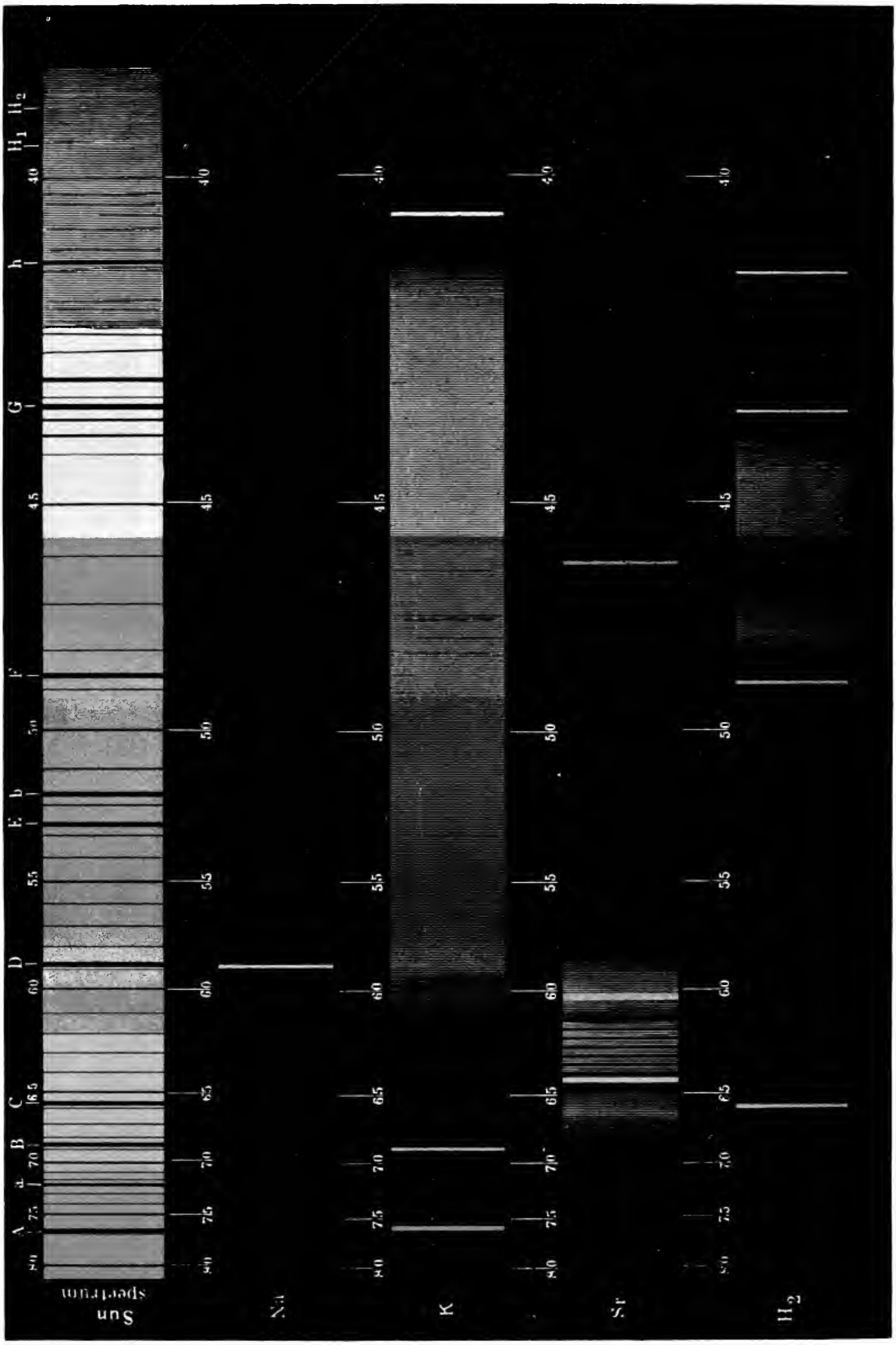
Sun spectrum
Na
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MANUAL

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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TENTH EDITION, THOROUGHLY REVISED.

WITH EIGHTY-TWO ILLUSTRATIONS, ONE COLORED SPECTRA PLATE,

AND

EIGHT COLORED PLATES REPRESENTING SIXTY-FOUR CHEMICAL REACTIONS.

LEA & FEBIGER,
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1912.

Authority to use for comment the Pharmacopœia of the United States of America (Eighth Decennial Revision), in this volume, has been granted by the Board of Trustees of the United States Pharmacopœial Convention; which Board of Trustees is in no way responsible for the accuracy of any translations of the Official Weights and Measures, or for any statement as to strength of Official Preparations.

PREFACE TO THE TENTH EDITION.

In this new edition the *Manual* preserves the plan and characteristics that have won for it the degree of approval shown in the exhaustion of the nine previous issues, each in several large printings. Numerous additions have been made, most of which are of fundamental importance, and again bring the Manual abreast of modern thought in chemistry to its date of issue. They embrace articles on the following subjects: Exothermic and endothermic reactions; reversible reactions and chemical equilibrium; mass action; extension of the articles on acids and bases; thermochemistry; a new chapter on solution, in which, among other matters, the solution of gases and Henry's law, freezing-points, boiling-points and osmotic pressure, Raoult's law and the laws of osmotic pressure are discussed, and the existence of ions foreshadowed; a new chapter on the theory of electrolytic dissociation, in which are considered the origin of the theory, ionic equilibrium, ionization of acids, bases, and salts, reactions on the ionic basis, activity of acids and bases, hydrolysis of salts, neutralization, electrolysis and Faraday's laws, etc.; electrolytic solution tension of metals; principle of the storage-battery; and ionic explanation of the action of indicators. Ionic relations are discussed in practically every chapter on acids and the metals, and a number of compounds have been added to the sections on inorganic and organic chemistry. Many of these are of medical interest, for example, sodium cacodylate, atoxyl and salvarsan, phenolphthalein, fluorescein, phenolsulphonephthalein.

The section on physiological chemistry has been rewritten and brought in line with present-day knowledge and theories. A table of international atomic weights on the oxygen = 16 basis has been added to the U. S. P. table of weights on the hydrogen = 1 basis.

It is hoped that with these alterations and additions the Manual will fully accomplish its object, viz., *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.*

As heretofore, the subject has been divided into seven parts, each one of which contains so much of the matter under consideration as is believed to be necessary for a fair understanding of the subject. At the same time care has been taken to place in the foreground all facts and data which are of direct interest to the physician, pharmacist. and dentist.

