine and iodine convert many of them into cymene. Many terpenes are therefore closely related to cymene, $C_{10}H_{14}$, and may be considered as dihydrocymene; others, however, show a quite different structure. They are oxidized quite readily with the formation of a number of organic acids, and unite with gaseous hydrochloric acid to form mono- or dihydrochlorides. With bromine they often form characteristic tetrabromides, $C_{10}H_{16}Br_4$. They readily yield compounds with nitrosyl chloride, of the formula $C_{10}H_{16}.NOCl$, known as nitrosochlorides, and with the oxides of nitrogen compounds of the formulas $C_{10}H_{16}.N_2O_3$ and $C_{10}H_{16}.N_2O_4$, known as nitrosites and nitrosates respectively. The terpenes are almost all optically active, and most of them exist both in dextro- and in lævorotatory modifications.

*Pinene* is the chief constituent in most of the volatile oils obtained from the coniferæ, and is also found largely in other volatile oils.

*Oil of turpentine*, $C_{10}H_{16}$, is chiefly composed of pinene. It is a thin, colorless liquid of a characteristic aromatic odor, and an acrid, caustic taste; it is insoluble in water, soluble in alcohol, and an excellent solvent for resins and many other substances. When treated with hydrochloric-acid gas direct combination takes place and a white solid substance of the composition $C_{10}H_{16}HCl$ is formed, which is known as pinene hydrochloride, or *artificial camphor*, on account of its similarity to camphor both in appearance and odor.

*Experiment* 71.—Through 10 or 20 c.c. of oil of turpentine pass a current of hydrochloric-acid gas for some time, or until a quantity of a solid substance has separated. Collect this substance, which is artificial camphor, upon a filter; notice its characteristic odor. Heat some of it; hydrochloric acid is set free.

*Camphene* is the only solid hydrocarbon of the terpene group, and occurs in the oil from Pinus Sibirica. It is obtained by heating the above pinene hydrochloride with alcoholic potash.

*Limonene* is the principal constituent of orange oil, and is found in a large

number of other oils, as the dextro modification. Lævolimonene occurs in pine-needle oil.

*Dipentene* is the inactive modification of limonene, and can be prepared by heating pinene, camphene, sylvestrene, or limonene to 250°–270° C. for several hours.

**Terebene, Terebenum,** consists chiefly of dipentene with other hydrocarbons, and is obtained from oil of turpentine by mixing it with sulphuric acid, distilling, washing the distilled oil with soda solution, redistilling, and collecting the portions which pass over at a temperature of 155°–165° C. (311°–329° F.). Terebene resembles oil of turpentine in most respects, but has not the unpleasant odor of this oil.

*Sylvestrene* is found in Swedish and Russian oil of turpentine.

*Phellandrene* is widely distributed in volatile oils; notably in the water-fennel oil and eucalyptus oil.

**Sesquiterpenes, $C_{15}H_{24}$.**—These are likewise widely distributed in the vegetable kingdom, and are very similar in their general properties to the terpenes proper, but have a higher boiling-point. Of those, well characterized, may be mentioned: *cadinene,* from oil of cade and a large number of other volatile oils; *caryophyllene,* from oil of cloves; *humulene,* from oil of hops; *santolene,* from oil of sandalwood; *cedrene,* from oil of cedarwood; and *zingiberene,* from oil of ginger.

**Rubber** (*Caoutchouc*).—Rubber is the dried milky juice found in quite a number of trees growing in the tropics. It consists chiefly of hydrocarbons of the terpene series, having a very large molecular weight and a complex molecular structure.

The commercial article is yellowish-brown, has a specific gravity of 0.92 to 0.94, is soft, flexible, insoluble in water and alcohol but soluble in carbon disulphide, ether, chloroform, and benzene. It is not acted upon by dilute mineral acids; concentrated nitric and sulphuric acid, as well as chlorine, attack it after a time. It is hard and tough in the cold; when heated it becomes viscous at 125° C. (257° F.), and fuses at 170°–180° C. (347°–356° F.) to a thick liquid, which, on cooling, remains sticky, and only regains its original character after a long time.

*Vulcanized rubber* is India rubber which has been caused to enter into combination with from 7 to 10 per cent. of sulphur by heating together the two substances to a temperature of 130°–150° C. (266°–302° F.). Vulcanized rubber differs from the natural article by possessing greater elasticity and flexibility, by resisting the action of solvents, reagents and atmosphere to a higher degree, and by not hardening when exposed to cold.

*Hard rubber, vulcanite, or ebonite,* is vulcanized rubber, containing from 20 to 35 per cent. of sulphur, and often also tar, white-lead, chalk, or other substances. It is hard, tough, and susceptible of a good polish.

**Preservation of Rubber.**—Various substances have been recommended for preserving articles of rubber. For undeteriorated rubber, it is said that a 3 per cent. solution of either phenol or aniline is the best, while for deteriorated rubber, or such as has been exposed many times to boiling water, a 1 per cent. solution of potassium pentasulphide is best, the restorative properties of the latter depending on the absorption of the sulphur from the pentasulphide. The articles are immersed in the solutions in vessels of appropriate shape. It has been observed that black rubber immersed in the aniline solution undergoes an increase in volume. For example, rubber tubing shows a marked increase in length.

**Gutta-percha.**—Gutta-percha is the concrete juice of a tree—Isonandra gutta. It resembles India rubber both in composition and properties. At ordinary temperature it is a yellowish or brownish, hard, somewhat flexible, but scarcely elastic substance; when warmed it softens, and is plastic above 60° C. (140° F.); at the temperature of boiling water it is very soft. It is insoluble in water, alcohol, dilute acids and alkaline solutions; soluble in oil of turpentine, carbon disulphide, and chloroform.

## Oxygen Derivatives of Terpenes.

**Stearoptens or Camphors** are substances closely related to the terpenes and to cymene both in physical and chemical properties; while terpenes are liquid, camphors are crystalline solids. Borneo camphor has the composition $C_{10}H_{18}O$, while the camphor found in the camphor-trees of China and Japan has the composition $C_{10}H_{16}O$.

*Camphor, Camphora,* $C_{10}H_{16}O$ (*Laurinol*), forms white, translucent masses of a tough consistence and a crystalline structure; it has a characteristic, penetrating odor and poisonous properties; in the presence of a little alcohol or ether it may be pulverized; it is nearly insoluble in water, but soluble in alcohol, ether, chloroform, etc.; boiled with bromine it forms the *monobromated camphor,* camphora monobromata, $C_{10}H_{15}BrO$, a white crystalline substance having a mild camphoraceous odor and taste. Heating with nitric acid converts camphor into camphoric acid, $C_8H_{14}(CO_2H)_2$, a colorless, crystalline, fusible substance having an acid taste; it is slightly soluble in water, readily in alcohol and ether.

**Cineol, Eucalyptol, $C_{10}H_{18}O$.**—Cineol is found in the volatile oils of different species of eucalyptus, as also in the oils of some other plants. It is liquid at the ordinary temperature, but solidifies when cooled to a little below the freezing-point of water. It has an aromatic, distinctly camphoraceous odor.

**Menthol, $C_{10}H_{19}OH$** (*Mint-camphor*).—Found together with a terpene in oil of peppermint, and separates in crystals on cooling the oil. Menthol is nearly insoluble in water, fuses at 43° C. (109° F.), and boils at 212° C. (414° F.). It has the characteristic odor of peppermint.

*Terpin hydrate, Terpini hydras,* $C_{10}H_{20}O_2.H_2O$, is the hydrate of the diatomic alcohol terpin, and is formed from pinene under the

influence of alcohol and nitric acid. It forms colorless crystals, melting at 117° C. (243° F.), is readily soluble in alcohol, but sparingly soluble in water, ether, or chloroform.

**Resins** are obtained, together with the essential oils, from plants. Mixtures of a resin and a volatile oil are known as *oleo-resins*, while mixtures of a resin or oleo-resins and gum are known as *gum-resins*. The name *balsam* is also used for a certain group of oleo-resins.

The resins are mostly amorphous, brittle bodies, insoluble in water, but soluble in alcohol, ether, fatty and essential oils; they are fusible, but decompose before being volatilized; they all contain oxygen and exhibit somewhat acid properties.

*Turpentine*, the oleo-resin of the conifers, contains besides the oil of turpentine a resin called *colophony*, *rosin*, or *ordinary resin*, consisting chiefly of the anhydride of *abietic acid*, $C_{44}H_{64}O_5$.

*Copaiva balsam* consists of a volatile oil and a resin, the latter being principally copaivic acid, $C_{20}H_{30}O_2$.

Of fossil resins may be mentioned *amber* and *asphalt*, the latter having most likely been formed from petroleum.

## 53. ALKALOIDS.

**General Remarks.**—The basic substances found in plants are grouped together under the name of alkaloids, this term signifying alkali-like, in allusion to the alkaline or basic properties of these substances. They show their derivation from ammonia to a more or less marked degree, as, for instance, in their power to combine with acids to form well-defined salts, to combine with platinic chloride to form insoluble double compounds, etc.

The compounds formed by the direct combination of alkaloids with acids are, in the case of oxygen acids, named like other salts of these acids, for instance, sulphates, nitrates, acetates, etc. In the case of halogen acids, however, a different method has been adopted, because it would be incorrect to apply the terms chlorides and bromides to substances formed, not by the combination of chlorine or bromine with other substances, nor by the replacement of hydrogen in the respective hydrogen acids of these elements, but by direct combination of these acids with the alkaloids. The terms *hydrochloride* and *hydrobromide* have been adopted by the U. S. P. for the compounds obtained by direct union of alkaloids with hydrochloric and hydrobromic acids. Formerly the terms *hydrochlorate* and *hydrobromate* were used.

Alkaloids are found in the leaves, stems, roots, barks, and seeds of

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QUESTIONS.—What substances are known as terpenes: where are they found in nature? Give the composition of the principal groups of terpenes. Mention the general properties of essential oils, and name some of the important ones. What is the source of rubber; how is it converted into vulcanized and hard rubber? State the composition and properties of camphor.

various plants; it often happens that a certain alkaloid is found in the different species of one family, and it is often the case that various alkaloids of a similar composition are found in the same plant.

**General Properties of Alkaloids.**—1. They combine with acids to form well-defined salts, and are set free from the solutions of these salts by alkalies and alkali carbonates.

2. In most cases those containing no oxygen are volatile liquids, those containing oxygen are non-volatile solids.

3. The volatile alkaloids have a peculiar disagreeable odor, reminding of ammonia; the non-volatile alkaloids are odorless.

4. Most solid alkaloids fuse at a temperature above 100° C. (212° F.) without decomposition, but are decomposed when the heat is raised much beyond the fusing-point.

5. Most alkaloids are insoluble, or nearly so, in water, but soluble in alcohol, chloroform, benzene, acetic ether, and many also in ether.

6. The hydrochlorides, sulphates, nitrates, acetates (and most other salts) of alkaloids are either soluble in water, or in water which has been slightly acidulated, and also in alcohol; but they are insoluble, or nearly so, in ether, acetic ether, chloroform (except veratrine and narcotine), amyl alcohol (except veratrine and quinine), benzene, and benzin.

7. The solid alkaloids, as well as their salts, may be obtained in a crystalline state.

8. Most alkaloids are white, have a very strong, generally bitter, taste, and act very energetically upon the animal system.

9. From the aqueous solutions of alkaloid salts, the solid alkaloids are precipitated by alkali hydroxides, in an excess of which reagents some alkaloids (morphine, for instance) are soluble. Alkali carbonates and bicarbonates liberate all, and precipitate most alkaloids; strychnine, brucine, veratrine, atropine, and a few rare alkaloids are not precipitated by bicarbonates.

Most alkaloids give precipitates with tannic acid, picric acid, phospho-molybdic acid, potassium mercuric iodide; and the higher chlorides of platinum, gold, and mercury. These precipitates are similar in properties and composition to those formed with ammonia.

Most alkaloids give beautiful color reactions when treated with oxidizing agents, such as nitric acid, chloric acid, chromic acid, ferric chloride, chlorine-water, etc.

A solution of mercuric-potassium iodide, $HgI_2.2KI$, made by dissolving 13.546 grams of mercuric chloride and 49.8 grams of potassium iodide in 1000 c.c. of water, is known as *Mayer's solution*. This precipitates all alkaloids, forming with them white or yellowish-white, generally crystalline compounds. The solution has been used for volumetric determination of alkaloids, but the method is now discarded, as the results are not accurate. (In most cases the alkaloid replaces the potassium in the potassium-mercuric iodide.)

Phospho-molybdic acid, mentioned above as a reagent for alkaloids, is prepared as follows: 15 grams of ammonium molybdate are dissolved in a little

ammonia-water and diluted with water to 100 c.c. This solution is poured gradually into 100 c.c. of nitric acid, specific gravity 1.185, and to this mixture is added a warm 6 per cent. solution of sodium phosphate as long as a precipitate is produced. This precipitate is collected on a filter, washed and dissolved in very little sodium hydroxide solution; the solution is evaporated to dryness, further heated until all ammonia has been expelled and the residue dissolved in 10 parts of water. To this solution is added a quantity of nitric acid sufficient to redissolve the precipitate which is formed at first. This reagent gives precipitates not only with the alkaloids, but also with the salts of potassium and ammonium.

**General Mode of Obtaining Alkaloids.**—The disintegrated vegetable substance (bark, seeds, etc.) is extracted with acidified water, which dissolves the alkaloids. When the alkaloid is volatile, it is obtained from this solution by distillation, after having been liberated by an alkali.

Non-volatile alkaloids are precipitated from the acid solution by the addition of an alkali, and the impure alkaloid thus obtained is purified by again dissolving in an acid and reprecipitating, or by dissolving in alcohol and evaporating the solution.

As the quantity of alkaloids in plants, and consequently in the aqueous extract made from them, is often so small that the precipitation process gives unsatisfactory results, a second method known as the *shaking-out process* is often employed for the separation of alkaloids. In using this process the concentrated aqueous extract, to which a suitable alkaline precipitant has been added, is agitated with a liquid (such as chloroform) not miscible with water and acting as a solvent upon the alkaloids. The operation is performed in an apparatus known as *separator* or *separatory funnel*, consisting of a globular or cylindrical glass vessel, provided with a well-fitting stopper and an outlet-tube containing a glass stopcock. Having introduced into this vessel the extract and solvent, the latter is made to dissolve the alkaloids present by a rapid rotation of the separator. As the aqueous solution and the solvent do not mix, but form two distinct layers one above the other, they may be conveniently separated by opening the stopcock until the heavier liquid has run out. By evaporation of the liquid, used as a solvent, the alkaloids may be obtained in a more or less pure condition.

**Assay methods.**—As the medicinal value of many drugs, such as opium, cinchona bark, etc., as also that of the galenical preparations, such as tinctures, extracts, etc., obtained from such drugs, depends chiefly on the alkaloids present, and as the quantity of the alkaloids in drugs varies considerably, the U. S. P. gives specific assay methods for the estimation of the percentage of the alkaloids contained in drugs or in certain preparations.

These assay methods must be closely followed by the analyst, as otherwise results may be obtained which are either too high or too low. This is due to the fact that these methods in many cases do not give absolutely correct results, but give results sufficiently accurate for all practical purposes, provided the directions of the Pharmacopœia are closely followed. To bring about a standard and uniformity in alkaloidal strength is the object of these assay methods.

**Antidotes.**—In cases of poisoning by alkaloids the stomach-pump and emetics (zinc sulphate) should be applied as soon as possible; astringent liquids may be given, because tannic acid forms insoluble compounds with most of the alkaloids. In some cases special physiological antidotes are known, and should be used.

**Detection of Alkaloids in Cases of Poisoning.**—The separation and detection of poisonous alkaloids in organic matter (food, contents of stomach, etc.), especially when present in very small quantities, as is generally the case, is one of the most difficult tasks of the toxicologist, and none but an expert who has made himself thoroughly familiar with the methods of discovering minute quantities of organic poisons in the animal system should undertake to make such an analysis in case legal proceedings depend on the result of the chemist's report.

Of the various methods applied for the separation of alkaloids from organic matter, the following may be mentioned:

The substance to be examined is properly comminuted (if this be necessary) and repeatedly digested at 40° to 50° C. (104° to 122° F.) with water slightly acidulated with sulphuric acid. The filtered liquids (containing the sulphates of the alkaloids) are evaporated over a water-bath to a thin syrup, which is mixed with three or four times its own volume of alcohol; this mixture is digested at about 35° C. (95° F.) for several hours, cooled, filtered, and again evaporated nearly to dryness. (By this treatment with alcohol many substances soluble in the acidified water, but insoluble in diluted alcohol, are eliminated and left on the filter, while the alkaloids remain in solution as sulphates.)