In the first part, treating of chemical physics, the student finds a brief discussion of those physical conditions of matter which have a close relationship to chemical phenomena, and also of the principles which lead to an understanding of many of the instruments, such as the spectroscope, polariscope, etc., which he uses in his chemical operations.

The second part treats of those principles of chemistry which are the foundation of the science, and enters briefly into a discussion of theoretical views regarding the constitution of matter. Though the authors prefer to present these theories to their classes at the proper times during the course of lectures, they do not deem it desirable to have them scattered throughout the work, believing it better to assemble them compactly in print, so that the student may be able to study them after having acquired some knowledge of chemical phenomena.

The third and fourth parts are devoted to the consideration of the non-metallic and metallic elements and their compounds. While the periodic law furnishes a most admirable basis for a scientific classification of elements, yet their consideration according to a *strict* adherence to periodicity does not seem advisable in this book. For this reason the old classification of metals and non-metals, organic and inorganic compounds has been retained, since experience has shown it to be well adapted for the instruction of beginners in chemistry.

The fifth part 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 is added giving official methods for volumetric determinations.

The sixth part treats of organic chemistry. Though it is impossible to include within the limits of this text-book an extended consideration of a branch of chemical science 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 general character, and a knowledge of the bodies which are most important in medical science.

The seventh and last part gives the principal facts of physiological chemistry. Special care has been taken also to introduce here the most modern methods for chemical examination in clinical diagnosis.

The authors will be grateful for any suggestions looking to the improvement of the book.

The authors wish to express here their obligations to G. Howard White, Jr., M. D., by whom the section on physiological chemistry was rewritten.

W. S.
D. B.

BALTIMORE, 1912.

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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 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.*[1] 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[2] 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 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 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.

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[1] It has been shown lately that matter may exist in a fourth state as *radiant* matter. This condition will be considered later.

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

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

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.

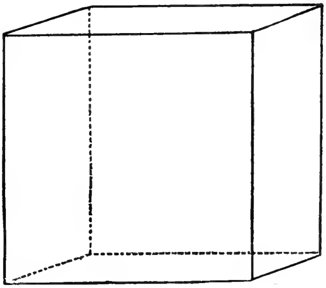
Not all matter can form crystals; some substances never have been obtained in a crystallized state, such as starch, gum, glue, etc. A solid substance showing no crystalline structure whatever is called *amorphous.*

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 be made up of particles of both substances,

Crystal Systems. The study of crystals forms an extensive field, known as crystallography. The limited scope of this book forbids any detailed study of crystals, and the reader must be referred to the large works on chemistry or works on crystallography for such information. But a brief description of the classification of crystals may not be out of place here.

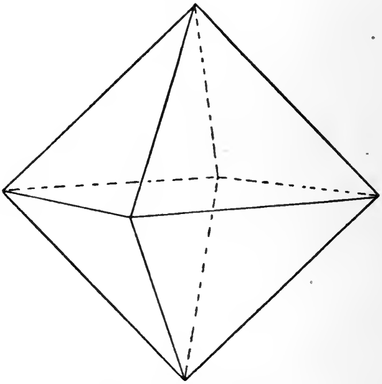
All crystals are referred to *axes* or imaginary lines drawn through the center. The great variety of forms of crystals depends upon the number and length of these axes and their relative inclination—that is, the angles at which they intersect. All crystal forms have been divided into two large groups, the *orthometric* and the *clinometric*, and these have been further subdivided into six systems. Orthometric refers to the fact that the axes intersect at right angles, while clinometric means that the axes intersect at oblique angles.

FIG. 1.



The cube.

FIG. 2.



Regular octahedron.

The orthometric group includes the following systems:

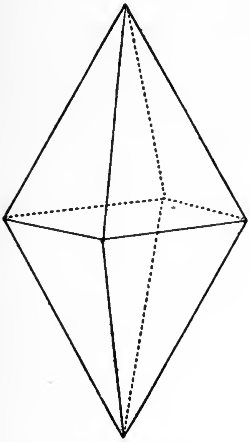
(1) Regular system, also known as the monometric, cubic, octahedral, or tessular system.

The crystals have three axes of equal length and intersecting at right angles. The fundamental forms of this system are the cube and the octahedron (Figs. 1 and 2). Some substances crystallizing in this system are alum, phosphorus, arsenic trioxide, diamonds, alkali iodides, chlorides, fluorides, and cyanides, and many metals and their sulphides.

(2) Quadratic system, also known as the dimetric, square prismatic, or tetragonal system.

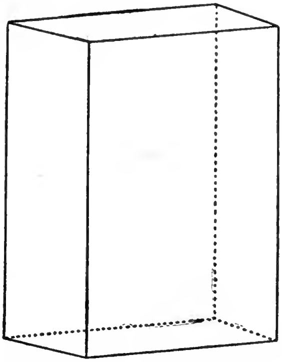
The crystals have three axes intersecting at right angles, two of which are of equal length and one either longer or shorter than the other two. The fundamental forms of this system are the quadratic octahedron (also known as square-based double pyramid) and the right square prism (Figs. 3 and 4).

FIG. 3.



Quadratic octahedron.

FIG. 4.

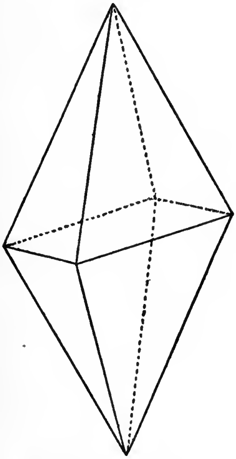


Right-square or quadratic prism.

Some substances crystallizing in this system are potassium ferrocyanide, calomel, nickel sulphate, tin, tin oxide, magnesium sulphate, zinc sulphate.

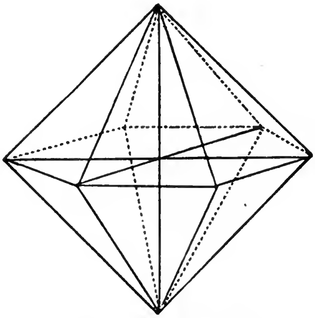
(3) Rhombic system, also known as the trimetric or right prismatic system.

FIG. 5.



Rhombic octahedron.

FIG. 6.



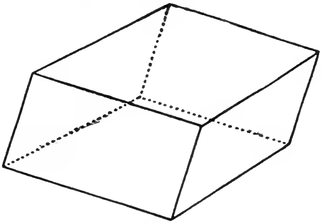
Double six-sided pyramid.

The crystals have three unequal axes intersecting at right angles. The fundamental form of this system is the rhombic octahedron or right rhombic double pyramid (Fig. 5). Some substances crystallizing in this system are potassium sulphate and nitrate, resorcin, zinc sulphate, citric acid, iodine, Rochelle salt, mercuric chloride, barium chloride, tartar emetic, codeine, salicylic acid, piperin, Epsom salt, silver nitrate, ammonium sulphate, cream of tartar.

(4) Hexagonal or rhombohedral system.

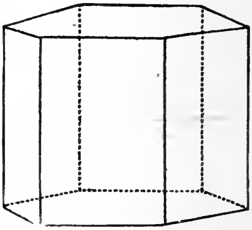
The crystals have four axes, three of which are of equal length, while the fourth is either longer or shorter than the other three. The three equal axes are in the same plane and intersect at an angle of 60°, while the fourth axis intersects these at right angles. The fundamental form is the double six-sided pyramid. The rhombohedron and regular six-sided prism are modifications of this system (Figs. 6, 7, and 8). Some substances crystallizing in this system are sodium nitrate, camphor, graphite, ammonium chloride, ice, calcspar, thymol, metallic bismuth and antimony, arsenic, silicic acid.

FIG. 7.



Rhombohedron.

FIG. 8.



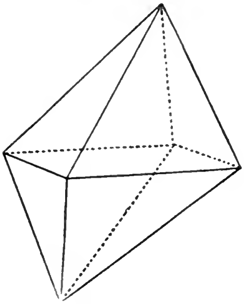
Six-sided prism.

The clinometric group includes the following systems:

(5) Monoclinic system, also known as the monosymmetric, clinorhombic, or oblique prismatic system.

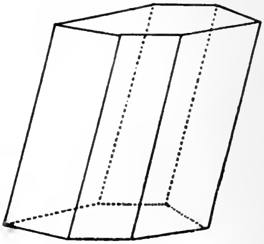
The crystals have three unequal axes, two intersecting at oblique angles and both intersecting the third at right angles. The fundamental forms of this system are the monoclinic double pyramid or octahedron and the monoclinic prism (Figs. 9 and 10). Some substances crystallizing in this system are ferrous sulphate, borax, lead acetate, cupric acetate, tartaric acid, potassium chlorate, and sodium acetate, sulphate, thiosulphate, phosphate, and carbonate.

FIG. 9.



Monoclinic double pyramid.

FIG. 10.



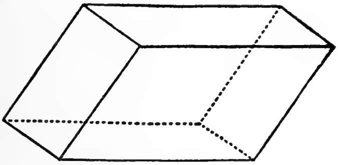
Monoclinic prism.

(6) Triclinic system, also known as the asymmetric, clinorhombohedral, or doubly oblique prismatic system.

The crystals are the most unregular of all, having three unequal axes, all intersecting at oblique angles. The fundamental forms of this system are the triclinic prism and the triclinic octahedron or double pyramid (Figs. 11 and 12). Some substances crystallizing in this system are copper sulphate, potassium dichromate, gypsum, boric acid, manganous sulphate.

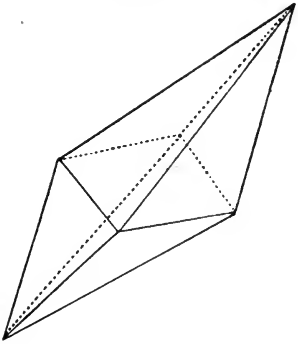
The pyramidal form is found in all the systems, while the cube is confined to the regular system, and prisms occur in all but the regular system.

FIG. 11.



Triclinic prism.

FIG. 12.



Triclinic octahedron.

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 acetanilid, 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, sulphur, 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 terms 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.

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[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.

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 measure 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 represent 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.

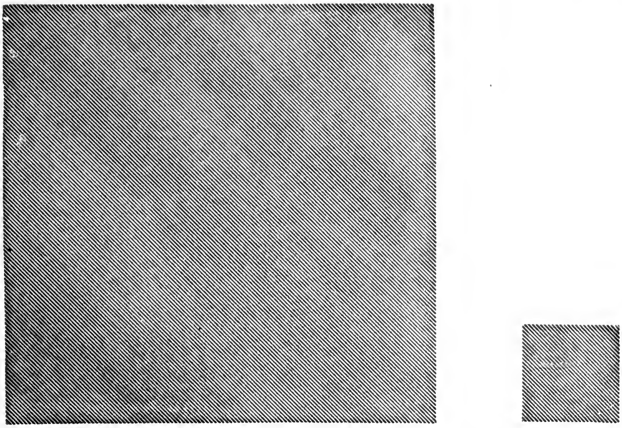
Divisibility. All matter admits of being subdivided into smaller particles, and this property is called divisibility. The processes by which we accomplish the comminution of a solid substance may be of a mechanical nature, such as cutting, crushing, grinding; but beside these modes of subdivision we 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. 13), or that the water consisted of small particles of a given size, which now exist in the steam again as such,

Fig. 13.



with the only difference that they are more widely separated from each other (Fig. 14).

Fig. 14.

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 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 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 milions 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

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[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.

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 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 proportional 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 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, gramme, 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 capacity is the cubic decimeter called *liter* (1.0567 U. S. quart), and the unit of weight is the weight of one cubic centimeter of water at the temperature of its greatest density, 4° C. (39.2° F.), and this unit is called *gramme* (15.43+ grains). One liter of water, equal to 1000 cubic centimeters, at its greatest density weighs 1000 grammes or one kilogram. While gramme is the unit for weights up to a kilogram, the latter is the unit for all larger weights, and is generally abbreviated to *kilo* (2.2046 pounds, avoirdupois).

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 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 a unit volume of water at 4° C. (39.2° F.) is 1 gramme, 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 grammes in air and 2 grammes in water, the loss being 4 grammes, 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 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. We have so far considered the gravity of solids and liquids only, and the next question will be: Do gases also possess weight—are they also attracted by the earth? 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, which would, therefore, be the height of the column of water required.

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 as 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.