A little water is now added to the residue, and this solution, which should yet have a slight acid reaction, is shaken with about three times its own volume of acetic ether, which dissolves some coloring and extractive matters, but does not act upon the alkaloid salts. The two strata of liquids which form on standing in a tube are separated by means of a pipette, and the operation is repeated, if necessary, *i. e.*, if the ether should have been strongly colored

The remaining acid aqueous solution is next slightly supersaturated with sodium carbonate, which liberates the alkaloids. Upon now shaking the solution with acetic ether, all alkaloids are dissolved in this liquid, which, after being separated from the aqueous solution, leaves upon evaporation, at a low temperature, the alkaloids generally in a sufficiently pure state for recognition by special tests. It may, however, be necessary to purify the residue further by neutralizing with an acid, allowing to crystallize in a watch-glass, and separating the small crystals from adhering mother-liquor.

The above method for detecting alkaloids in the presence of organic matter generally answers the requirements of students.

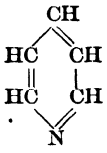
The practical toxicologist has in most cases of poisoning some data (deduced from the symptoms before death, or from the results of the post-mortem examination) pointing to a certain poison, which, of course, facilitate his work considerably.

**Classification of Alkaloids.**—While the constitution of many alkaloids has as yet not been determined, others have been shown to be derivatives, or to contain the nuclei of either pyridine, quinoline, or

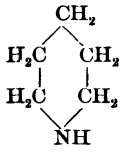
isoquinoline. Closely related to pyridine are the liquid bases coniine, nicotine, and sparteine, as also the solid alkaloids atropine, cocaine, ecgonine, and others. Among alkaloids derived from quinoline are those found in cinchona bark and in nux vomica. Related to isoquinoline are the opium alkaloids.

### The Pyridine Group of Alkaloids.

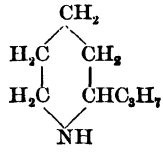
The close relationship between pyridine and some of the vegetable alkaloids may be shown by considering the structure of pyridine and coniine:



Pyridine.



Piperidine.



Coniine.

Piperidine has been made by adding 6 atoms of hydrogen to pyridine by means of sodium and alcohol; coniine, which is propyl-piperidine, was the first true alkaloid prepared artificially.

**Piperin,** $C_{17}H_{19}NO_3$.—This compound is found in black and white pepper. While it is isomeric with morphine, it differs widely from it in all its properties. It can hardly be called an alkaloid, as it has no alkaline reaction, is but feebly basic, and does not show the general alkaloidal reactions. It forms colorless or pale yellowish crystals which are, when first put in the mouth, almost tasteless, but produce on prolonged contact a sharp, biting sensation.

Piperin dissolves in concentrated sulphuric acid with a dark blood-red color, which disappears on dilution with water. Treated with nitric acid it turns rapidly orange, then red.

**Coniine,** $C_8H_{17}N$.—Coniine occurs in conium maculatum (hemlock), accompanied by two other alkaloids. It is a colorless, oily liquid, having a disagreeable, penetrating odor.

**Pilocarpine,** $C_{11}H_{16}N_2O_2$.—Found in the leaflets of pilocarpus species. The alkaloid crystallizes with difficulty; its solutions in ether, alcohol, or water have an alkaline reaction. It is a white, crystalline powder, which dissolves in fuming nitric acid with a faint greenish tint. The aqueous solution is precipitated by most of the common reagents for alkaloids. The hydrochloride and nitrate are official.

**Nicotine,** $C_{10}H_{14}N_2$.—Tobacco leaves contain from 2 to 8 per cent. of nicotine, which is a colorless, oily liquid, having a caustic taste and a disagreeable, penetrating odor. It gives with hydrochloric acid a violet, with nitric acid an orange, color.

**Sparteine,** $C_{15}H_{26}N_2$.—This alkaloid, found in scoparius (broom, Irish broom), is a colorless, oily liquid, turning brown on exposure to air and light. It has a slight aniline-like odor.

**Sparteine Sulphate,** $C_{15}H_{26}N_2H_2SO_4 + 5H_2O$, is obtained by saturating the alkaloid with sulphuric acid; it is a colorless, crystalline salt, readily soluble in water. An ethereal solution of the salt, to which a few drops of ammonia-water have been added, deposits, on the addition of an ethereal solution of iodine, minute dark greenish-brown crystals.

## The Tropine Group of Alkaloids.

**Atropine** (*Atropina*), $C_{17}H_{23}NO_3 = 289.19$ (*Daturine*).—Obtained from Atropa belladonna. It is a white, crystalline powder, having a bitter and acrid taste and an alkaline reaction; it is sparingly soluble in water, but very soluble in alcohol and chloroform. The commercial article generally contains a small quantity of hyoscyamine. *Atropine sulphate,* $(C_{17}H_{23}NO_3)_2.H_2SO_4$, is a white, crystalline powder, easily soluble in water.

**Analytical Reactions.**—1. Atropine dissolves in concentrated sulphuric acid without color. This solution is not colored by nitric acid (difference from morphine), and not at once by potassium dichromate (difference from strychnine).

2. A mixture of atropine and nitric acid, when evaporated to dryness over a water-bath, leaves a yellow residue, which turns violet on the addition of a few drops of an alcoholic solution of potassium hydroxide and a fragment of the same reagent.

3. On warming a mixture of atropine and concentrated sulphuric acid a pleasant odor, reminding of roses and orange flowers, is evolved. The addition of a few fragments of potassium dichromate changes this odor to that of bitter almond.

4. Solutions of atropine dilate the pupil of the eye to a marked extent.

**Homatropine,** $C_{16}H_{21}NO_3$.—This alkaloid is obtained by the condensation of tropine and mandelic acid. The hydrobromide is official. It is a white crystalline powder, and resembles atropine in its mydriatic properties.

**Hyoscyamine,** $C_{17}H_{23}NO_3$.—Found in small quantities together with hyoscine in the seeds of Hyoscyamus niger (henbane), and in some other plants belonging to the solanaceæ.

Hyoscyamine resembles atropine closely in most of its chemical, physical, and physiological properties, but the corresponding salts of the two alkaloids crystallize in different forms; the *hydrobromide* is official.

Hyoscyamine differs from atropine by yielding with gold chloride a precipitate which, when recrystallized from a hot aqueous solution, acidified with hydrochloric acid, deposits lustrous, golden-yellow scales.

**Scopolamine,** $C_{17}H_{21}NO_4$.—This is an alkaloid obtained from Scopola and other plants of the Solanaceæ. It is known only in an amorphous, semisolid state, but the salts, of which the *hydrobromide* is official, crystallize readily. Scopolamine evaporated to dryness

on a water-bath with a few drops of fuming nitric acid leaves a nearly colorless residue which turns violet on the addition of some alcoholic solution of potassium hydroxide.

**Cocaine** (*Cocaina*), $C_{17}H_{21}NO_4$ = **303.18.**—This alkaloid is found in the leaves of the South American shrub Erythroxylon coca, in quantities varying from 0.15 to 0.65 per cent. It is a white crystalline powder, soluble in about 600 parts of water, easily soluble in alcohol, ether, and chloroform; it fuses at 98° C. (208° F.). A fragment of cocaine placed on the tongue causes the sensation of numbness without acrid or bitter taste; the solution in water is faintly bitter.

Cocaine heated with acids in sealed tubes is decomposed into methyl alcohol, benzoic acid, and *ecgonine*, showing it to be methyl-benzoyl-ecgonine:

$$\underset{\text{Cocaine.}}{C_{12}H_{21}NO_4} + 2H_2O = \underset{\text{Methyl alcohol.}}{CH_3HO} + \underset{\text{Benzoic acid.}}{C_6H_5CO_2H} + \underset{\text{Ecgonine.}}{C_9H_{15}NO_3}.$$

Ecgonine is found in the coca leaves as benzoyl-ecgonine, $C_9H_{15}(C_7H_5O)NO_3 + 4H_2O$; this is a white, crystalline substance from which cocaine may be obtained by heating it with methyl-iodide. The mother-liquors obtained in the manufacture of cocaine from the leaves contain the alkaloid in an amorphous state and possibly one or two other alkaloids, one of which has been named *hygrine*. Whether these alkaloids are contained in the coca-plant, or are products of the decomposition of cocaine, are questions not yet decided.

Of the various salts of cocaine, the *hydrochloride*, $C_{17}H_{21}NO_4HCl$, is official. This salt crystallizes from alcohol in short, anhydrous prisms; from aqueous solution, however, with two molecules of water, which are completely expelled at a temperature of 100° C. (212° F.). The anhydrous salt fuses at 190° C. (374° F.) and is readily soluble in water; this salt solution has a somewhat more bitter taste than the alkaloid itself.

**Analytical Reactions.**—1. Cocaine salts are precipitated from an aqueous solution as follows: Platinum chloride produces a yellowish-white, mercuric chloride a white flocculent, picric acid a yellow pulverulent, the alkali carbonates and hydroxides a white precipitate, which latter is soluble in ammonia.

2. To a cocaine solution, strongly acidified with hydrochloric acid, add some potassium dichromate, when an orange-colored crystalline precipitate of cocaine chromate forms.

3. Add 1 c.c. of a 3 per cent. solution of potassium permanganate to 1 centigram of cocaine hydrochloride dissolved in 2 drops of water; a violet precipitate forms which appears brownish-violet when collected on a filter.

4. Boil a small quantity of cocaine solution for a few minutes with dilute sulphuric acid; neutralize carefully with potassium hydroxide and then add a few drops of ferric chloride solution. A pale, brownish-yellow precipitate of basic ferric benzoate will form.

**Substitutes for Cocaine.**—Several synthetics have been introduced to take the place of cocaine. Some of these are the following:

**Alypin,** $(CH_3)_2N.CH_2.C(C_2H_5)(C_6H_5COO).CH_2.N(CH_3)_2.HCl$, is the hydrochloride of the benzoyl-ethyl-tetramethyldiamino derivative of secondary propyl alcohol. It is a white hygroscopic powder, very soluble in water and alcohol, of a neutral reaction and bitter taste. It is a local anesthetic, claimed to be equal to cocaine, but not a mydriatic, and less toxic than cocaine. It is used externally in a 10 per cent. solution and hypodermically in a 1 to 4 per cent. solution.

**Betaeucaine Hydrochloride** (*Betaeucainæ hydrochloridum*), $C_5H_7N.(CH_3)_3(C_6H_5-COO).HCl$, is a salt of trimethyl-benzoyl-hydroxypiperidine. It is a white powder, soluble in 30 parts of water and in 35 parts of alcohol. Its solutions can be boiled without change, and are precipitated by alkalies or carbonates; 5 c.c. of a 1 per cent. aqueous solution of the salt gives no permanent precipitate on the addition of 5 c.c. of mercuric chloride test solution. If cocaine or alphaeucaine be present, a precipitate will be formed. It is a local anesthetic like cocaine, but weaker, and does not dilate the pupil or contract the bloodvessels. It is used in a 2 to 3 per cent. solution in the eye, and 5 to 10 per cent. solution or ointment on other parts.

**Holocaine hydrochloride,** $CH_3.C(:N.C_6H_4.OC_2H_5)(.NH.C_6H_4.OC_2H_5).HCl$, is the salt of a basic condensation product of paraphenetidin and acetparaphenetidin (phenacetin). It forms colorless, neutral or faintly alkaline crysta's, odorless, slightly bitter, and producing transient numbness on the tongue. It is soluble in 50 parts of water, easily in alcohol. The solution is precipitated by alkalies and carbonates and the alkaloidal reagents. Porcelain should be used in making solutions, as alkali from glass causes a turbidity.

The salt is a local anesthetic like cocaine, but having a quicker effect and antiseptic action. As 1 per cent. solution is employed. It is more toxic than cocaine.

**Pelletierine tannate** of the U. S. P. is a mixture of the tannates of four alkaloids (punicine, iso-punicine, methyl-punicine, and pseudo-punicine) obtained from Punica Granatum.

## The Quinoline Group of Alkaloids.

**Cinchona Alkaloids.**—The bark of various species of cinchona contains a number of alkaloids, of which the most important are quinine, cinchonine, quinidine, and cinchonidine. These alkaloids exist in the bark in combination with a peculiar acid, termed *kinic acid.* The quantity and relative proportion of the alkaloids vary widely in different barks, but the official bark should contain not less than 5 per cent. of total alkaloids, and at least 4 per cent. of anhydrous ether-soluble alkaloids.

**Quinine** (*Quinina*), $C_{20}H_{24}N_2O_2.3H_2O$ = **378.26.**—This formula represents the official alkaloid, but it is also known as anhydrous, and in combination with either one or two molecules of water. The anhydrous quinine is a resinous substance, while the crystallized quinine is a white, flaky, amorphous or crystalline powder, having a very bitter taste and an alkaline reaction. It is nearly insoluble in water, but soluble in alcohol, ether, ammonia water, chloroform, and dilute acids. When heated to about 57° C. (134° F.) it melts; at 100° C. (212° F.) it loses 2 molecules of water, the remainder being expelled at 125° C. (257° F.).

**Quinine Sulphate** (*Quininæ Sulphas*), $(C_{20}H_{24}N_2O_2)_2H_2SO_4.7H_2O$ = **872.58.**—This salt, containing two molecules of the alkaloid in combination with one of sulphuric acid and seven of water, is the common form of quinine sulphate. It forms snow-white, silky, light and fine, needle-shaped crystals, fragile and somewhat flexible, making a very light and easily compressible mass; it has a very bitter taste and a neutral reaction; it is soluble in 720 parts of cold and in 30 parts of boiling water; soluble in 65 parts of alcohol, but nearly insoluble in ether and chloroform; it readily dissolves in diluted sulphuric or hydrochloric acid.

**Quinine Bisulphate** (*Quininæ Bisulphas*), $C_{20}H_{24}N_2O_2.H_2SO_4.7H_2O$ = **548.39.**—This salt is formed when the common sulphate is dissolved in an excess of diluted sulphuric acid. It crystallizes in colorless, silky needles, has a strongly acid reaction, and is soluble in 8.5 parts of water.

**Quinine Dihydrochloride** (*Quininæ Dihydrochloridum*), $C_{20}H_{24}N_2O_2.2HCl$ = **397.15.**—This is an acid salt of quinine. It is a white powder, odorless and very bitter. One gram is soluble in 0.6 c.c. of water and 12 c.c. of alcohol. It is slightly soluble in chloroform and still less in ether. Quinine hydrochloride is soluble in 18 parts of water, less than its own weight of alcohol or chloroform, and in 240 parts of ether.

**Quinine and Urea Hydrochloride** (*Quininæ et Ureæ Hydrochloridum*), $C_{20}H_{24}N_2O_2.CO(NH_2)_2.2HCl.5H_2O$ = **547.28.**—This double salt occurs as translucent prisms or as a white powder of very bitter taste. One gram dissolves in 0.9 c.c. of water and 2.4 c.c. of alcohol. It contains 58 per cent. of anhydrous quinine.

**Quinine Tannate** (*Quininæ Tannas*), is somewhat variable in composition, containing from 30 to 35 per cent. of anhydrous quinine. It is a pale yellow, odorless, tasteless amorphous powder, slightly soluble in water, chloroform or ether, somewhat more soluble in alcohol.

| | | |
|---|---|---|
| Quinine hydrochloride, | $C_{20}H_{24}N_2O_2.HCl.2H_2O$ | = 396.68 |
| Quinine hydrobromide, | $C_{20}H_{24}N_2O_2.HBr.2H_2O$ | = 423.16 |
| Quinine salicylate, | $2(C_{20}H_{24}N_2O_2.C_7H_6O_3)H_2O$ | = 942.50 |

The above three salts are obtained by treating quinine with the respective acids; they are white, crystalline substances; the first two are easily, the salicylate is sparingly, soluble in water.

*Iron and quinine citrate* is a scale compound obtained by dissolving ferric hydroxide and quinine in citric acid, evaporating, etc.

**Analytical Reactions.**—1. Quinine or its salts, dissolved in water or in dilute acids, give, after having been shaken with fresh chlorine-water, or bromine-water, an emerald-green color on the addition of ammonium hydroxide. (Plate VI, 4). The reaction is readily shown by treating 10 c.c. of a solution (about 1 in 1500) with 2 drops of bromine-water, and then with an excess of ammonia-water. The green color is due to the formation of thalleioquin.

2. Solutions of quinine, treated with chlorine water, then with fragments of potassium ferrocyanide, turn pink, then red on the addition of ammonium hydroxide not in excess.

3. Solutions of quinine give with ammonia water a white precipitate of quinine, which is readily dissolved in an excess of ammonia. The precipitate is also soluble in about twenty times its own weight of ether (the other cinchona alkaloids requiring larger proportions of ether for solution).