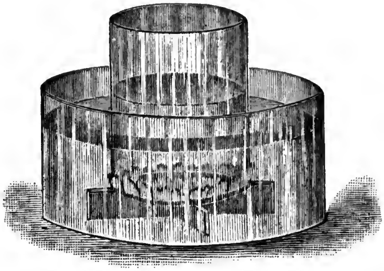
Diffusion is exhibited also by solids, even at ordinary temperature. Sir W. Roberts-Austen placed gold and lead in contact four years at 18° C., and found the surfaces united. Gold had penetrated the lead to more than 5 millimeters from the surface, while within 0.75 millimeter from the surface gold 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. 15), 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, whilst at the same time water passes over to the salt solution

Fig. 15.



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 phenomena 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 of 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.*

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 the 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 temperatures 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.

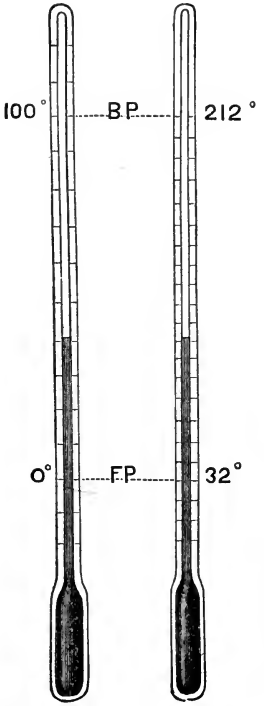
Expansion is a very important thing which must be taken into account by constructors, for example, of bridges, railroad beds, etc. Also in very careful physical measurements, expansion of glass apparatus, solutions, barometers, etc., must be carefully noted.

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. 16.) Degrees of temperature below the zero point of either instrument are designated by —, *i. e.*, minus.

As 100 degrees centigrade are equivalent to 180 degrees Fahrenheit, it follows that 1 degree C. = 1.8 degree F., or 1 degree F. = $\frac{10}{18}$ 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.

Fig. 16.



Centigrade. Fahrenheit.
Thermometric scales.

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 of 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 gramme 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 phenomena, 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 gramme of a substance fuse. Different substances have different latent heats of fusion, but water (ice) has the greatest. To melt 1 gramme of ice at 0° C. to water at 0° C. requires 80 calories, or as much heat becomes latent as will raise 1 gramme 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. 69. 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 every one. 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 gramme 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 gramme of water at 100° C. into steam at 100° C., as would raise 535.9 grammes 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.

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 atmospheres 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.

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?

3. LIGHT.

Light a form of energy. It has been shown in the preceding chapter that a heated body sends forth waves through the ether, which in striking a cooler body cause its molecules to vibrate more quickly—*i. e.*, heat it to a higher temperature. But an increased molecular motion may produce other effects than heat, as we may observe by heating an iron bar, which, when sufficiently hot, will emit light. That light is different in effect from heat, though both come from the same hot body, may be observed in the action of luminously hot bodies on certain chemicals; for example, the silver salts, which undergo a change in their chemical composition. The action of sunlight on photographic plates is an excellent illustration.

The explanation of these phenomena is that ether waves of diverse characters produce different effects. Thus, the waves coming to us from the sun may affect the sense of touch, and we call the effect heat; they may affect the sense of sight, and we term it light; or they may affect the composition of matter, when we speak of it as chemical action. But in all these results we have simply different manifestations of some form of radiant energy. *Light is that form of energy which may be appreciated by the organ of vision.*

Color. Both heat- and light-producing waves or oscillations are propagated through ether with the same velocity, viz., at the rate of 300,000 kilometers, or 186,000 miles, per second; but the waves differ in regard to length and in the amplitude of vibration. Waves of a particular limited range of frequency (477,000,000 millions to 699,000,000 millions per second) when falling upon the eye produce a sensation of light. Of these, the slowest—*i. e.*, the waves with the least frequency and the greatest wave-length—produce a sensation of red light; as the frequency increases, the sensation produced by them is successively that which is termed orange, yellow, green, blue, indigo, and violet light.

Ether waves of frequency too limited to be visible are called *infra-red waves;* they have, however, great heating power when falling upon a substance. On the other hand, there are waves of greater frequency than those which produce a sensation of violet; they are also invisible, but have the power of producing chemical action; they are called *ultra-violet* or *actinic waves.* There is no inherent difference between any of the different kinds of waves here mentioned; indeed, they all may be produced at the same time by the same body.

In what is called daylight there is a mixture of waves of different frequencies, affecting our eye simultaneously in such a manner that none of the specific colors predominates. The reason that even under the influence of this white light most objects show a distinct color is not, as might be supposed, an inherent color possession of these objects, but an effect of the light. Without light all objects are black—*i. e.*, without light there is no color. There is a great diversity in the behavior of different substances toward white light. It may either be absorbed or reflected, or partly absorbed and partly reflected. If all be absorbed, black is the result; if all rays except the red ones be absorbed, the body appears red, etc.

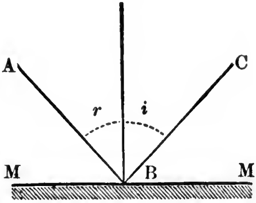
Not only has the number of wave oscillations per second been determined, but also their length. The longest waves are those producing heat; the shortest ones are the actinic waves. Between them are the light waves ranging from 650 millionths of a millimeter in length for red light, to 442 millionths of a millimeter in length for violet light.

Light rays. Light travels through homogeneous media, as air, water, and glass, in straight lines, and a very narrow cylinder of light is called a *ray*, *beam*, or *pencil* of light. Those bodies which readily transmit luminous rays are said to be *transparent*, those not transmitting light are called *opaque*, while *translucent* bodies are those permitting light to pass through them to a limited extent.

A body may be self-luminous, like the sun or a flame; or it may be luminous by reflected light, like the moon or any object that is illuminated by daylight or by any luminous body.

Light of itself is invisible, as can be shown by admitting a sunbeam through a small hole into a dark room. If the air be free from dust, the beam is invisible; but if the eye, or any object upon which it may strike, is placed in its path, we are made aware of its presence, not by seeing the light, but by seeing the object which emits it or intercepts it.

FIG. 17.



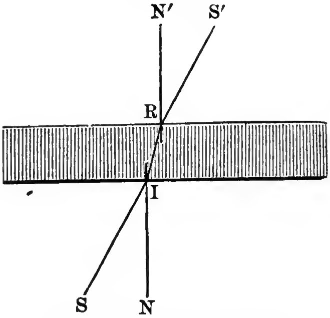
Reflection.

Reflection. When a ray of light strikes a mirror or a polished surface obliquely we notice that a ray of light is thrown off or *reflected* from the mirror. On measuring the angle i (Fig. 17) made by the entering or *incident* ray CB and a perpendicular NB, and the angle r made by the reflected ray AB and the perpendicular, they will be found equal. In other words, in plane mirrors the angle of incidence is always equal to the angle of reflection.

Upon this reflection depends the formation of the image seen in mirrors. If a reflecting surface were an absolutely smooth plane, it would be invisible, and we would see in it simply the images of other subjects. Most objects are not bounded by absolutely smooth surfaces, and, consequently, the light which falls upon them is scattered or diffused, thus rendering them visible in all directions.

Refraction. While a light ray travels 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, 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.

Fig. 18.

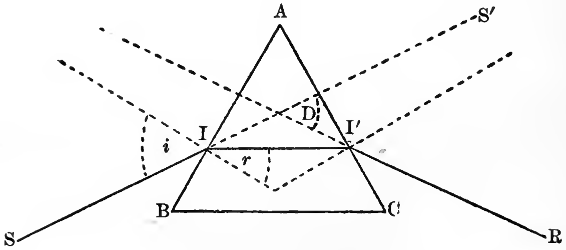


Refraction by a parallel plate.

In Fig. 18, 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, 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

Fig. 19.



Refraction through a prism.

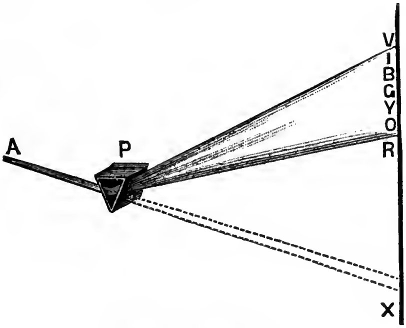
the angle between them is called the *refracting angle.* Triangular glass prisms are generally used.

In Fig. 19, 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. 19, 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 less refracted, violet most. Such a band of colors is known as the *prismatic spectrum.*

In Fig. 20, 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, and its separation into different colors, are called *dispersion.*

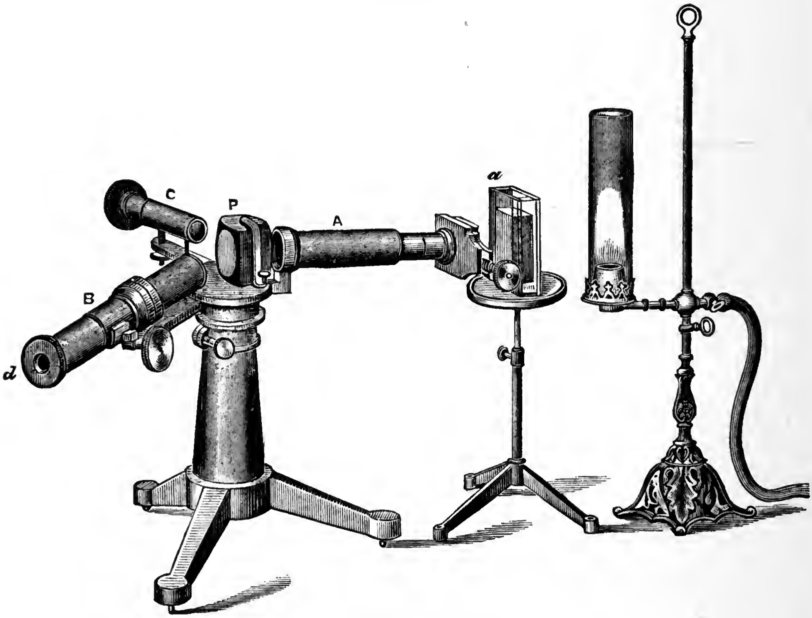
FIG. 20.



Prismatic spectrum.

The spectroscope is an instrument that serves for conveniently observing the spectrum. Differently constructed instruments are employed, of which Fig. 21 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.

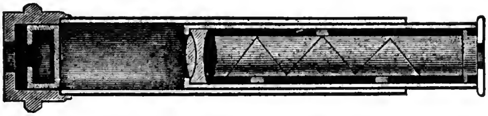
FIG. 21.



Spectroscope.

A second form of spectroscope, known as the direct-vision spectroscope, is shown in Fig. 22. 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 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 colors 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. 22.



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 accompanying 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.

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. 23, where a piece of Iceland spar (crystallized calcium carbonate) is placed over reading matter.

Fig. 23.

Double refraction.

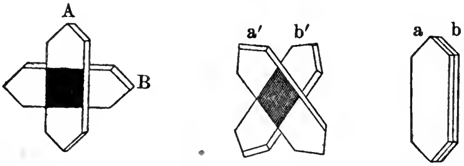
If a pinhole be made through a card, and the card be placed over a crystal of Iceland spar and held before the eye toward the light, there will appear to be two holes, with light shining through each. If the crystal be made to rotate in a plane parallel with the card, then one of the holes will appear to remain nearly at rest, while the other rotates about it. These facts show that a ray of light on entering 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 refracting double. 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. 24, 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.*

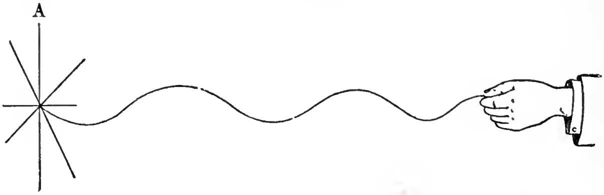
FIG. 24.



Tourmaline plates.

In order to understand polarization of light, we should bear in mind that the particles of ether undulate in a variety of planes perpendicular to the line of propagation. We assume 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. 25. According to whether we move the hand horizontally, obliquely, or vertically, the undulations will lie in a horizontal, oblique, or vertical plane, as represented at A.

FIG. 25.

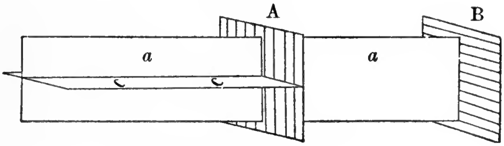


Undulation in a cord.

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 will proceed in that plane. If, however, the slit of one card be set at a right angle to that of another card placed over the string, then 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. 26, 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 in the same plane, a string may be made to vibrate through these gratings parallel to the rods, but when set at a right angle this becomes impossible.

Fig. 26.