4. Most solutions of quinine, especially when acidulated with sulphuric acid, show a vivid blue fluorescence.

5. Neutral solutions of quinine are precipitated by alkali oxalates.

6. Quinine and its salts form colorless solutions with concentrated sulphuric acid. A dark or red color indicates the presence of other organic substances.

**Quinidine, $C_{20}H_{24}N_2O_2$.**—Isomeric with quinine; it gives, like the latter, a green color with chlorine water and ammonia, and forms fluorescent solutions. Unlike quinine, it is precipitated from neutral solutions by potassium iodide.

**Cinchonine, $C_{19}H_{22}N_2O$.**—This alkaloid is found in cinchona bark in quantities varying from 0.5 to 3 per cent. It crystallizes without water, forming white needles: it is almost insoluble in water, soluble in 116 parts of alcohol or in 163 parts of chloroform, readily soluble in dilute acids.

By dissolving the alkaloid in sulphuric acid is obtained:

Cinchonine sulphate, *Cinchoninæ sulphas*, $(C_{19}H_{22}N_2O)_2H_2SO_4.2H_2O$. It is a white, crystalline substance. Cinchonine differs from quinine by its greater insolubility in ether, by its insolubility in ammonia-water, by not forming fluorescent solutions, and by not giving a green color with chlorine-water and ammonia.

**Analytical Reactions.**—1. Chlorine water added to the solution of a cinchonine salt produces a yellowish-white precipitate insoluble in excess of ammonia.

2. Potassium ferrocyanide solution added to a neutral solution of cinchonine produces a white precipitate soluble in excess of the reagent. Upon adding an acid to this solution a golden-yellow precipitate is formed.

3. With alkali hydroxides, carbonates, and bicarbonates, cinchonine salts form white precipitates insoluble in ammonia.

**Cinchonidine, $C_{19}H_{22}N_2O$.**—An alkaloid isomeric with cinchonine; soluble in 75 times its weight of ether. The sulphate, which crystallizes with 3 molecules of water, is official.

**Emetine Hydrochloride** (*Emetinæ Hydrochloridum*), **$C_{30}H_{44}N_2O_4.2HCl$ = 569.31.**—This is a salt of the alkaloid emetine which occurs in ipecac. It contains variable amounts of water of crystallization. It occurs as a white, crystalline powder, freely soluble in water or alcohol, and when exposed to light gradually darkens.

**Strychnine** (*Strychnina*), $C_{21}H_{22}N_2O_2 = 334.20$.—This alkaloid is found, together with brucine, in the seeds and bark of different varieties of Strychnos, and is generally obtained from nux vomica. Strychnine is a white, crystalline powder, having an intensely bitter taste, which is still perceptible in solutions containing 1 in 700,000. It is nearly insoluble in water and in ether, soluble in chloroform and in dilute acids.

Strychnine has strong basic properties and is one of the most powerful poisons known, one-quarter of a grain having caused death within a few hours.

By dissolving it in sulphuric acid or nitric acid the official *strychnine sulphate, strychninæ sulphas*, $(C_{21}H_{22}N_2O_2)_2.H_2SO_4.5H_2O$, or *strychnine nitrate, strychninæ nitras*, $C_{21}H_{22}N_2O_2.HNO_3$, is obtained.

**Analytical Reactions.**—1. Strychnine dissolves in sulphuric acid and nitric acid without color.

2. A fragment of potassium dichromate, drawn through a solution of strychnine in concentrated sulphuric acid, produces momentarily a blue, then brilliant violet color, which slowly passes to cherry red, then to rose pink, and finally to yellow. This reaction may still be noticed with $\frac{1}{50000}$ grain of strychnine (Plate VI).

3. *Sonnenschein's Test.* When to a very small quantity of strychnine, dissolved in a drop of sulphuric acid, some ceroso-ceric oxide is added, and the mixture is stirred with a glass rod, a deep blue color is produced, changing soon to violet, and finally remaining cherry red. One part of strychnine in one million parts of water can thus be recognized. The reagent may be made by heating cerium oxalate to redness and dissolving it in 30 times its weight of sulphuric acid.

4. Solutions of strychnine give with diluted solution of potassium dichromate a yellow, crystalline precipitate, which, when collected, washed, and heated with concentrated sulphuric acid, shows the play of colors described in test 2. A play of colors similar to the above is shown under identical conditions by mixtures of other alkaloids; for instance, by morphine containing 10 per cent. of hydrastine.

5. Neutral solutions of strychnine give yellow precipitates with the chlorides of gold and platinum and with picric acid; a white precipitate with mercuric chloride, potassium hydroxide, and with chlorine-water; a greenish-yellow precipitate with potassium ferro-cyanide.

**Brucine, $C_{23}H_{26}N_2O_4.4H_2O$.**—This alkaloid is found associated with strychnine in various species of Strychnos. It is readily soluble in alcohol, amyl alcohol, and chloroform, but sparingly soluble in cold water and in ether.

**Analytical Reactions.**—1. To 1 c.c. of water add 5 drops of nitric acid and 5 milligrams of brucine; a deep blood-red color results. Heat the liquid until it has assumed a yellow color, then add 9 c.c. of cold water and a few milligrams of sodium thiosulphate (or a small crystal of stannous chloride); a beautiful amethyst or violet color results (Plate VI, 6).

2. Fresh chlorine-water, added drop by drop to a concentrated brucine solution, produces a red color, turning violet, and becoming colorless on addition of an excess of chlorine.

**Veratrine** (*Veratrina*).—This is a mixture of alkaloids obtained from the seed of Asagræa officinalis. It is a white, amorphous, rarely crystalline powder, highly irritating to the nostrils; nearly insoluble in water, readily soluble in alcohol.

**Analytical Reactions.**—1. Concentrated sulphuric acid gives with veratrine first a yellow, then reddish-yellow, intense scarlet, and finally, violet-red color. (Plate VI, 8.) The yellow or orange-red solution exhibits, by reflected light, a greenish fluorescence.

2. Veratrine, when heated with concentrated hydrochloric acid, dissolves with a blood-red color.

3. Bromine-water colors veratrine violet.

4. Veratrine forms with nitric acid a yellow solution.

## The Isoquinoline Group of Alkaloids.

**Opium.**—Opium is the concrete, milky exudation obtained, in the Orient, by incising the unripe capsules of papaver somniferum poppy. Chemically, opium is a mixture of a large number of substances, containing besides glucose, fat, gum, albumin, wax, volatile and coloring matter, meconic acid, etc., not less than sixteen or eighteen different alkaloids, many of which are, however, present in minute quantities.

Ordinary opium should contain not less than 9 per cent., and when dried at 85° C. (185° F.) not less than 12 per cent. nor more than 12.5 per cent. of morphine, to be the official article. Dried and powdered opium, after having been exhausted with purified petroleum benzin, is the *deodorized opium* of the U. S. P.

**Morphine** (*Morphina*), $C_{17}H_{19}NO_3.H_2O$ = **303.18** (*Morphia*).—A white crystalline powder, or colorless, shining, prismatic crystals, odorless, of a bitter taste, and an alkaline reaction to litmus: almost insoluble in ether and chloroform, very slightly soluble in cold water, soluble in 300 parts of cold, and 36 parts of boiling, alcohol; heated for some time at 100° C. (212° F.) it becomes anhydrous; at 254° C. (489° F.) it melts, forming a black liquid.

The following salts are official:

| | | |
|---|---|---|
| Morphine hydrochloride, | Morphinæ hydrochloridum, | $C_{17}H_{19}NO_3.HCl.3H_2O$. |
| Morphine sulphate, | Morphinæ sulphas, | $(C_{17}H_{19}NO_3)_2H_2SO_4.5H_2O$. |

The above two salts are white, and soluble in water.

**Analytical Reactions.**—1. Morphine or a morphine salt sprinkled upon nitric acid assumes an orange-red color, and then produces a reddish solution, gradually changing to yellow. (Plate VI, 1.)

2. Neutral solution of ferric chloride causes a blue color with morphine or with neutral solutions of morphine salts; the color is

changed to green by an excess of the reagent, and is destroyed by free acids or alcohol, but not by alkalies. (Plate VI, 2.)

3. A fragment of iodic acid added to a strong solution of a morphine salt is decomposed, with liberation of iodine, which imparts a violet color to chloroform upon shaking the latter with the mixture.

4. A mixture of 2 parts of morphine and 1 part of cane-sugar added to concentrated sulphuric acid gives a rose-red color.

5. Morphine dissolves in cold, concentrated sulphuric acid, forming a colorless solution, which, after standing for several hours, turns pink or red on the addition of a trace of nitric acid.

6. Aqueous or acid solutions of morphine salts are precipitated by alkaline hydroxides: the precipitated morphine is soluble in potassium or sodium hydroxide, but not in ammonium hydroxide.

7. Neutral solutions of morphine afford yellow precipitates with the chloride of gold or platinum, with potassium chromate or dichromate, and with picric acid, but not with mercuric chloride.

**Diacetylmorphine** (*Diacetylmorphina, Heroin*), $C_{17}H_{17}(C_2H_3O_2)_2NO$.—It is obtained by heating morphine with acetyl chloride. It is a white powder, having a bitter taste, alkaline reaction, and practically insoluble in water, easily soluble in hot alcohol. It readily forms salts with acids, the one usually employed being the official *hydrochloride*, $C_{17}H_{17}(O.C_2H_3O)_2NO.HCl.H_2O$, which is a white powder, of bitter taste, soluble in 2 parts of water and in alcohol. It is precipitated by alkalies, carbonates, and alkaloid reagents.

**Apomorphine, $C_{17}H_{17}NO_2$.**—When morphine is heated for some hours with an excess of hydrochloric acid, under pressure to 150° C. (302° F.), it loses water and is converted into apomorphine, a crystalline alkaloid valuable as an emetic.

*Apomorphine hydrochloride*, $C_{17}H_{17}NO_2.HCl$, which is official, is a grayish-white salt which turns greenish when exposed to light and air.

**Analytical Reactions.**—1. Nitric acid produces a deep purple color fading to orange.

2. Sulphuric acid containing a trace of nitric acid produces a blood-red color fading to orange.

3. Sulphuric acid containing a trace of selenious acid produces a dark blue color, fading to violet, then turning black.

4. Sulphuric acid containing a trace of ferric chloride produces a pale blue color.

**Codeine** (*Codeina*), $C_{18}H_{21}NO_3.H_2O = 317.19$.—A white crystalline powder, sparingly soluble in cold water, easily soluble in alcohol and chloroform. It is neutral to litmus and has a faintly bitter taste. Codeine has been found to be morphine methyl-ether, and is made synthetically by heating morphine with methyl-iodide.

Codeine combines with acids to form salts soluble in water, of which the following are official:

| | | |
|---|---|---|
| Codeine phosphate, | Codeinæ phosphas, | $C_{18}H_{21}NO_3.H_3PO_4.2H_2O$. |
| Codeine sulphate, | Codeinæ sulphas, | $(C_{18}H_{21}NO_3)_2.H_2SO_4.5H_2O$. |

**Analytical Reactions.**—1. On adding to 5 c.c. of an aqueous solution of codeine (1 : 100) 10 drops of bromine-water, shaking so as to redissolve the precipitate formed, and adding after a few minutes some ammonia-water, the liquid assumes a claret-red tint. (Plate VI, 3.)

2. Codeine heated with sulphuric acid containing a drop of nitric acid gives a blood-red color.

3. Codeine, dissolved in sulphuric acid, forms a colorless liquid, which, upon being warmed with a trace of ferric chloride, becomes deep blue.

4. Crystals of codeine sprinkled upon nitric acid assume a red color, but the acid will acquire only a yellow, not a red color. (Difference from morphine.)

5. Sulphuric acid containing a trace of selenious acid gives a green color, changing rapidly to blue, and then slowly back to grass green.

**Ethylmorphine Hydrochloride** (*Æthylmorphinæ Hydrochloridum, Dionin*), $C_{19}H_{23}O_3N.HCl.H_2O$.—This is the hydrochloride of the ethyl ester of morphine, which is similar to codeine, the methyl ester of morphine, and is prepared in the same manner as the latter. It is a white, odorless, slightly bitter powder, soluble in 7 parts of water and 2 parts of alcohol; insoluble in ether and chloroform. It is distinguished from morphine salts by its insolubility in excess of alkali. Some authorities claim that it possesses no advantage over codeine.

**Narcotine,** $C_{22}H_{23}NO_7$, and **Narceine,** $C_{23}H_{27}NO_8.3H_2O$, are white crystalline opium alkaloids, which are almost insoluble in water, soluble in alcohol. Concentrated sulphuric acid forms with narcotine a solution which is at first colorless, but turns yellow in a few minutes, and purple on heating. Narceine dissolves in concentrated sulphuric acid with a gray-brown color, which changes to red when heated.

**Cotarnine Hydrochloride** (*Cotarninæ Hydrochloridum, Stypticin*), $C_{12}H_{13}O_3N.HCl$. —This is a salt of cotarnine, a product of the hydrolysis of narcotine. Cotarnine is obtained by boiling narcotine for a long time with water, or by heating it with dilute nitric acid. The salt is a yellow powder, soluble in water and in alcohol. Its solution gives, with iodine solution, a brown precipitate of cotarnine periodide. It is a hemostatic, analgesic, and uterine sedative.

**Meconic Acid,** $C_7H_4O_7.3H_2O$.—A tribasic acid, characteristic of opium, in which it exists to the extent of 3 or 4 per cent., most likely combined with the alkaloids. It is a white, crystalline substance, soluble in water and alcohol.

Meconic acid forms with ferric chloride a blood-red color, which is not affected by dilute acids or by mercuric chloride (different from ferric sulphocyanate), but disappears on the addition of stannous chloride and of the alkali hypochlorites. This test may be used in cases of poisoning to decide whether opium or morphine is present.

**Hydrastine, Hydrastina,** $C_{21}H_{21}NO_6$ = **383.18.**—Found together with berberine in the rhizome of Hydrastis Canadensis (golden seal) in quantities varying from 0.1 to 0.2 per cent. It can also be made synthetically. Hydrastine crystallizes in four-sided, colorless prisms; it fuses at 131° C. (268° F.), is insoluble

in water and benzin, soluble in about 2 parts of chloroform, 124 parts of ether, and 135 parts of alcohol at the ordinary temperature.

Hydrastine answers to all the general tests for alkaloids; treated with concentrated sulphuric acid it shows a yellow color, turning red, then purple on heating. Concentrated nitric acid produces a yellow color, changing to orange. The fluorescence noticed in solutions of hydrastine or its salts is due to products formed from it by oxidation. While hydrastine itself crystallizes very readily, especially from solutions in acetic ether, its salts can scarcely be obtained in crystals.

**Hydrastine Hydrochloride,** $C_{21}H_{21}NO_6.HCl$, is official. It is a white, odorless, hygroscopic powder, which is very soluble in water and in alcohol, slightly soluble in chloroform, and still less soluble in ether.

**Hydrastinine, $C_{11}H_{11}NO_2$.**—When hydrastine is treated with oxidizing agents it is converted into hydrastinine, the *hydrochloride* of which is official, $C_{11}H_{11}NO_2.HCl$. This salt has a pale yellow color, a bitter, saline taste, and is soluble in 0.3 part of water, and also readily soluble in alcohol, but difficultly soluble in ether or chloroform. A dilute aqueous solution of the salt (up to about 1 in 100,000) has a decided blue fluorescence.

**Berberine, $C_{20}H_{17}NO_4$.**—Found in a number of plants (Berberis vulgaris, Hydrastis Canadensis, etc.) belonging to entirely different families. It is a yellow, crystalline substance, soluble in 7 parts of alcohol, 18 parts of water, insoluble in ether, chloroform, and benzene.

Berberine not only forms well-defined, readily crystallizing salts with acids, but it also enters into combination with a number of other substances, as, for instance, with alcohol, ether, chloroform, etc. Some of these compounds crystallize well, as for instance, berberine-chloroform, $C_{20}H_{17}NO_4.CHCl_3$.

## The Xanthine Alkaloids.

Caffeine and theobromine are xanthine derivatives and are closely connected with uric acid, as shown in chapter 50. They show the properties of alkaloids to a much less degree than the majority of the compounds considered in this chapter; they do not act on red litmus and are but feebly basic.

Theobromine has been obtained from xanthine, $C_5H_4N_4O_2$ (a base found in animal liquids), by treating its lead compound with methyl-iodide, $CH_3I$, when lead iodide and dimethyl-xanthine are formed. By introducing a third methyl group into the molecule of theobromine trimethyl-xanthine, *i. e.*, caffeine or theine is formed. These facts show the close relationship between the active principles of the vegetable substances used so extensively in the preparation of the beverages, coffee, tea, and chocolate. And again, these principles show a relationship to a series of substances (such as xanthine, uric acid, and others) which are found in animal fluids.