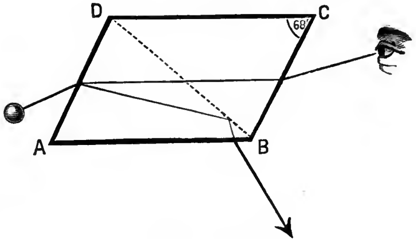
Explanatory diagram of the action of tourmaline plates.

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, polarimeters, or, in a special case, saccharimeters. 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. 27 represents a section of this prism. DB 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's 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.

Fig. 27.



Nicol's prism.

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's 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's 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 direction 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.*

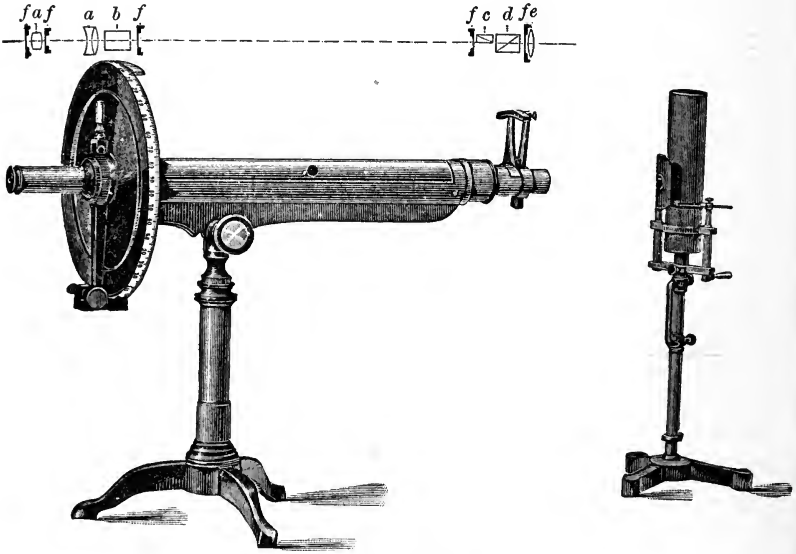
The degree of rotation varies with the quantity of substance in solution for a definite length of a column of the latter, and hence is used to determine the percentage strength, for example, that of sugar in urine and other liquids. Polariscopes are therefore valuable quantitative analytical instruments.

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. 28 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.

FIG. 28.



Lippich's polariscope.

Chemical effects of light. The well-known bleaching effect that sunlight has on many dye-stuffs 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.

QUESTIONS.—What are our views regarding the nature and propagation of light? Explain reflection, refraction, and dispersion of light. What is the prismatic spectrum, and how is it obtained? Give a full explanation of the spectroscope and of its use in chemical analysis. Define continuous, bright-line, and absorption-spectra, and state the conditions under which they are formed. What is meant by double refraction and by polarization of light? Mention the essential parts of the polariscope, and the use made of it in chemical analysis. How are the different colors produced under the influence of white light? What is revealed to us by the Frauenhofer lines in the solar spectrum? Explain the terms dextrorotatory, levorotatory, and optically inactive substances.

4. ELECTRICITY.

Electricity generated by friction. When a glass tube is rubbed with a piece of silk, it will be found to have acquired the property of attracting light bodies, such as scraps of paper, sawdust, etc. Moreover, if the tube be brought close to the face, a sensation similar to that produced by the contact of a cobweb will be experienced. If a knuckle be held near the tube, a peculiar noise is heard, and a spark may be seen to pass between the tube and the knuckle.

These phenomena show that the tube has acquired peculiar properties by friction. It is said to be electrified, and the name *electricity* is given to the cause producing these phenomena. The term electricity is derived from the Greek electron, amber, in which substance the property of attracting light objects after the application of friction was first noticed about twenty-five hundred years ago.

Conductors and non-conductors. Besides glass and amber, there are many substances, such as sulphur, sealing-wax, hard rubber, etc., which can be readily electrified by friction. On the other hand, a bar of metal cannot be electrified unless it be fitted to a glass rod, a piece of rubber, or to certain other substances, and held by this handle while being rubbed with flannel. Moreover, it can be shown that a piece of glass or sulphur will attract particles —*i. e.*, becomes electrified—at that spot only where it has been rubbed, while a tube of metal, fastened to a suitable handle, becomes electrified over the whole surface of the tube. These facts show that electricity when generated in such bodies as glass, sulphur, and rubber, remains where it has been produced, while in metals it immediately spreads over the whole mass.

Bodies of the first kind, such as glass, etc., are said to be *non-conductors,* while materials such as metals are said to be *conductors.* A non-conductor is often called an *insulator,* and a conductor supported by a non-conductor is said to be *insulated.*

The reason that conductors, such as metals, cannot be electrified by friction unless held by a non-conductor, is that the human body is a good conductor, and therefore carries off the electricity as quickly as it is generated.

No substance is absolutely non-conducting, but the difference in this power possessed by what are termed good conductors and non-conductors is very great. Of conductors, may be mentioned: All metals, charcoal, acids, saline solutions, living animals and vegetables, water, moist earth and stones. Non-conductors are: Shellac, rubber, resins, sulphur, wax, glass, silk, wool, porcelain, dry paper and dry air.

Duality of electricity. For a further study of electrical phenomena the simple instrument known as the electric pendulum or pith-ball electroscope may be used. It consists of a pith-ball suspended by a silk fibre from an insulated support. When an electrified glass rod is brought near the ball, the latter is attracted; but as soon as it touches the rod the attraction is changed to repulsion, which lasts as long as the ball retains the electricity it has acquired by contact. The same phenomena may be shown by employing any other electrified body, for example a piece of sealing-wax, sulphur, etc., in place of the glass rod. If while the pith-ball exhibits repulsion for the glass electrified resin is brought near the ball, it is attracted by the resin; and when it is repelled by the resin it is attracted by the glass. These phenomena clearly show that the electricity developed on the resin is not of the same kind as that developed on the glass. They exhibit opposite forces toward any third electrified body, each attracting what the other repels. They have accordingly received names which indicate opposition. The electricity which glass acquires when rubbed with silk is called *vitreous* or *positive,* and that which resin acquires by friction with flannel, *resinous* or *negative* electricity.