**Caffeine** (*Caffeina*), **$C_8H_{10}N_4O_2.H_2O$ or $C_5H(CH_3)_3N_4O_2.H_2O = 212.13$** (*Trimethyl-xanthine, Theine, Guaranine*), occurs in coffee, tea, Paraguay tea, and a few other plants. It forms fleecy masses of long, flexible, silky needles, which are soluble in about 45 parts of water

and in 53 parts of alcohol; it has a slightly bitter taste and a neutral reaction.

Caffeine is dissolved by sulphuric acid without color; when evaporated to dryness with hydrochloric acid and a little potassium chlorate the mass assumes a purple color on holding it over ammonia-water.

Two volumes of a saturated solution of caffeine in water mixed with one volume of mercuric chloride solution form after a short time large crystals of caffeine-mercuric chloride.

*Citrated caffeine* (U. S. P.) is obtained by adding caffeine to a solution of citric acid and evaporating the mixture to dryness.

**Caffeine Sodio-Benzoate** (*Caffeinæ Sodio-Benzoas*).—This is a mixture of caffeine and sodium benzoate, containing when dried to constant weight at 80° C. from 46 to 50 per cent. of anhydrous caffeine. It is a white, slightly bitter powder, soluble in 1.1 parts of water, less soluble in alcohol, practically neutral to litmus.

**Theobromine, $C_7H_8N_4O_2$** (*Dimethyl-xanthine*).—Found in the seeds of Theobroma cacao, a tree growing in the tropics. It is white, crystalline, sparingly soluble in cold water, alcohol, and ether, volatilizes without decomposition at 290° C. (554° F.), has a neutral reaction, but forms with acids well-defined salts.

**Theobromine Sodio-Salicylate** (*Theobrominæ Sodio-Salicylas, Diuretin*), $C_7H_7N_4O_2.Na + C_7H_5O_3.Na$. —This is a double salt of theobromine-sodium and sodium salicylate. It is obtained by dissolving in water molecular proportions of sodium hydroxide, theobromine, and sodium salicylate, and evaporating the solution to dryness. It is a white powder, containing, when dried over sulphuric acid, not less than 46.5 per cent. of theobromine, readily soluble in water, and easily decomposed by exposure to carbon dioxide or by acids. It is incompatible with acids, bicarbonates, borates, phosphates, ferric salts, chloral, etc. Its effects are like those of theobromine, but it has the advantage of greater solubility.

**Theophylline** (*Theophyllina, Dimethyl-xanthine*), $C_7H_8N_4O_2.H_2O = 198.12$.—This is isomeric with theobromine, and occurs in small amounts in tea leaves. It is also made synthetically. Theophylline occurs as a white, odorless, bitter powder, which is permanent in the air. One gram dissolves in 100 c.c. of cold, but much less of hot water, and in 80 c.c. of alcohol. It is sparingly soluble in ether, but readily soluble in solutions of caustic alkalies and in ammonia water.

## Unclassified Alkaloids.

**Physostigmine, $C_{15}H_{21}N_3O_2$** (*Eserine*).—Found in the seeds of Physostigma venenosum (Calabar bean). The pure alkaloid does not crystallize well, is almost tasteless, and assumes gradually a reddish tint. The *salicylate* is official. It is a white or yellowish-white crystalline powder, which has a bitter taste. The salicylate is sparingly soluble in water.

**Analytical Reactions.**—1. Five milligrams of physostigmine dissolved in 2 c.c. of ammonia water yield a yellowish-red liquid which, on evaporation on a water-bath, leaves a blue or bluish-gray residue, soluble in alcohol, forming a blue solution. Upon supersaturation

with acetic acid this becomes violet and exhibits a strong reddish fluorescence. The violet solution leaves on evaporation a residue which is first green and afterward blue. (Plate VI, 7.)

2. Physostigmine or its salts give with calcium oxide and water a red liquid which turns green on heating.

**Aconitine** (*Aconitina*) $C_{34}H_{47}NO_{11}$ = **645.38.**—Found in various species of aconitum to the amount of about 0.2 per cent. It is a white crystalline powder, requiring for solution 3200 parts of water or 22 parts of alcohol.

Aconitine is one of the most poisonous substances known and should never be tasted except in highly diluted solutions, which cause a characteristic tingling sensation when brought in contact with the mucous surfaces of the tongue. A dilute aqueous solution is precipitated by alkalies, tannic acid, mercuric potassium iodide, but only concentrated solutions yield precipitates with platinic chloride, mercuric chloride, and picric acid.

Any soluble salt of aconitine in dilutions of 1 : 1000 produces with a drop of potassium permanganate solution a blood-red precipitate of aconitine permanganate.

**Colchicine** (*Colchicina*), $C_{22}H_{25}NO_6$ = **399.21.**—This alkaloid is obtained from Colchicum. It is a pale yellow, amorphous powder or leaflets, having a very bitter taste. It is soluble in 22 parts of water and very soluble in alcohol and chloroform. It melts at 142° C. (288° F.). Sulphuric acid produces a citron-yellow color, changed to greenish blue, then to red, and finally to yellow by the further addition of nitric acid. Excess of potassium hydroxide changes this to red.

**Ptomaines** (*Putrefactive or Cadaveric Alkaloids*).—It has been known for a long time that vegetable, and more especially animal matter, when in a state of decomposition (putrefaction) acts generally as a poison, both when taken as food or when injected under the skin. Though many attempts had been made to isolate the poisonous products, this was not accomplished successfully until the years 1873 to 1876, by Francesco Selmi, of Italy. He demonstrated that a great number of basic substances can be extracted from putrid matter by treating it successively with ether, chloroform, amyl alcohol, and other solvents. He also showed that these substances resemble vegetable alkaloids in many respects, and assigned to them the name ptomaines, derived from πτῶμα, that which is fallen, *i. e.*, a cadaver.

Although Selmi did not succeed in isolating any of the ptomaines completely (he experimented with extracts only) his investigations stimulated other scientists, and by the united efforts of many workers our knowledge of ptomaines has now advanced so far, that general statements can be given in regard to their origin, composition, physical and chemical properties, action upon the animal system, etc.

**Formation of Ptomaines.**—It has been shown in chapter 41 that albuminous substances under favorable conditions undergo a decom-

position termed putrefaction. Presence of moisture, a suitable temperature, and the action of a ferment are the essential factors in putrefaction. The ferments are living organized beings, termed germs, bacteria, bacilli, microbes, organized ferments, etc.

It is during the growth, development, and multiplication of these microörganisms that the decomposition of the albuminous substances into simpler forms of matter takes place. A full explanation of the exact mode of the formation of decomposition-products from organic matter by the action of bacteria has not been furnished yet, but we do know that ptomaines are found among these products. We also know that certain bacteria split up organic molecules in a certain direction, *i. e.*, with the formation of certain products. We also know that while microörganisms live chiefly in dead organic matter, they also have the power of existing and multiplying in the living organism, causing the decomposition of living tissues, often with the formation of ptomaines.

**General Properties of Ptomaines.**—Ptomaines resemble vegetable alkaloids in all essential properties. Some contain carbon, hydrogen, and nitrogen only, corresponding to the volatile alkaloids, such as coniine and nicotine, while others contain oxygen also, corresponding to the fixed alkaloids.

Ptomaines and alkaloids both have the basic properties and the power to combine with acids to form well-defined salts; they have in common a number of characteristic reactions, such as the formation of precipitates with the chlorides of platinum, mercury, gold, as also with tannic acid, phospho-molybdic acid, picric acid, etc.; and both show corresponding solubility and insolubility in the various solvents generally used for the extraction of alkaloids.

Ptomaines not only possess the general characters of true alkaloids, but even the often highly characteristic color-tests of the latter are in some cases almost identical with those of ptomaines. Thus, ptomaines have been found which resemble in their chemical properties as well as in their physiological action upon the animal system, the alkaloids morphine, atropine, strychnine, coniine, digitaline, etc.

Many attempts have been made to find some characteristic properties by which to differentiate between the putrefactive and the vegetable alkaloids, but practically without results. It is true that most vegetable alkaloids are optically active, while ptomaines are inactive, but it does not often happen that ptomaines are obtained in such quantities as to permit of an exact determination of optical properties.

Under these conditions it is evident that the toxicologist has a most difficult task, when called upon to examine a body (especially when already in a state of decomposition) for alkaloidal poisons. How many times, in former years, chemists may have unjustly claimed the presence of poisonous vegetable alkaloids in material given them for examination, we cannot say, but we do know of a number of cases

of recent date in which such claims were shown to be based upon errors, made in consequence of the close analogy between ptomaines and alkaloids.

While the poisonous properties of some ptomaines are well marked, others are more or less inert. The poisonous ptomaines are now often termed *toxines*, in order to distinguish them from the inert basic products of putrefactive changes.

The toxins are of special interest to the physician, because it is now known that *infectious diseases are caused by the poisonous products formed by the growth, multiplication, and degeneration of microorganisms in the living body.* This statement is of far-reaching importance, as it opens a new field for investigation in connection with the treatment of infectious diseases.

**Non-poisonous Ptomaines.**—A number of these basic substances have been known for a long time. Some of them are also formed by other processes than those of putrefaction, and the term ptomaines may therefore be not well chosen for all of them. However, the close relationship between these substances unites them into a natural group, of which the following members may be mentioned:

*Methylamine*, $NH_2.CH_3$, the simplest organic base that can be formed, has been found in decomposing herring, pike, haddock, poisonous sausage, cultures of comma bacillus on beef-broth, etc. It is an inflammable gas of strong ammoniacal odor.

*Dimethylamine*, $NH(CH_3)_2$, has been found in putrefying gelatin, decomposing yeast, poisonous sausage, etc. It is, like the former, a gas at ordinary temperature.

*Trimethylamine*, $N(CH_3)_3$, has been shown for a long time to occur in some animal and vegetable tissues. Its presence has been demonstrated in leaves of chenopodium, in the blood of calves, in human urine, etc., but it also occurs as a product of putrefaction in yeast, meat, blood, ergot, etc. It is a liquid, possessing a strong, fish-like odor. Boiling-point 9° C. (48° F.).

*Ethylamine*, $NH_2.C_2H_5$; *Diethylamine*, $NH.(C_2H_5)_2$; *Triethylamine*, $N.(C_2H_5)_3$; *Propylamine*, $NH_2.C_3H_7$; *Neuridine*, $C_5N_2H_{14}$, are other non-poisonous volatile ptomaines belonging to the amine group, while of the non-volatile amides may be mentioned: *Mydine*, $C_8H_{11}NO$; *Pyocyanine*, $C_{14}H_{14}NO_2$; *Betaine*, $C_5H_{13}NO_3$, etc.

**Poisonous Ptomaines.**—While no strict line of demarcation can be drawn between poisonous and non-poisonous substances, the following list of ptomaines embraces those which cause serious disturbances when brought into the animal system:

*Isoamylamine*, $C_5H_{13}N$, a colorless, strongly alkaline liquid, has been found in putrefying yeast and in cod-liver oil. It is strongly poisonous, producing rigor, convulsions, and death.

*Cadaverine*, $C_5H_{14}N_2$, occurs very frequently in decomposing animal tissues, and seems to be a constant product of the growth of the comma bacillus, irrespective of the soil on which it is cultivated. It is a syrupy liquid, possessing

an exceedingly unpleasant odor, resembling that of coniine. The substances which have been described by various scientists as "animal coniine" were most likely cadaverine. This base is not very poisonous, but is capable of producing intense inflammation, necrosis, and suppuration in the absence of bacteria.

*Neurine*, $C_5H_{13}NO$, is a base which has been obtained by boiling protagon with baryta, and has been formed by synthetical processes. It also occurs, however, frequently in decomposing meat. It is exceedingly poisonous, even in small doses. Atropine possesses a strong antagonistic action toward neurine, and the injection of even a small quantity is sufficient to dispel the symptoms of poisoning by neurine.

*Choline* (*Trimethyl-oxyethyl-ammonium hydroxide*), $N(CH_3)_3.C_2H_5O.OH$, has been found in animal tissues, in a number of plants (hops, ergot, Indian hemp, white mustard, etc.), and in putrid matters. It is a colorless fluid of oily consistency, has strongly basic properties, and is extremely unstable. By removal of the elements of water choline is converted into the strongly poisonous neurine. On the other hand, choline by oxidation is converted into *muscarine*, a ptomaine even more poisonous than neurine.

*Mytilotoxine*, $C_6H_{15}NO_2$, is the poison found in poisonous mussels. It has a strong paralysis-producing action, resembling curara in that respect.

*Typhotoxine*, $C_7H_{17}NO_2$, is looked upon as the specific toxic product of the activity of Koch-Eberth's typhoid bacillus. The poison throws animals into a paralytic or lethargic condition, so that they lose control over the muscles and fall down helpless. Simultaneously frequent diarrhœic evacuations take place, and death follows in from one to two days.

*Tetanine*, $C_{13}H_{30}N_2O_4$, has been obtained from cultures of tetanus microbes, from the amputated arm of a tetanus patient, and from the brain and nerve tissues of persons who died from tetanus. It produces in animals the symptoms characteristic of tetanus, such as tonic and clonic convulsions. While mice and rabbits are strongly affected by tetanine, dogs and horses seem to be but slightly susceptible to its action.

*Mydatoxine*, $C_6H_{13}NO_2$, has been obtained from human internal organs which were kept for four months at a temperature varying from $-9°$ to $+5°$ C. (16° to 41° F.). It is an alkaline syrup, which does not possess strong toxic properties.

*Tyrotoxicon.* The composition of this highly poisonous ptomaine has not been established yet. It has been found in decomposing milk, in poisonous cheese, ice-cream, and cream-puffs.

*Spasmotoxine.* Composition yet unknown. Obtained from cultures of the tetanus-germ on beef-broth. Produces violent convulsions.

**Leucomaines.**—The basic substances formed in the living tissues by retrograde metamorphosis, during normal life, are known as leucomaines, in contradistinction to the ptomaines, or basic products of putrefaction. To the group of leucomaines belong many substances known long ago, such as creatine, creatinine, xanthine, guanine, and others. Most of these bodies are non-poisonous, but some have been discovered of late, possessing strong poisonous properties. The accumulation of these substances in the body, because of incomplete excretion or oxidation, produces auto-intoxication.

## 54. PROTEINS.

**Occurrence in Nature.**—Proteins form the chief part of the solid and liquid constituents of the animal body; they occur in blood, tissues, muscles, nerves, glands, and all other organs; they are also found in small quantities in nearly every part of plants, and in larger quantities in many seeds. They have never yet been formed by artificial means, but are almost exclusively products of vegetable and animal life.

**General Properties.**—The word protein (formerly proteid) refers to a member of that group of substances which consist, so far as is known at present, essentially of combinations of $\alpha$-amino-acids[1] and their derivatives, *e. g.*, amino-acetic acid or glycocoll; $\alpha$-amino-propionic acid or alanine; phenyl-$\alpha$-amino-propionic acid or phenyl-alanine; guanidine-amino-valeric acid or arginine, etc., and are therefore essentially polypeptides. The various proteins resemble one another closely in their properties. Their composition is so complex that, as yet, no chemical formula has been assigned to them with any certainty; they all contain carbon, hydrogen, oxygen, and nitrogen; most contain sulphur, several phosphorus, and some iron. Various other metallic and non-metallic elements have been found in certain proteins.

Nearly all proteins are amorphous, non-diffusible, colorless, odorless, nearly tasteless, and non-volatile. When heated under such conditions that the volatile products formed are not burnt at all, or only partially, a disagreeable odor is noticed, due chiefly to ammonia derivatives. Proteins vary in solubility; all are optically active, most of them being lævorotatory, while hæmoglobin and the nucleo-proteins are dextrorotatory. Proteins are distinguished by the ease with which they undergo chemical change under the influence of

[1] Greek letters are, in some cases, used to indicate the position of substituting groups in a molecule. In organic acids, the carbon atom next to the carboxyl group (COOH) is designated by $\alpha$, the next one by $\beta$, the next one by $\gamma$, etc. Thus, lactic acid is $\alpha$-hydroxy-proprionic acid, $CH_3CHOH.COOH$; alanine is $\alpha$-amino-propionic acid, $CH_3.CHNH_2.COOH$; glycocoll is $\alpha$-amino-acetic acid, $CH_2NH_2.COOH$; hydracrylic acid is $\beta$-hydroxy-propionic acid, $CH_2OH.CH_2COOH$.