On repeating the experiment with other substances, it is found that all electrified bodies behave like either glass or resin. An electrified body is spoken of as being *charged* with electricity; the charge may be either positive or negative. Experiments show that, whenever electricity of one kind is developed, whether by friction or other means, an equal quantity of the opposite kind is simultaneously developed. Thus, in rubbing glass and silk the glass is charged with positive, the silk with negative electricity. If a conductor receives two charges of electricity of equal quantity but opposite kind, it exhibits no trace of electricity, the two charges having neutralized one another.

The kind of electricity which a body obtains by friction with another body evidently depends on the nature of the bodies. For instance, if glass be rubbed with cat's skin the glass becomes charged with negative, but if rubbed with silk it becomes charged with positive electricity. In the following "potential series" any one of the bodies named becomes positively electrified when rubbed with one of the bodies following, but negatively electrified when rubbed with one of those which precede it:

1. Cat's skin.
2. Flannel.
3. Ivory.
4. Glass.
5. Silk.
6. Human body.
7. Wool.
8. Metals.
9. Sealing-wax.
10. Resin.
11. Sulphur.
12. Gutta-percha.

When an electrified body is brought to its normal condition it is said to be *discharged.* The discharge may take place slowly through the air, or rapidly by bringing the charged body in contact with the earth directly or by means of a conductor, such as the human body or a piece of wire. The discharge may be accompanied by a flash of light, called a *spark.*

Induction. A body charged with electricity will exert an influence upon surrounding unelectrified bodies and destroy the neutral condition existing in them, attracting to the surface next to the electrified body a charge the opposite to that which it contains. But while one kind of electricity is drawn toward the original electrified body, an equal quantity of the opposite kind of electricity is driven toward the farther extremity of the bodies which are under the influence of the electrified body. This action exerted by an electrified body on another body is called *induction.*

Induction of bodies connected with the earth can last only so long as they are under the influence of the electrified body, because as soon as this is removed the induced electricity is immediately carried off by the earth. But if an insulated body be brought near one that is electrified, and while under its influence be touched at the end opposite to the electrified body so as to carry off the electricity there gathered, then on removing the electrified body the previously neutral body will be found to be electrified with a charge opposite in character to that of the originally electrified body. This method of imparting electricity is called *charging by induction.* Induction furnishes us the explanation of the attraction and repulsion of light materials by electrified bodies. A positively excited body decomposes the normal charge present in other bodies, and if sufficiently light they move toward the excited body, discharging their negative electricity and becoming charged positively through contact; they are now repelled, as both bodies are electrified alike.

Electrical machines. Electricity produced by friction or by induction is called *static electricity,* or electricity at rest, to differentiate it from *current electricity*, or electricity in motion, which will be considered later. Various machines have been constructed to generate static electricity. In the older forms of such machines friction between glass plates or glass cylinders and pads of silk served as the generating source. In the newer and more powerful forms of static machines, such as the Toepler-Holtz machines, induction chiefly is used to generate the electricity.

Nature of Electricity.—The most modern theory of the nature of electricity teaches that it is a manifestation of some manner of strain set up in the hypothetical ether. But this theory cannot be discussed to advantage in this volume. However, the following lines may assist the student in getting an idea of what electricity is, and how it acts.

It has been stated that energy is a universal property of matter, and that energy, like matter, can neither be created nor destroyed. But energy, like matter, can be changed from one form to another, or from one place to another. According to whether energy manifests itself in masses, in molecules, or in atoms, we speak of mass energy, molecular energy, and atomic energy. Mass energy becomes manifest in the attractions due to gravitation, such as the fall of bodies; in magnetic attractions, as when a magnet attracts iron; in electric attractions, as when an electrified body attracts light particles of matter. Molecular energy manifests itself in heat, in light, in magnetism, and in electricity. Just what the difference is between the different kinds of molecular motion that produce in one case heat, in others light or electricity, has never been discovered. It is supposed to be in the form of undulations or vibrations, the heat undulations having one form, the electric undulations another form, so that while both kinds of motion are found in the same body at the same time, they do not interfere with each other.

Exactly as in the case of heat and light, we have to assume that the propagation of electricity through space takes place in the ether. There is, moreover, a mutual reaction between the vibratory motion of the molecules and the undulatory motion of the ether, the vibrations producing the undulations, and the undulations, in turn, producing the vibrations; just as the vibratory strokes of an oar produce waves, which in turn may produce vibrations in other oars resting in the water.

The conclusion, therefore, to which we come in regard to the nature of electricity is this: Electricity is a manifestation of energy believed to consist in undulations of the ether and vibrations of the grosser molecules of matter.

We see, then, that electricity is neither energy nor matter, but, like heat, light, and sound, it is an effect produced by energy on matter. But as the effect cannot be separated from its cause, it is convenient to speak of it as *electric energy*, in the same sense as we speak of mechanical enegy, vital energy, heat energy, or energy in any other form in which it becomes manifest as associated with matter.

To obtain electricity, energy in some other form must be expended, whether it be the energy of our body expended in rubbing together pieces of glass and silk, or the energy of chemical action, as in a battery cell, or the potential energy of coal used in the mechanical working of a dynamo. All methods of generating electricity bring about a disturbance of the electrical equilibrium existing under normal conditions in all matter. Whenever this equilibrium is disturbed there is a tendency to re-establish it, and it is during the process of re-establishing the equilibrium that work is done electrically.

One of the principal reasons that electrical phenomena offered great difficulties to the investigator is that the electric undulations taking place in the ether produce no effect whatever on our senses. Waves of air in striking certain nerves in the ear produce the sensation of sound; waves of ether affect certain other nerves in such a manner as to produce the sensations of heat and light, but man has no nerves that are affected by electric or magnetic waves—*i. e.*, he is magnetically and electrically blind and deaf. The slow development of the science of electricity was due to this fact.

Magnetism. The native iron ore known as lodestone or magnetite (ferrous ferric oxide) has the power of attracting bits of steel or iron, and also possesses the property of pointing north and south when suspended by a thread. Pieces of iron may be caused to acquire the same properties, and all bodies possessing them are called *magnets*, while *magnetism* is the term used to designate the magnetic condition of matter.

Any bar of steel or iron may be magnetized by drawing over it lengthwise a magnet; but while a piece of hard steel will remain a magnet almost indefinitely, soft iron loses its magnetism very readily. A pivoted or suspended magnet always places itself in the direction of the "magnetic meridian" of the earth—*i. e.*, nearly north and south. The end of the magnet pointing north is called its *north pole*, the other its *south pole*. On bringing one pole of a magnet near a suspended magnet it is found that with magnetism, as with electricity, like poles repel and unlike poles attract each other. There exists also magnetic induction, corresponding to induction by electricity. This can be shown by placing a bar of iron near a magnet, when it is found that the end of the bar nearest the north pole is converted into a south pole, and *vice versa*.