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QUESTIONS.—State the general physical and chemical properties of alkaloids. Give a general method for the extraction and separation of alkaloids from vegetables. Mention the chief constituents of opium. Mention the properties of morphine and its salts; give tests for them. Mention the principal alkaloids found in cinchona bark. State the physical and chemical properties of quinine and cinchonine. Which of their salts are official, and by what tests may these alkaloids be recognized and distinguished from each other? Give tests for strychnine, brucine, atropine, and veratrine. What is the chemical relationship between xanthine, caffeine, and theobromine? Mention properties of, and give tests for, cocaine. Mention the characteristic physical, chemical, and physiological properties of ptomaines.

reagents, ferments, or variations in temperature; they all undergo the process of putrefaction, which has been considered in chapter 41.

By boiling with dilute acids or alkalies, and also by the action of certain enzymes, the proteins undergo hydrolytic cleavage, forming many simpler compounds. (The terms hydrolytic cleavage and hydrolysis refer to a splitting up of complex molecules, while water or its constituents are taken up at the same time.)

**Classification.**—The classification here used is the one which has been adopted by the American Society of Biological Chemists and the American Physiological Society, and is as follows:

I. Simple Proteins.—a, *Albumins;* b, *Globulins;* c, *Glutelins;* d, *Prolamines,* or *Alcohol-soluble proteins;* e, *Albuminoids;* f, *Histones;* g, *Protamines.*

II. Conjugated Proteins.—a, *Nucleoproteins;* b, *Glycoproteins;* c, *Phosphoproteins;* d, *Hæmoglobins;* e, *Lecithoproteins.*

III. Derived Proteins:

1. Primary protein derivatives: a, *Proteans;* b, *Metaproteins;* c, *Coagulated proteins.* 2. Secondary protein derivatives: a, *Proteoses;* b, *Peptones;* c, *Peptides.*

## I. Simple Proteins.

These are protein substances which yield only $\alpha$-amino-acids or their derivatives by hydrolysis.

The simple proteins occur in all animal and vegetable organisms. In the animal body they are the most prominent solid constituents of the muscles, glands, and blood-serum, and are found to a greater or less extent in all tissues, secretions, and excretions. The percentage composition of simple proteins is as follows:

| | |
|---|---|
| Carbon | 50.0 to 55.0 per cent. |
| Hydrogen | 6.5 " 7.3 " |
| Nitrogen | 15.0 " 18 0 " |
| Oxygen | 21.0 " 24.0 " |
| Sulphur | 0.3 " 2.5 " |

A few simple proteins contain phosphorus to the extent of 0.42–0.85 per cent., and a few contain also a trace of iron.

The nitrogen of proteins is split off in four forms, viz., as ammonia, as diamino-acids, as monamino-acids, and as a guanidine residue. Part of the nitrogen is easily split off as ammonia by the action of alkalies.

By boiling proteins with alkalies, part of the sulphur is split off as sulphide, while the remainder can be obtained as sulphate, after fusing the residue with potassium nitrate and sodium carbonate. As about one-half of the total sulphur present is obtained by each operation, it is assumed that there are at least two atoms of sulphur in the protein molecule.

When acted upon by enzymes or other hydrolytic agents, the

simple proteins form first proteins of lower molecular weight, which are diffusible and not coagulated by heat. By the prolonged action of certain ferments (trypsin, bacteria, etc.), or by long boiling with acids, they give rise to the formation of amino-acids (tyrosine, leucine, aspartic, and glutamic acids), of the hexone bases (lysine, arginine, histidine), and a number of undefined bodies.

In solubility the simple proteins vary; some are soluble in water, others only in water containing either acids, alkalies, or certain neutral salts, while yet others are insoluble. The soluble proteins are converted into insoluble modifications by the action of heat or certain reagents. This change is called coagulation, and is distinguished from precipitation by the fact that proteins when once coagulated cannot return to their original condition. The temperature at which coagulation takes place depends on the nature of the protein present, the reaction of the solution, and the presence of neutral salts.

An alkaline solution of a protein will not coagulate on boiling; a neutral solution will do so partially; a solution showing an acid reaction will be coagulated completely on boiling, provided the quantity of neutral salt present be not too small, and the protein solution not too dilute.

### Tests for Simple Proteins.

*a.* Coagulation or precipitation tests.

(Use a solution made by dissolving 1 part of white of egg in about 10 parts of a 2 per cent. sodium chloride solution.)

1. *Heat test.* To 5 c.c. of protein solution add a few drops of dilute acetic acid, and heat. The protein is completely coagulated.

2. *Heller's test.* Place 1 c.c. of nitric acid in a test-tube, and allow a few cubic centimeters of protein solution to flow down the side of the tube, taking care that the liquids do not mix. A white, opaque ring of coagulated protein forms at the line of junction. (Strong sulphuric, hydrochloric, and metaphosphoric acids coagulate proteins in the same way.)

3. To 5 c.c. of protein solution add solution of cupric sulphate; repeat with solutions of mercuric chloride, lead acetate, and silver nitrate. In all cases coagulation takes place. (These reactions explain the use of proteins, such as the white of egg, as antidotes in cases of poisoning by metallic compounds.)

4. To 5 c.c. of protein solution add a few drops of acetic acid and some potassium ferrocyanide solution; coagulation takes place.

5. Saturate 10 c.c. of protein solution with ammonium sulphate; all proteins are precipitated except peptones.

6. Solutions of picric, trichloracetic, phosphotungstic, phosphomolybdic, tannic, taurocholic, and nucleic acids, potassium mercuric iodide, alcohol, all precipitate proteins under special conditions.

*b.* Color tests.

(Use any dry protein.)

1. *Xanthoproteic reaction.* Heat a small quantity of protein with concentrated nitric acid; the protein, or the solution, turns yellow. Allow it to cool, and add an excess of ammonia: the color changes to orange.

This reaction is due to the presence of the tyrosine and the tryptophane radicals in the protein molecule.

2. *Millon's reaction.* Pour a few cubic centimeters of water on a small quantity of protein; add 1 c.c. of Millon's reagent, and boil: a purple-red color develops. (Millon's reagent is made by dissolving 10 grams of mercury in the same weight of pure nitric acid, and adding to the cool solution 2 volumes of water.) This reaction is given by tyrosine.

3. *Biuret reaction.* Boil a small quantity of protein with 5 c.c. of solution of sodium hydroxide, and after cooling add one or two drops of dilute solution of cupric sulphate: a violet to pink color is obtained, according to the amount of copper-solution and the nature of the protein. (It may be necessary to heat the solution before a distinct color appears.)

This reaction is given by biuret, hence its name.

(*a*) **Albumins.**—These substances are soluble in water and are precipitated from their aqueous solution by large quantities of mineral acids and by saturation of their solution with ammonium sulphate. In a solution containing 1 per cent. of neutral salt they are coagulated between 60° and 75° C. (140° and 167° F.).

They include ovalbumin (white of egg); serum-albumin of blood-serum and serous fluids; lactalbumin of milk; and vegetable albumins.

(*b*) **Globulins.**—These compounds are insoluble in water, but dissolve in water containing from 0.5 to 1 per cent. of some neutral salt. The solution coagulates on heating, is precipitated by saturation with magnesium sulphate or sodium chloride, and by the addition of an equal volume of saturated solution of ammonium sulphate. Globulins are precipitated if the salt be removed from their solution by dialysis.

Serum- or para-globulin of blood, lacto-globulin of milk, and fibrinogen are globulins.

(*c*) **Glutelins.**—Glutelins are simple proteins insoluble in all neutral solvents, but readily soluble in very dilute acids and alkalies. They occur in abundance in the seeds of cereals.

(*d*) **Prolamines or Alcohol-soluble Proteins.**—These are soluble in 70 to 80 per cent. alcohol, and in dilute acids and alkalies, but insoluble in water, absolute alcohol, and other neutral solvents. Similar to glutelins, they are found chiefly in the vegetable kingdom. For instance, *zein* is found in maize, *gliadin* in wheat, *hordein* in barley, etc.

(*e*) **Albuminoids.**—Simple proteins which possess essentially the same chemical structure as the other proteins, but are characterized by great insolubility in all neutral solvents. They occur chiefly as constituents of the skeleton, of the skin and its appendages, and exist, as a rule, in an insoluble condition. To the albuminoids belong: Keratins, elastin, collagen, and a few other substances.

*Keratins* occur as the principal constituents of the horny portion of the skin and its appendages. A special keratin, neurokeratin is found in the nervous system. The keratins contain proportionately more sulphur than other proteins, part of it in very loose combination. The darkening of the hair by the use of a lead comb, forming black lead sulphide, is due to the action of this sulphur. The products of deep cleavage of the keratins are the same as those of the proteins, but with relatively greater quantities of the sulphurized products, mainly in the form of cystine.

Keratins dissolve slowly in cold caustic alkalies, more rapidly on heating. They are insoluble in water, alcohol, ether, and in gastric and pancreatic juices. They give the xanthoproteic, biuret, and Millon's reactions.

*Elastin* occurs in the connective tissue, particularly in yellow elastic fiber; it contains very little sulphur (less than 0.5 per cent.), and yields on deep cleavage the same products as simple proteins, giving, however, glycocoll, little glutamic acid, and no aspartic acid.

Elastin is insoluble in water and in cold solutions of caustic alkalies; it dissolves slowly in alkalies on boiling and in cold sulphuric acid; it is easily dissolved by warm nitric acid, as also by the action of proteolytic enzymes. It shows the same color-reactions as the keratins.

*Collagen* occurs in the fiber of connective tissue. *Ossein*, the chief organic constituent of bone, is a collagen; and *chondrin*, a constituent of cartilage, is collagen mixed with a small quantity of other material.

On boiling with water (more readily with acidified water) collagen is converted into gelatin, while the latter, when heated to 130° C. (266° F.), is converted into collagen. (Collagen may therefore be considered an anhydride of gelatin.)

Gelatin yields no tryptophane, no tyrosine, and contains a rather small percentage of sulphur.

(*f*) **Histones.**—Soluble in water and insoluble in very dilute ammonia, and, in the absence of ammonium salts, insoluble even in an excess of ammonia; yield precipitates with solutions of other proteins. On hydrolysis they yield a large number of amino-acids, among which the basic ones predominate, such as arginine and histidine, while others of them are absent (cystine, tyrosine).

(*g*) **Protamines.**—Simpler polypeptides than the proteins included in the preceding groups. They are soluble in water, uncoagulable by heat, have the property of precipitating aqueous solutions of other

proteins, possess strong basic properties, and form stable salts with strong mineral acids. They are the simplest natural proteins.

## II. Conjugated Proteins.

Substances which contain the protein molecule united to some other molecule or molecules otherwise than as a salt.

(*a*) **Nucleoproteins.**—These are compounds of one or more protein molecules with nucleic acid. They occur chiefly in the cell nuclei, but are found also in the protoplasm. Nucleoproteins yield, on digestion with pepsin, a simple protein, usually a histone or a protamine, and nuclein. Nuclein is generally but not always resistant to peptic digestion. On treatment with caustic alkali it is split into protein and nucleic acid, which is the important portion of the nucleoproteins. This nucleic acid consists of a carbohydrate group linking together nitrogenous bases and phosphoric acid. As there are many different nucleic acids these constituent groups vary within certain limits. The carbohydrates may be pentose or hexose. The nitrogenous bases may be one or more purine bodies (guanine, adenine, etc.), or pyrimidine derivatives (thymine, cytosine, uracil). The phosphoric acid is said to be metaphosphoric acid. The purine bodies in nucleins are the origin of the uric acid of human urine.

The nucleoproteins give all the color reactions, are soluble in water containing a small quantity of alkali, and are precipitated from this solution by acetic acid. They are dextro-rotatory.

(*b*) **Glycoproteins.**—Compounds of the protein molecule, with a substance or substances containing a carbohydrate group other than a nucleic acid. This carbohydrate group is capable of reducing cupric oxide.

(*c*) **Phosphoprotein.**—Compounds of the protein molecule with some, as yet undefined, phosphorus-containing substance other than a nucleic acid or lecithin. *Caseinogen*, the principal protein constituent of milk belongs to this group.

(*d*) **Hæmoglobins.**—Compounds of the protein molecule, with hæmatin or some similar substance. Hæmoglobins form the coloring-matters of the blood. On hydrolysis they yield a simple protein and a substance called hæmochromogen, which contains iron and is readily oxidized to hæmatin.

(*e*) **Lecithoproteins.**—Compounds of the protein molecule with lecithins. (See Index for Lecithins.)

## III. Derived Proteins.

These substances are derivatives of proteins, and are obtained from them by hydrolytic changes of various kinds, *e. g.*, through the action of acids, alkalies, heat, or enzymes.

**1. Primary Protein Derivatives.**—Derivatives of the protein molecule apparently formed through hydrolytic changes which involve only slight alterations of the protein molecule.

(*a*) **Proteans.**—Insoluble products which apparently result from the incipient action of water, very dilute acids, or enzymes on proteins originally soluble.

(*b*) **Metaproteins.**—Products of the further action of acids and alkalies, whereby the molecule is so far altered as to form products soluble in very weak acids and alkalies, but insoluble in neutral fluids. The two principal metaproteins are the alkali metaprotein or alkali albuminate and the acid metaprotein or acid albuminate.

*Alkali metaprotein* is formed when native proteins are acted upon by alkalies to such an extent that part of the nitrogen, and occasionally sulphur also, is eliminated from the molecule. The change takes place slowly at the ordinary temperature, more rapidly on heating.

*Acid metaprotein* is obtained by digesting a native protein with dilute acid.

(*c*) **Coagulated Proteins.**—Insoluble products, which result from the action of heat on their solutions, or from the action of alcohols on the protein. The nature of the process of coagulation is unknown; the result is the formation of protein substances insoluble without decomposition. In the liver and other glands coagulated proteins have been found. Hard-boiled white of egg and fibrin are coagulated proteins.

**2. Secondary Protein Derivatives.**—Products of the further hydrolytic cleavage of the protein molecule by acids, alkalies, superheated steam, or enzymes.

(*a*) **Proteoses.**—Soluble in water, uncoagulated by heat, and precipitated by saturating their solutions with ammonium sulphate or zinc sulphate.

(*b*) **Peptones.**—Soluble in water, uncoagulated by heat, and not precipitated by saturating their solutions with ammonium sulphate. They are the result of the digestion of proteins; their solutions in water are readily diffusible. The peptones are divided into antipeptones, hemi-peptones, and ampho-peptones. Here again the properties of the different classes are not definite.

The proteoses and peptones give a biuret reaction showing more red color than the natural proteins.

(*c*) **Peptides.**—Definitely characterized combinations of two or more amino-acids, the carboxyl group of one being united with the amino group of the other with the elimination of a molecule of water. The peptones are peptides or mixtures of peptides, the latter term being at present used to designate those of definite structure, such as polypeptides, dipeptides, etc.

## Products of Proteolysis.

Proteolysis is the change affected in proteins during their digestion, and is brought about by the action of bodies termed proteolytic agents, or enzymes. The products formed vary in quantity and composition with the nature of the proteins and enzymes, and depend also on the condition under which the changes take place. While the compounds grouped together as proteins differ widely in their properties, yet the end-products of any proteolysis will consist of a few *amino-acids* and *nitrogenous bases*. This would indicate that there exists a close relation between the different proteins, the difference being due more to the atomic arrangement within the molecule than to the quality and quantity of the elements present in protein molecules.

These decomposition products of proteins are:

(1) **Monamino-acids:**

Glycocoll (amino-acetic acid), $CH_2.NH_2.CO_2H$.
Alanine (amino-propionic acid), $C_2H_4.NH_2.CO_2H$.
Valine (amino-iso-valeric acid), $C_4H_8.NH_2.CO_2H$.
Aspartic acid (amino-succinic acid), $C_2H_3.NH_2.(CO_2H)_2$.
Glutamic acid (amino-pyrotartaric acid), $C_3H_5.NH_2.(CO_2H)_2$.
Phenylalanine (phenyl-amino-propionic acid), $C_6H_5.C_2H_3.NH_2\ CO_2H$.
Iso-leucine (amino-methyl-ethyl-propionic acid), $C_6H_{10}\ NH_2.CO_2H$.
Leucine (amino-caproic acid), $C_5H_{10}.NH_2.CO_2H$.
Serine (amino-oxypropionic acid), $C_2H_3(OH).NH_2.CO_2H$.
Proline (pyrrolidine-carboxylic acid), $C_4H_7.NH.CO_2H$.
Oxyproline (oxypyrrolidine-carboxylic acid), $C_4H_7O.NH.CO_2H$.
Tryptophane (indol-amino-propionic acid), $C_{11}.H_{12}N_2O_2$.
Cystine (disulphide of amino-thio-propionic acid (cysteine), $(C_2H_3S.NH_2.CO_2H)_2$.
Tyrosine (oxyphenyl-amino-propionic acid), $C_8H_8O.NH_2.CO_2H$.

(2) **Diamino-acids (hexone bases):**

Arginine (guanidine-amino-valeric acid), $C_6H_{14}N_4O_2$.
Histidine (amino-imidazol-propionic acid), $C_6H_9N_3O_2$.
Lysine (diamino-caproic acid), $C_6H_{14}N_2O_2$.

An enormous amount of work is being done in the attempt to solve the protein molecule by studying these substances (proteoses, peptones, peptides, amino-acids) obtained by proteolysis. They are successively simpler, more soluble, and more diffusible as the proteolysis proceeds. The constitution of many of these simpler decomposition products has now been well substantiated (amino-acids). It has been found possible to make a beginning in the synthesis of protein by forming combinations of amino-acids, linking the carboxyl group of one to the amino group of another, with the elimination of a molecule of water. This procedure can be repeated, and substances have been formed containing thirty-six or more amino-acid molecules. These substances are apparently entirely analogous to the peptides derived

from the proteins, as some of them give a biuret test, are acted upon by proteolytic enzymes (erepsin), and have other common properties. It is probable, therefore, that this grouping is one of the many forms of combination that must be present in the protein molecule. While all of these amino-acids have been found in protein, they are not necessarily all present in any one protein, and in different proteins they are present in markedly different proportions. Experimental work is beginning only now to show the significance of these differences in the proteins. The molecular weights of the proteins cannot be determined by any known methods, and the actual structural constitution is entirely unknown.

As leucine and tyrosine are readily isolated their more important properties are stated here.

**Tyrosine,** $C_6H_4.OH.C_2H_3(NH_2)CO_2H$ (*Para-oxyphenyl-amino-propionic Acid*).—This is obtained from all proteins, except collagen and reticulin, by trypsin digestion, by prolonged boiling with dilute acids or alkalies, by fusion with alkaline hydroxides, and by putrefaction. Tyrosine is generally found with leucine; both these substances have nearly the same physiological properties and pathological significance. They occur in the intestine during the digestion of proteins, and, pathologically, they are found in atheromatous cysts, in pus, in abscess and gangrene of the lung, in the urine during yellow atrophy of the liver, and in phosphorus poisoning.

Tyrosine crystallizes in colorless, fine, silky needles, often tufted. It is very slightly soluble in water, more so in the presence of alkalies and mineral acids, insoluble in alcohol and ether.

**Leucine,** $C_5H_{10}.NH_2.CO_2H$ (*Amino-caproic Acid*).—This is a constant product of the cleavage of proteins. It is easily soluble in hot water, less so in cold water, soluble in alcohol, insoluble in ether. It is easily soluble in acids and alkalies, forming crystalline compounds with mineral acids. When impure, leucine crystallizes in rounded lumps which often show radiating striations. When pure it forms white, glittering, flat crystals.

## Enzymes (Ferments).

Enzymes, as mentioned in chapter 41, are substances that decompose others without themselves undergoing permanent change, *i. e.*, they are catalysts. The activity of all enzymes is impeded by accumulation of the products of the fermentation. The activity of enzymes is controlled by the temperature and character of the solution in which they act. There is a certain temperature at which every enzyme is most active—the "optimum" temperature. A higher temperature first impairs, and then destroys its activity. All enzymes are destroyed by heating to 100° C. (212° F.) with water. Cooling impairs their activity; but even after freezing they regain their power when carefully brought to the proper temperature. Some act best in neutral, others in either acid or alkaline, solution of certain concentration. The action of enzymes is in many cases reversible. Thus, ethyl butyrate is split by lipase into ethyl alcohol and butyric acid; and under certain conditions lipase will produce the opposite

effect and cause the combination of alcohol and butyric acid with the formation of ethyl butyrate.

As it has been shown that living "organized ferments" owe their activity to the enzymes which they secrete, there is less stress laid now upon the distinction between organized and unorganized ferments, and the term ferment is reserved mainly for yeast.

The chemical composition of the enzymes is not known. As yet, no enzyme has been prepared in the pure state; they may be extracted from the cells by means of water and glycerin. The solution in glycerin is very stable. When in solution they are easily obtained by precipitation of some other substance from the same solution, the enzyme being carried down with the precipitate. The activity of their solution is generally destroyed by heating to 80° C. (176° F.).

The quantitative estimation of enzymes is based on the amount of decomposition-products formed, or the amount of material decomposed in a given time and under certain conditions.

Enzymes occur widely distributed in animal and vegetable organisms, and possess great diversity of function. At present, enzymes are classified according to the nature of the changes they produce; the more prominent groups are:

*Amylases* or *amylolytic enzymes*, converting starches into simple sugars: ptyalin, amylopsin, malt, diastase.

*Proteases* or *proteolytic enzymes*, converting proteins into peptone or simpler compounds: pepsin, trypsin.

*Steatases* or *steatolytic enzymes*, splitting fats: steapsin.

*Invertases* or *inverting enzymes*, splitting sugar: invertin.

*Coagulases* or *coagulating enzymes*, converting soluble proteins into insoluble forms: rennin.

*Oxidases* or *oxidizing enzymes*. Oxidases produce oxidation in the presence of oxygen, peroxidases (catalases), only in the presence of a peroxide. Oxygenases are theoretical enzymes, capable of first combining with oxygen and then transferring it to some other substance.

Of *glucoside-splitting enzymes* has been mentioned in chapter 51, *emulsin* or *synaptase*, which decomposes amygdalin, while *myrosin* acts on sinigrin found in mustard seed.

Not infrequently the enzymes of the body are secreted in an inactive state, and are then spoken of as *zymogens* or *pro-enzymes*. These zymogens become active in the presence of certain supplementary substances. These substances are called *kinases* if of organic nature, and *activators* if of inorganic nature. Thus, enterokinase is the kinase of trypsinogen, converting it into trypsin, while hydrochloric acid is the activator of pepsinogen, converting it into pepsin.

The following three enzymes are mentioned here because they furnish official preparations.

**Pepsin.**—Pepsin is one of the active principles of gastric juice,

capable of converting albumin, in the presence of hydrochloric acid into soluble peptones. While pure pepsin is not known, a number of preparations containing more or less of this ferment are sold as pepsin. They are obtained by different processes of extraction from the glandular layer of fresh stomachs from healthy pigs.

*Pepsin*, U. S. P., should be either a fine, white, or yellowish-white, amorphous powder, or consist of thin, pale yellow or yellowish, transparent or translucent grains, scales or spongy masses, free from offensive odor. It should be capable of digesting not less than 3000 times its own weight of freshly coagulated and disintegrated egg albumin. One part of pepsin dissolves in 50 parts of water to a more or less opalescent solution. It is practically insoluble in alcohol, chloroform or ether. In solution pepsin is incompatible with alkalies, alkaline earths, or alkali carbonates. It is inactive in a solution of hydrochloric acid of more than 0.5 per cent. In a dry state pepsin is not injured in a temperature of 100° C. but in solution its activity is destroyed above 70° C. Details of the assay of pepsin are given in the U. S. Pharmacopœia.

**Pancreatin**, U. S. P.—This preparation is a mixture of the enzymes existing in the pancreas of warm-blooded animals, and is usually obtained from the fresh pancreas of the hog. It consists principally of amylopsin, trypsin, and steapsin. It is a yellowish or grayish, almost odorless powder, soluble in water to the extent of 90 per cent., insoluble in alcohol. It has the power to digest proteins, and should convert not less than twenty-five times its own weight of starch into sugar. Pancreatin acts best in neutral or faintly alkaline media, being rendered inert by more than traces of mineral acids, or large amounts of alkali hydroxides. Excess of alkali carbonates inhibits its activity. Details of the assay of pancreatin are given in the U. S. Pharmacopœia.

**Diastase**, U. S. P.—This is a mixture containing amylolytic enzymes obtained from an infusion of malt. It should convert not less than 50 times its weight of potato starch into sugars. It occurs as a yellowish-white powder or in translucent scales, and is odorless and tasteless. It converts starch into dextrin and maltose, but gradually loses this power on keeping or quickly by heating its solution above 85° C., or by the addition of much acid. It is practically insoluble in alcohol, its aqueous solution is more or less turbid. Details of the assay of diastase are given in the U. S. Pharmacopœia.

**Saliva, Ptyalin.**—Saliva is the mixed secretion of the parotid, submaxillary, sublingual, and buccal glands. The quantity secreted in a day varies from 600 to 1500 c.c. The flow is easily excited by reflex stimulation, as by the smell or sight of food, or by chewing of some insoluble substances. Saliva appears as a viscid, frothy, tasteless, inodorous liquid, of a sp. gr. of 1.002 to 1.008. The reaction to litmus is generally slightly alkaline, but may become acid under pathological conditions. Saliva as it appears in the mouth contains food particles

and numerous microörganisms. The average composition of saliva is as follows:

| | |
|---|---|
| Water | 99.49 |
| Mucin and epithelium | 0.13 |
| Fatty matter | 0.11 |
| Ptyalin, maltase, and other organic matter | 0.12 |
| Salts | 0.15 |

The salts are alkali and earthy phosphates, carbonates and chlorides, and potassium sulphocyanate. The latter occurs in variable quantity in the saliva of different individuals. Pathologically, saliva may contain sugar in diabetes, melanin in Addison's disease, bile-pigment in icterus. Leucine and urea have been found in saliva during uremia. The iodides and some other drugs are habitually secreted by the salivary glands. This function is used in measuring the rapidity of absorption.

*Ptyalin*, the diastatic enzyme, occurs in the saliva of all animals except the pure carnivora. It is characterized by its action in converting starch into sugar. It acts best at 40° C. (104° F.), in a neutral solution, although it is active in a weak alkaline solution, and [illegible] in acid solution up to 0.2 per cent. of mineral acid.

The conversion of starch into sugar by ptyalin is a progressive hydrolysis. The first change is the formation of soluble starch, which gives a blue color with iodine. Soluble starch is s[illegible] to maltodextrin and erythrodextrin; the latter gives a red color with iodine. [illegible] liter[illegible]extrins are next split and yield maltose, maltodextrin, and achroödextr[illegible] are not colored by iodine. From achroödextrin more maltodextrin and [illegible]ose are derived, and finally the hydrolysis results in the formation of maltose with some maltodextrin. The maltose is converted into glucose by the action of the enzyme maltase.

*Experiment* 72.—Mix intimately 1 gram of starch with 10 c.c. of water, pour this mixture into 90 c.c. of boiling water and stir until a smooth paste is formed. Place 10 c.c. of paste in a test-tube, heat to 40° C. (104° F.), add 1 c.c. of saliva and 1 c.c. of 1 per cent. solution of sodium carbonate, mix well, and keep at the stated temperature. At the expiration of one minute take out a drop of the mixture, place it on a white plate, and add a drop of dilute iodine solution. The mixture will turn blue. Repeat testing the mixture, which is to be kept at the same temperature, every minute until iodine has no longer any effect on the solution, indicating the conversion of all starch into simple sugars. With normal saliva the color reaction will cease within six minutes; a longer time would indicate an insufficient quantity of ptyalin in the saliva used for the experiment.

When the solution no longer is affected by iodine add to 1 c.c. of solution 6 c.c. of alcohol: a precipitate of dextrin is formed. Allow the digestion to proceed for half an hour, then heat some of the digested mixture with Fehling's solution: the formation of red cuprous oxide shows the conversion of starch into glucose.

*Action of acids and alkalies on salivary digestion.* In each of three test-tubes, A, B, and C, place 5 c.c. of starch paste, prepared as above, and 1 c.c. of saliva.

To A add 3 c.c. of 0.25 per cent. hydrochloric acid; to B add 3 c.c. of 1 per cent.. sodium carbonate. Keep the tubes at 40° C., and note the time required for the disappearance of the iodine color reaction with the contents of each tube. The reaction will disappear first in B, then in C, and finally in A.

In order to obtain saliva for experimental purposes a small glass rod or a piece of rubber should be placed in the mouth. This will stimulate the flow of saliva, which is to be collected and filtered.

**General Tests for Mixed Saliva.**—1. Allow a few c.c. of saliva to stand a day or two: a cloudiness will be observed, due to the precipitation of calcium carbonate, which has been held in solution by carbon dioxide.

2. Acidify saliva with acetic acid: a precipitate of mucin is formed insoluble in an excess of the acid.

3. Apply the xanthoproteic, Millon's, and biuret reactions for proteins (see page 603).

4. Acidify with acetic acid and add ferric chloride: a red color, due to the formation of ferric sulphocyanide, is produced.

**Dried Thyroids** (*Thyroideum Siccum*).—The thyroid gland is a very vascular organ situated in front and on either side of the upper windpipe. Numerous extracts of the thyroid are upon the market. The preparation of the Pharmacopœia is the cleaned, dried, and powdered glands of the sheep, freed from fat. It is a yellowish amorphous powder, partially soluble in water.

*Thyreoidectin* and *rodagen* are unofficial preparations prepared respectively from the blood and from the milk of animals from which the thyroids have been removed. Their action is stated to be exactly the opposite of that of the thyroid preparations

The thyroid gland, and also [illegible], have some influence on sugar metabolism, which is not yet understo[illegible] The thyroid gland contains iodine in some form of protein combination, known as *thyro-iodine;* this compound contains 9.3 per cent. of iodine. Its administration in cases of dwarfism and idiocy, and myxœdema is attended with remarkable improvement.

**Dried Suprarenals** (*Suprarenalum Siccum*).—These are the cleaned, dried, and powdered suprarenal glands of the sheep or ox, freed from fat. A light yellowish, amorphous powder, partially soluble in water. The suprarenal glands contain a substance which has the power of constricting the bloodvessels of the body, and thus causing a great but transient rise in blood-pressure. This substance has been found to be methylamino-ethanol-dioxy-benzene, $C_6H_3(OH)_2.CH(OH).CH_2.NH.CH_3$. It is used particularly to produce local anemia, and is called by various names: suprarenalin, suprarenin, adrenalin, epinephrin.

The dried gland is used very little in medicine, having been supplanted almost entirely by adrenalin chloride.

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QUESTIONS.—To which class of substances is the term protein applied, and which elements enter into their composition? How are proteins classified, and how do these groups differ from each other? Describe three color-reactions of proteins. Mention the conditions necessary for the coagulation of a protein solution by heat; and state how coagulation differs from precipitation. Describe the products of proteolysis. Describe the nucleoproteins. Give a full description of the nature and action of enzymes. State the composition and properties of tyrosine and leucine. Mention three enzymes that are official; state their sources and their function in the process of digestion.

# APPENDIX.

## TABLE OF WEIGHTS AND MEASURES.

*Measures of length.*

| | | | | | |
|---|---|---|---|---|---|
| 1 millimeter | = | 0.001 | meter | = | 0.03937 inch. |
| 1 centimeter | = | 0.01 | meter | = | 0.3937 inch. |
| 1 decimeter | = | 0.1 | meter | = | 3.937 inches. |
| 1 meter | | | | = | 39.37 inches. |
| 1 decameter | = | 10 | meters | = | 32.8083 feet. |
| 1 hectometer | = | 100 | meters | = | 328.083 feet. |
| 1 kilometer | = | 1000 | meters | = | 0.62137 mile. |
| 1 yard or 36 inches | | | | = | 0.9144 meter. |
| 1 inch | | | | = | 25.4 millimeters. |

*Measures of capacity.*

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 milliliter | = | 1 c.c. | = | 0.001 | liter | = 0.0021 U. S. pint. |
| 1 centiliter | = | 10 c.c. | = | 0.01 | liter | = 0.0211 U. S. pint. |
| 1 deciliter | = | 100 c.c. | = | 0.1 | liter | = 0.2113 U. S pint. |
| 1 liter | = | 1000 c.c. | | | | = 1.0567 U. S. quart. |
| 1 decaliter | | | = | 10 | liters | = 2.6417 U. S. gallons. |
| 1 hectoliter | | | = | 100 | liters | = 26.417 U. S. gallons. |
| 1 kiloliter | | | = | 1000 | liters | = 264.17 U. S. gallons. |
| 1 U S gallon | | | | | | = 3785.43 c.c. |
| 1 imperial gallon | | | | | | = 4543.5 c.c. |
| 1 minim | | | | | | = 0.06 c.c. |
| 1 fluidrachm | | | | | | = 3.70 c.c. |
| 1 fluidounce | | | | | | = 29.57 c.c. |
| 1 liter | | | | | | = 33.81 fluidounces. |

*Weights.*

| | | | | | |
|---|---|---|---|---|---|
| 1 milligram | = | 0 001 | gramme | = | 0.015 grain |
| 1 centigram | = | 0 01 | gramme | = | 0 154 grain |
| 1 decigram | = | 0 1 | gramme | = | 1 543 grain |
| 1 gramme | | | | = | 15.432 grains |
| 1 decagram | = | 10 | grammes | = | 154.324 grains |
| 1 hectogram | = | 100 | grammes | = | 0.268 pound Troy. |
| 1 kilogram | = | 1000 | grammes | = | 2.679 pounds Troy. |
| 1 kilogram | | | | = | 2.2046 pounds avoirdupois. |
| 1 grain Troy | | | | = | 0.0648 gramme. |
| 1 drachm Troy | | | | = | 3.888 grammes. |
| 1 ounce Troy | | | | = | 31.103 grammes. |
| 1 ounce avoirdupois | | | | = | 28.350 grammes. |
| 1 pound avoirdupois | | | | = | 453.592 grammes. |

*Commercial weights and measures of the U. S. A.*

1 pound avoirdupois = 16 ounces.
1 ounce = 437.5 grains.
1 gallon = 231 cubic inches.
1 gallon = 4 quarts = 8 pints.
1 pint of water weighs 7291.2 grains at a temperature of 15.6°.

*Apothecaries' weights.*

The apothecaries' ounce is of the same value as the now obsolete English Troy ounce.

| | | | | |
|---|---|---|---|---|
| 1 ounce | = | 8 drachms | = | 480 grains. |
| 1 drachm | = | 3 scruples | = | 60 grains. |
| 1 scruple | | | = | 20 grains. |
| 1 ounce | | | = | 31.103 grammes. |
| 1 grain | | | = | 64.799 milligrams. |

*Apothecaries' fluid measures.*

These are derived from the U. S. gallon; the liquid pint of this gallon is identical in value with the apothecaries' pint.

| | | | | |
|---|---|---|---|---|
| 1 pint | = | 16 fluidounces | = | 7680 minims. |
| 1 fluidounce | = | 8 fluidrachms | = | 480 minims. |
| 1 fluidrachm | | | = | 60 minims. |

*Jewelers' weight.*

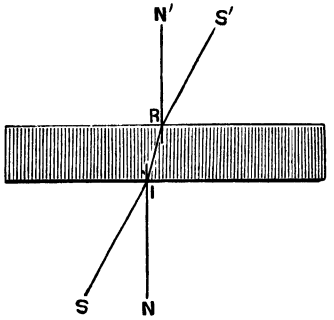
| | | | | |
|---|---|---|---|---|
| 1 carat | = | 0.205 gramme | = | 3.163 grains. |

## SPECTROSCOPE.

This instrument is a very useful adjunct to qualitative chemical analysis. To understand its action, a discussion of the principle of refraction and of dispersion of light is necesary.

**Refraction.**—While a ray of light moves in a straight line through homogeneous media, the ray is bent when passing from a medium of one density to that of another density, as from air to glass or to water. Under these conditions, unless the ray enter perpendicularly, it is bent out of its course, still moving,

FIG. 45.

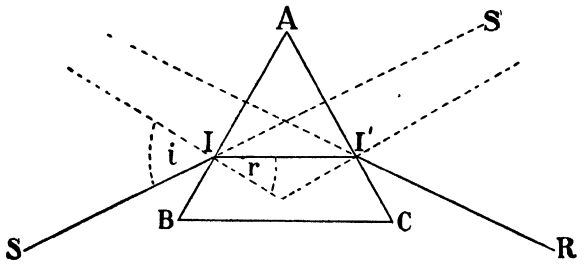



Refraction by a parallel plate.

however, in a straight path in the second medium, but in a different direction from that in the first. This bending of rays is known as *refraction*. It is refraction which causes a straight stick when held obliquely in clear water, to appear bent at the point of entering the water.

In Fig. 45 *SI* represents a ray of light entering a denser medium—say a plate of glass—with parallel sides. Here the ray is bent toward the perpendicular *N'R;* on leaving the denser medium and re-entering the air it is again bent,

FIG. 46.




Refraction through a prism.

but away from the perpendicular to such an extent that the rays *SI* and *RS'* (or rather their extensions) are parallel to one another.

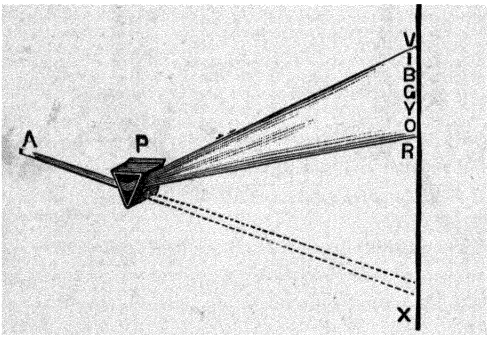
**Refraction through Prisms.**—A prism, in optics, is any transparent medium comprised between two plane surfaces inclined to each other. The intersection of the two planes is called the *edge*, and the angle between them is called the *refracting angle*. Triangular glass prisms are generally used.

In Fig. 46 *ABC* is a section of a prism. *A* is called the summit or apex, and *BC* the base. A ray of light, *SI*, falling upon the prism will not pass through it in a straight line, *SIS'*, but is bent out of its course twice, in accordance with the law of refraction, first from *I* to *I'*, and then to *R*. The amount of bending depends on the angle of the prism, its material, and the angle of incidence of the ray, shown in *i*, while *r* is the angle of refraction. The angle *D* represents the angle of deviation.

**Dispersion.**—In Fig. 46 the ray is represented by a single line throughout. In reality, matters are more complicated, as white light is made up of rays of different colors, each of which has a different angle of refraction. The result is that when a beam of white light falls on a prism it does not come through as white light, but the constituent colors are refracted at different angles, giving rise to a band of light containing all the colors of the rainbow, viz., red, orange, yellow, green, blue, indigo, violet; red being least refracted, violet most. Such a band of colors is known as the *prismatic spectrum.*

In Fig. 47 *A* represents a ray of light which if unbent would strike a screen at *X*, but the prism *P* intervening, the ray is refracted and at the same time resolved into its constituents, which form the spectrum, the colors of which are indicated by the initial letters. This spreading out of light into its different colors, is called *dispersion.*

FIG. 47.



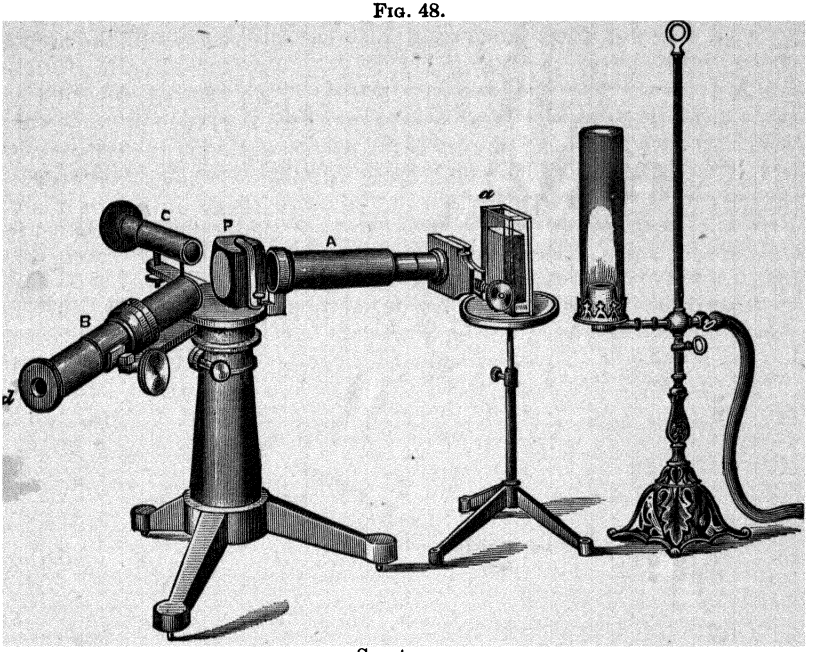

Prismatic spectrum.

**The Spectroscope.**—The spectroscope is an instrument that serves for conveniently observing the spectrum. Differently constructed instruments are employed, of which Fig. 48 represents the single-prism spectroscope, which is most largely used. It consists of the prism *P* and of three telescopes directed toward it. The light is permitted to enter the tube *A* through a narrow slit at its distal end, while at the other end a convex lens, called the collimator, serves to collect the light into nearly parallel beams. These beams pass through the prism where the dispersion is brought about, and the spectrum thus formed is observed at *d* through the telescope *B*. Through the third tube *C* a fine scale for measurement of the relative position of lines or colors is reflected to the eye of the observer. This scale is usually photographed on glass, and when illuminated by a candle or some other stronger light the image of the scale is directed upon the face of the prism in such a manner that it is reflected down the axis of the observing telescope, and is seen above or below the spectrum, according to the direction given to the axis of the scale tube. The glass vessel *a* serves as a container for a liquid to be examined spectroscopically.

A second form of spectroscope, known as the direct-vision spectroscope, is

shown in Fig. 49. It consists of a cylindrical tube provided with ocular and containing from three to seven prisms, a draw-tube with adjustable slit, and a collimator lens placed between them to render the rays parallel. The prisms placed opposite to one another are made of crown glass and flint glass, respectively. The dispersive power of the latter is nearly double that of crown glass, while the

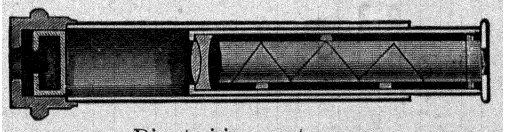
FIG. 48.




Spectroscope.

deviating powers of the two glasses do not differ much. The result is that a beam of light entering through the slit undergoes but little deviation from its original course, while there is sufficient dispersion between its color to produce a spectrum available for spectroscopic uses. When the luminous flame of a candle, oil, or gas is examined spectroscopically, it shows a *continuous spectrum*, *i. e.*, this white light has been decomposed into its constituents.

FIG. 49.



Direct-vision spectroscope.

**Bright Line Spectra.**—If into a non-luminous flame of a Bunsen burner a platinum wire which has been previously dipped into common salt (sodium chloride) be held, the flame will be colored yellow, and if it be examined by the spectroscope there will be seen a bright yellow line in the yellow part of the spectrum, while no other colors are visible. In thus examining salts of other metals

such as potassium, lithium, calcium, etc., by holding in the flame by means of platinum wire, it will be seen that each one gives a number of characteristic bands or lines in different parts of the spectrum, the remaining portion being quite dark. So characteristic are these spectra of different elements that they furnish a distinctive means of recognition; and indeed some elements have been discovered by this method. These spectra can be seen only when the substance is heated to a point where volatilization takes place, because gases alone show the property of giving discontinuous, or bright line, spectra, and no two gases give the same spectrum.

The reason that luminous flames give a continuous spectrum is that the luminosity is due to light emitted by particles of *solid* carbon floating in the burning gas. This shows that the spectroscope furnishes a reliable means of determining whether light proceeds from a luminous solid or a luminous gas, as all luminous solids and liquids give continuous spectra.

**Absorption Spectra.**—If the spectroscope is so arranged that a continuous spectrum is obtained from a strongly luminous flame, or from an electric light, and if then a little sodium chloride be evaporated in the flame of a Bunsen burner that has been placed between the slit and the luminous flame, it will be seen that the spectrum is no longer continuous, but that a black line intercepts it, a line holding precisely the position occupied by the yellow sodium line seen on a dark background when the luminous flame is removed. In repeating the experiment with the salts of various metals, we find like conditions, viz., the discontinuous bright-color spectra of individual metals are converted into spectra showing black lines in the continuous spectrum obtained from the luminous flame. (See spectra on plate facing title page.)

From these facts we may draw the conclusion that the vapors of different substances absorb precisely the same rays that they are capable of emitting. Such spectra are called *absorption spectra*, or *reversed spectra*.

Absorption spectra are also of interest because, if white sunlight be examined with a spectroscope of sufficiently high power, it is found not to be continuous, but to contain many hundreds of black lines, called after their discoverer *Frauenhofer lines*. The more prominent lines are designated by letters or numbers, as shown in the solar spectrum represented on the spectra plate. On comparing these lines in the sun spectrum with the positions of lines obtained by known elements, such as iron, sodium, calcium, etc., it is found that they correspond exactly to one another. The explanation given is this: The main body of the sun consists of a highly luminous mass surrounded by an atmosphere of cooler vapor. The luminous body would give a continuous spectrum, but the rays passing through the vapors of the sun's atmosphere are partly absorbed, and thus a large number of black lines are produced. Absorption-spectra are, furthermore, of great interest, because when light passes through certain liquids, such as blood or a solution of quinine sulphate, dark-line spectra are obtained, sufficiently characteristic to assist in the recognition of these substances.

From what has been said, we learn that we have three kinds of spectra, viz., continuous spectra, produced by luminous solids or liquids, and possibly by luminous gases under high pressure; bright-line spectra, produced by luminous vapors; and absorption spectra, produced by light that has passed through certain media.

The value of the spectroscope depends on the use made of it in *spectroscopic analysis*, as both the bright-line spectra and absorption spectra enable us to determine the nature of many substances, and to differentiate between elements present, not only on our globe, but in other celestial bodies likewise.

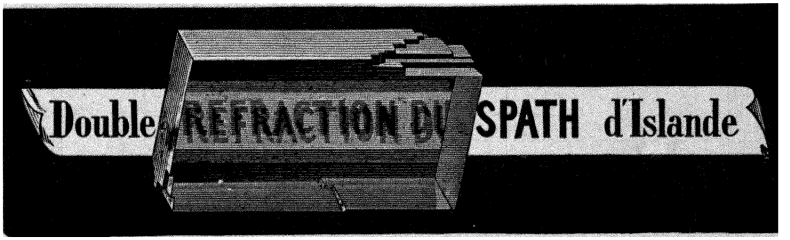
## OPTICAL ROTATION AND THE POLARISCOPE.

There are a number of substances which have a certain influence on so-called polarized light, which can be observed and measured by the instrument known as the polariscope. In many instances the use of the polariscope affords the simplest and most positive evidence of the identity or purity and quantity of such active substances. It is hoped that the following description will help the student to get the meaning of polarization of light and an understanding of the polariscope and its use.

**Double Refraction.**—A plate of glass will not interfere with reading printed matter over which the plate is laid. But in trying to read through several varieties of transparent crystalline substances a peculiar phenomenon is noticed; as then each letter will be duplicated, as shown in Fig. 50, where a piece of Iceland spar (crystallized calcium carbonate) is placed over reading matter.

If a pinhole be made through a card, and the card be placed over a crystal of Iceland spar and held before the eye toward the light, there will appear to be two holes, with light shining through each. If the crystal be made to rotate in a plane parallel with the card, then one of the holes will appear to remain nearly at rest, while the other rotates about it. These facts show that a ray of light on entering

FIG. 50.




Double refraction.

the crystal is divided into two parts, one of which obeys the law of regular refraction, and is called the *ordinary ray*, while the other which does not, is termed the *extraordinary ray*. This power of certain substances to refract light rays in two directions is known as *double refraction*.

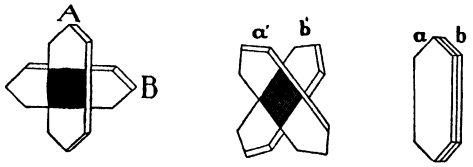
In all crystals which produce double refraction there is one direction (in some even two directions) in which an object, looked at through the crystal, does not appear double. The line through which double refraction is suspended is called the *optic axis*, and is a line around which the molecules appear to be arranged symmetrically.

**Polarization.**—The semitransparent mineral tourmaline is another substance which shows double refraction. Two rays, the ordinary and the extraordinary, are formed when a ray of light is passed through a plate of this substance, just as in the case of Iceland spar; but tourmaline possesses the peculiar property of absorbing the ordinary ray, while the extraordinary one passes through.

If two plates, cut parallel to the axis of the crystal, are laid upon each other in a crossed position, as *AB* in Fig. 51, it is found that light from the first plate is cut off by the second one, and darkness results. If one plate be turned round upon the other, it will be found that the combination is most transparent in two positions differing by 180 degrees, one of them, *ab*, being the natural position

which the plates originally occupied in the crystal. The combination is most opaque in the two positions at right angles with these, while intermediate positions such as *a'b'* show intermediate behavior. These facts show that light which has passed through one such plate is in a peculiar condition. It is said to be *plane-polarized.*

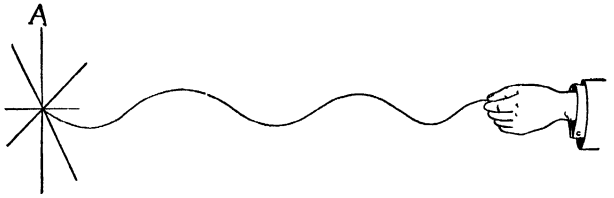
FIG. 51.




Tourmaline plates.

In order to understand polarization of light, we should bear in mind that the particles of the luminiferous ether undulate in a variety of planes perpendicular to the line of propagation. It appears that in polarized light the undulations of the ether particles take place in a single plane. These ether undulations may be compared to those taking place in a cord fastened at one end and shaken by the hand at the other end, as in Fig. 52. According to whether we move the hand

FIG. 52.

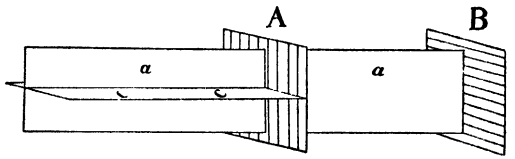



Undulation in a cord.

horizontally, obliquely, or vertically, the undulations will lie in a horizontal, oblique, or vertical plane, as represented at *A*.

If a cardboard, with a long slit in it, be held over the string, the string will vibrate in one plane only, viz., in that of the slit. Instead of one cardboard, two or more may be used, and as long as the slits are in one plane the vibrations

FIG. 53.




Explanatory diagram of the action of tourmaline plates.

will proceed in that plane. If, however, the slit of one card be set at a right angle to that of another placed over the string, vibrations will no longer be propagated.

To make the action of the tourmaline plates still more intelligible, we may compare it to that of a grating, *A*, Fig. 53, formed of parallel vertical rods which permit the passage of all vertical planes, as *aa*, but intercept that of horizontal planes, *cc*. As long as the rods of the gratings *A* and *B* are parallel, a string may

be made to vibrate through these gratings parallel to the rods, but when set at a right angle this becomes impossible.

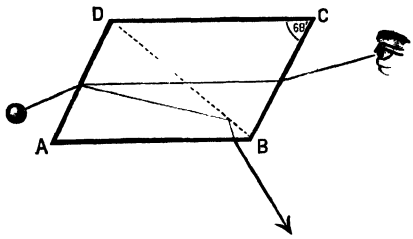
When a ray of light strikes a plate of tourmaline it permits the passage of those undulations which are parallel with its axis, but it absorbs those undulations which are in planes at right angles to its axis. The rays which pass through the plate produce the polarized light.

## POLARISCOPE.

As the unaided eye cannot differentiate between common and polarized light, instruments are constructed by which the phenomena of polarization can be studied, and these instruments are known as polariscopes or polarimeters. They all contain some substance, known as a polarizer, such as tourmaline, Iceland spar, etc., serving as a *polarizer* of light; and a second substance, called an *analyzer*, for the detection of that light. In the above experiment with tourmaline plates the first plate serves as a polarizer and the second as an analyzer.

The material used generally for polarization is Iceland spar, as it is more transparent than tourmaline. Instead of using plates of this material, prisms, known as *Nicol's prisms*, are made by sawing through a crystal from one obtuse angle to the other. The two parts, after their surfaces have been well polished, are joined by a transparent cement of Canada balsam. Fig. 54 represents a

FIG. 54.




Nicol's prism.

section of this prism. *BD* indicates the line where the crystal has been cut and cemented. A ray of light passing from the object to the side *AD* is doubly refracted in such a manner that the ordinary ray on striking the balsam is totally reflected to the side *AB*, and there refracted out of the crystal, while the extraordinary ray passes on and emerges at the side *BC* as a polarized ray. If this ray is now passed into a second Nicol prism parallel to the first, as if it were a continuation of the latter, it will pass through unchanged. If the second prism be turned through an angle of 90 degrees—that is, if the two prisms be *crossed*—the ray of light will be cut off entirely. The ray in the second prism becomes an ordinary one, and is totally reflected at the layer of balsam through the side of the prism and is lost, as in the case of the first prism. In intermediate positions between the crossed and the parallel ones the extraordinary ray from the first prism is decomposed in the second one partly into an ordinary and partly into an extraordinary ray. The former is reflected out of the prism, while the latter goes through, so that more and more light will pass through as the second prism is turned so as to approach parallelism to the first. Thus it is easily seen that a Nicol prism may serve, not only to produce polarized light, but also to detect such light.

Polarized light is extensively used in the examination of minerals and salts, as thin slices of crystals belonging to different crystallographic systems when

brought between two Nicol prisms show rings or bands of colors characteristic of the respective systems.

Many organic liquids and solids in solution have a peculiar action on polarized light. Such substances, for example, are sugars, tartaric acid, alkaloids, essential oils, etc. If two Nicol prisms are crossed so that no light is emitted, and a solution of sugar, for example, is placed in a glass tube between the prisms, light will pass. The sugar turns the plane of vibrations of the light as it comes from the first prism, and the effect is the same as if the second prism had been turned with respect to the first one as described above, where nothing intervened between the prisms. Substances which have such an effect on polarized light are said to *turn the plane of polarization*, and are called *optically active*. The amount of this turning or *rotation of the plane of polarization* can be measured by noting to what extent the second prism must be turned to the right or left to produce the original condition, namely, darkness.

Substances which act in such a manner that the analyzer must be turned to the right to produce darkness are called *dextrorotatory*, or *right-handed;* while those substances acting in the opposite manner are called *levorotatory*, or *left-handed*. Substances acting in neither way are called *optically inactive*.

The degree of rotation varies with the quantity of substance in solution for a definite length of a column of the latter, and hence is used to determine the percentage strength, for example, that of sugar in urine and other liquids. Polariscopes are therefore valuable quantitative analytical instruments.

All polariscopes consist essentially of a polarizer and an analyzer, with a tube between them for containing the substance to be examined, and a scale for reading the amount of rotation produced, all carried on a suitable metallic support. In addition to these essential parts, the polariscopes of different makers are provided with numerous contrivances rendering the instruments more perfect and the analytical results obtained more accurate.

Plates of crystalline substances, as quartz, have a noteworthy effect when placed in the path of polarized light between a polarizer and an analyzer. Not only do they prevent the light from being entirely shut off when the Nicol prisms are crossed, but they produce sharply defined appearances, as color tints, alternate lines of light and darkness, equal or unequal illumination of the two halves of the field of view, etc. The appearances depend on the particular arrangement and direction of cutting of the crystalline plates. A full explanation of the cause of these effects is beyond the scope of this work.

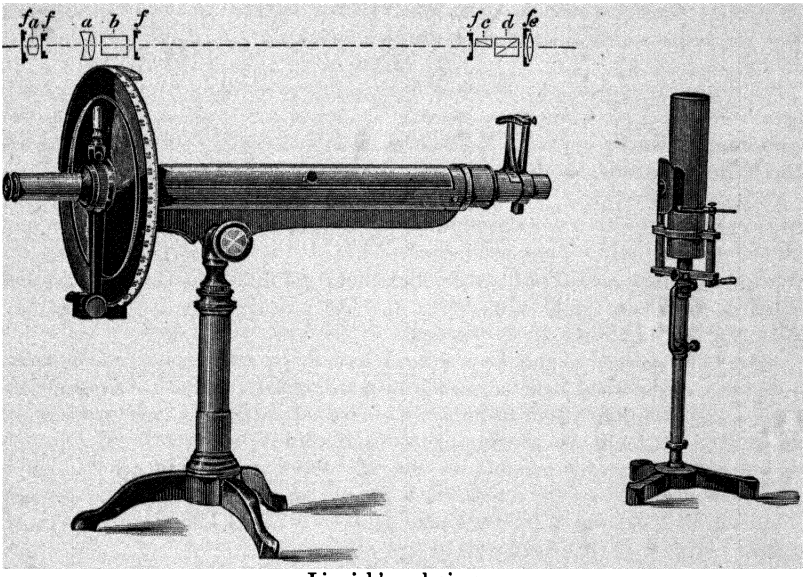
Fig. 55 shows Lippich's polariscope, used chiefly for sugar solutions. The optical arrangement is shown above the drawing of the instrument, and consists of a telescope, *aa*, the analyzer, *b*, a stationary polarizer, *c*, a movable polarizer, *d*, and the condensing lens *e; f* represents a number of diaphragms. The liquid to be examined is placed in the tube, and the rotatory power of the substance is determined by turning the polarizer to the right or left, as the case may require. The amount of turning necessary to establish the same conditions existing before the optically active substance was brought between the prisms is read off on the movable disk, which is provided with a scale. A lamp supplies the illumination by means of a flame colored yellow by sodium chloride fused on the end of platinum wire. Sodium light is monochromatic and corresponds with the line *D* of the solar spectrum. The readings are best made in a dark room.

The rotation of the plane of polarization either to the right or to the left of the zero point is directly proportional to the length of the column of liquid and to the density or the quantity of matter in 1 c.c. The rotation also is different for different temperatures. Hence in making determinations of the amount of rotation, the exact length of the column of liquid used and the temperature must be

recorded. Usually a tube of 50 or 100 mm. is used and a standard temperature of 20° or 25° C. is maintained. For saccharimeters the temperature is fixed at 20° C. by international agreement. The U. S. P. gives the amount of rotation that the official active liquids, such as volatile oils, etc., should show when examined in a specified length of tube and at 25° C. or some other specified temperature. If, in an actual test, there is considerable variation from the figures given in the U. S. P., there is reason to suspect that the article in question is inferior or adulterated.

A uniform basis for expressing optical rotation is in terms of the theoretical figure that would be obtained if the liquid had the sp. gr. 1 (that is, 1 c.c. weighed 1 gram) and for a column of liquid 100 mm. long. This is known as the *specific rotatory power* or *specific rotation*, and is usually expressed by the symbol $[\alpha]_D$, the letter D indicating that the reading is made with sodium light. The value of

FIG. 55.




Lippich's polariscope.

$[\alpha]_D$ is easily found from the data of an actual determination. In the case of substances that are liquid by nature, if $\alpha$ is the reading of the polariscope for a column L mm. long of a substance of sp. gr. d, then $\frac{\alpha}{d}$ would be the rotation if the sp. gr. could be reduced to 1 (since rotation varies directly as the sp. gr.), and $\frac{\alpha \times 100}{d \times L}$ would be the reading for a column of liquid 100 mm. long (since rotation varies directly as the length of the column of liquid). This, by definition, is the specific rotation; hence

$$I \quad [\alpha]_D = \frac{100 \times \alpha}{L \times d}.$$

In the case of solid substances, like cane-sugar, dextrose, tartaric acid, etc., which show optical rotation when dissolved and the solutions are examined in the polariscope, the specific rotatory power may be calculated as described above.

Let d be the sp. gr. of a solution of the solid, and p the number of grams of the solid in 100 grams of the solution. L the tube length and $\alpha$ the angle of rotation observed. Then $\frac{100}{d}$ = the volume in c.c. containing p grams of the solid, $p \div \frac{100}{d}$, or $\frac{p \times d}{100}$ = grams of substance in 1 c.c. of solution. $\alpha \div \frac{p \times d}{100}$, or $\frac{100 \times \alpha}{p \times d}$ = the degree of rotation that would be observed if 1 c.c. of the solution contained 1 gram of the active substance (since rotation varies directly with the density or amount of substance in solution). Finally, $\frac{100}{L} \times \frac{100 \times \alpha}{p \times d}$, or $\frac{10000 \times \alpha}{L \times p \times d}$ = the degree of rotation that would be observed for a column of 100 mm. length of the solution containing 1 gram of active substance in 1 c.c. of solution (since rotation varies directly with the length of the column of liquid). But, by definition this is the specific rotation; hence

$$\text{II} \quad [\alpha]_D = \frac{10000 \times \alpha}{L \times p \times d}$$

If c is the weight in grams of the active substance in 100 c.c. of the solution, the formula, calculated in the manner indicated above, is:

$$\text{III} \quad [\alpha]_D = \frac{10000 \times \alpha}{L \times c}.$$

The specific rotations have been determined for all active substances in a pure state, and are recorded in books.

Formulas II and III above are used in quantitative determinations of the amount of an active substance contained in a solution. We may illustrate by one example. Suppose a solution of cane-sugar, contained in a tube 188.8 mm. long, gave a rotation of 12.6°. The specific rotatory power of cane-sugar is 66.5°. Substituting these known factors in formula III, we have:

$$66.5 = \frac{10000 \times 12.6}{188.8 \times c} \text{ or } c = \frac{10000 \times 12.6}{188.8 \times 66.5}$$

$$c = \frac{126000}{12555.2} = 10.03$$

That is, 100 c.c. of the solution contained 10.03 gram of cane-sugar.

The polariscopes most generally used are the half-shadow instruments of Laurent and of Schmidt and Hänsch in which the two sides of the field of vision are capable of becoming unequally illuminated. Most of the instruments in use do not permit the angle of rotation to be read off in degrees of a circle, but give readings in terms of divisions of what is known as the sugar scale, the instruments being primarily adapted for use in the determination of the per cent. of cane-sugar.

The following factors are employed for converting divisions of the sugar scale into degrees of a circle.

1 division Laurent = 0.2167° angular rotation

1 division Schmidt and Hänsch = 0.346° angular rotation.

The light used in these instruments is sodium light.

## TABLE OF ELEMENTS AND ATOMIC WEIGHTS.

Adopted by the International Committee on Atomic Weights (1915). (O = 16.)

| Name. | Symbol. | Atomic weight. | Name. | Symbol. | Atomic weight. |
|---|---|---|---|---|---|
| Aluminum | Al | 27.1 | Neodymium | Nd | 144.3 |
| Antimony | Sb | 120.2 | Neon | Ne | 20.2 |
| Argon | A | 39.88 | Nickel | Ni | 58.68 |
| Arsenic | As | 74.96 | Niton (radium emanation) | Nt | 222.4 |
| Barium | Ba | 137.37 | Nitrogen | N | 14.01 |
| Bismuth | Bi | 208 | Osmium | Os | 190.9 |
| Boron | B | 11 | Oxygen | O | 16 |
| Bromine | Br | 79.92 | Palladium | Pd | 106.7 |
| Cadmium | Cd | 112.4 | Phosphorus | P | 31.04 |
| Cæsium | Cs | 132.81 | Platinum | Pt | 195.2 |
| Calcium | Ca | 40.07 | Potassium | K | 39.1 |
| Carbon | C | 12 | Praseodymium[3] | Pr | 140.6 |
| Cerium | Ce | 140.25 | Radium | Ra | 226.4 |
| Chlorine | Cl | 35.46 | Rhodium | Rh | 102.9 |
| Chromium | Cr | 52 | Rubidium | Rb | 85.45 |
| Cobalt | Co | 58.97 | Ruthenium | Ru | 101.7 |
| Columbium[1] | Cb | 93.5 | Samarium | Sm | 150.4 |
| Copper | Cu | 63.57 | Scandium | Sc | 44.1 |
| Dysprosium | Dy | 162.5 | Selenium | Se | 79.2 |
| Erbium | Er | 167.7 | Silicon | Si | 28.3 |
| Fluorine | F | 19 | Silver | Ag | 107.88 |
| Gadolinium | Gd | 157.3 | Sodium | Na | 23 |
| Gallium | Ga | 69.9 | Strontium | Sr | 87.63 |
| Germanium | Ge | 72.5 | Sulphur | S | 32.07 |
| Glucinum[2] | Gl | 9.1 | Tantalum | Ta | 181.5 |
| Gold | Au | 197.2 | Tellurium | Te | 127.5 |
| Helium | He | 3.99 | Terbium | Tb | 159.2 |
| Holmium | Ho | 163.5 | Thallium | Tl | 204 |
| Hydrogen | H | 1.008 | Thorium | Th | 232.4 |
| Indium | In | 114.8 | Thulium | Tm | 168.5 |
| Iodine | I | 126.92 | Tin | Sn | 119 |
| Iridium | Ir | 193.1 | Titanium | Ti | 48.1 |
| Iron | Fe | 55.84 | Tungsten | W | 184. |
| Krypton | Kr | 82.92 | Uranium | U | 238.5 |
| Lanthanum | La | 139 | Vanadium | V | 51 |
| Lead | Pb | 207.1 | Xenon | Xe | 130.2 |
| Lithium | Li | 6.94 | Ytterbium (Neoytterbium) | Yb | 172 |
| Lutecium | Lu | 174 | Yttrium | Yt | 89 |
| Magnesium | Mg | 24.32 | Zinc | Zn | 65.37 |
| Manganese | Mn | 54.93 | Zirconium | Zr | 90.6 |
| Mercury | Hg | 200.6 | | | |
| Molybdenum | Mo | 96 | | | |

[1] Also called Niobium, Nb. [2] Also called Beryllium, Be. [3] Also called Didymium, Di.

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