When a magnetized bar is dipped into iron filings, masses of the filings adhere to the two extremities—*i. e.*, to the two poles—while none are found at the centre. When a magnetic bar is cut in halves at the non-magnetic centre, two magnets are produced; and this cutting into smaller lengths may be continued indefinitely, with the result that each length, and finally each particle, possesses two poles and an intermediate neutral zone. This fact, as well as other considerations, has led to the assumption that each molecule of iron is a magnet in itself. In ordinary iron these little magnets are not arranged systematically, while in magnetized iron all the north poles point in one direction, all the south poles in the opposite direction. Moreover, it is supposed that each magnetic molecule is traversed by a closed electric circuit, which currents become parallel upon magnetization of ordinary iron. According to this theory, magnetism is a manifestation of electrical energy.

The shape given to magnets is usually that of a bar or of a horseshoe. A bar of soft iron laid over the poles of a horseshoe magnet is called an *armature;* it serves to retain the full power of the magnet.

When fine iron filings are sprinkled on a piece of glass or cardboard which has been placed over a magnet, the filings arrange themselves in lines radiating from either pole, forming graceful curves from pole to pole. These lines, called *lines of magnetic force,* represent the resultant of the combined action of the two poles, the space surrounding a magnet as far as its influence extends being termed its *magnetic field.* A magnetic needle placed anywhere in this field follows the lines of magnetic force, always assuming a position tangent to the magnetic curve.

The explanation given for the fact that the magnetic needle points north and south is that the earth itself is an immense magnet, possessing two magnetic poles which are close to the geographical poles.

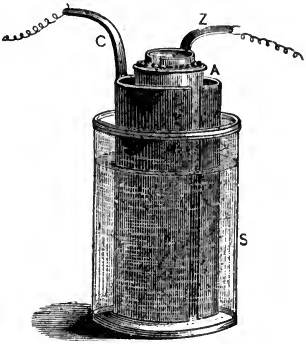
Electricity generated by chemical action. On placing a strip of ordinary zinc in diluted sulphuric acid, bubbles of hydrogen gas are evolved on its surface and the zinc gradually dissolves; a piece of platinum placed in the acid is not affected at all. If, however, strips of zinc and platinum are placed in a vessel containing diluted acid, on connecting the plates above the liquid by a conductor, for instance by a piece of copper wire, characteristic changes take place. First, the evolution of gas stops on the zinc, while bubbles of hydrogen escape from the surface of the platinum. Next, on placing the connecting wire near a magnetic needle, this is turned from its course—*i. e.,* deflected. And again, on cutting the wire and placing the tongue between the two ends, a metallic taste and a tingling sensation are perceived. All these phenomena cease as soon as the connection between the plates is broken, and reappear when connection is again established.

Undoubtedly something takes place in the wire while the plates are in the diluted acid. Further investigation shows that during the action of the acid on the metals electricity is generated, which travels through the wire, imparting to it characteristic properties.

Galvanic or voltaic cells. In place of zinc, platinum, and sulphuric acid, many other materials may be used to bring about the conditions described in the preceding paragraph ; indeed, electricity is generated whenever two solids (plates or cylinders are generally used), conductors themselves and connected by a conductor, are placed in a liquid that has the power to act chemically on one of the solids. Any such arrangement is termed a *galvanic* or *voltaic* cell. Here chemical action causes the generation of electricity, resulting in the zinc-platinum cell in the splitting up of sulphuric acid, H_2SO_4, the hydrogen, H_2, escaping from the platinum plate, while the group SO_4 combines with the zinc, forming zinc sulphate, $ZnSO_4$, which dissolves in the water.

Many combinations are employed in the different cells for generating electricity. Fig. 29 represents the *Daniell cell.* It consists of the glass jar S, containing a saturated solution of cupric sulphate, in which stands the copper cylinder C. Inside of this cylinder fits a porous cell, A, containing sulphuric acid, and into this dips the zinc plate Z.

Fig. 29.



Daniell's cell.

Chemically pure zinc is scarcely acted on by diluted sulphuric acid ; ordinary zinc contains metallic impurities, and as these are in contact with zinc, they set up a galvanic action, and thus bring about the chemical changes above described.

What is believed to take place in any galvanic cell is that the electrolytic fluid—*i. e.*, the active agent in the liquid state—is split up into two component parts, called *ions*, and that these ions, charged with positive and negative electricity, respectively, unload these charges on the two plates, while an equalizing effect is brought about through the connecting wire. In other words, there is a constant disturbance of the electrical equilibrium through chemical action, and a tendency to re-establish the equilibrium, which tendency produces the current.

One of the plates (platinum, in the case cited above) is known as the *positive electrode* or *anode*, while the other one (zinc) is the *negative electrode* or *cathode* of the cell. The same terms are used also to designate the terminals of the wires leading from the two plates, which terminals are called also + and − poles.

Whenever the plates are connected by the conducting wire electricity passes from the anode through the wire to the cathode, and through the liquid back to its point of origin. This continuous motion is called the *electric current,* and the different parts through which the current passes are known as the *circuit.* Whenever the connection is broken at any point the circuit is said to be open; otherwise it is closed. If the circuit be open, both plates become charged with positive and negative electricity, respectively; but as there is no conductor to carry off these charges, further accumulation stops, and chemical action ceases until the circuit is again closed.

Whenever two or more galvanic cells are connected so as to use in one circuit the electricity generated by all the cells, the arrangement is spoken of as a *galvanic battery;* at present this term is likewise applied to a single cell.

Electromotive force. The fact that electricity flows continuously in a closed circuit containing a galvanic cell shows that the cell has the power of setting electricity in motion, and this power is designated as *electromotive force* (E. M. F.), *electrical tension,* or *potential.* It is the result of the tendency to re-establish equilibrium, and depends upon the difference in the electrical condition of the two plates; the greater this difference the greater the E. M. F.

The action of an electric battery may be compared to a pump sending water from a reservoir through a pipe to a higher elevation; the water will return to its former level with a certain force, depending on the height to which it has been lifted, and the water while descending can be made to do mechanical work—turn a wheel or set in motion other machinery. Similarly the current of electricity on its return trip can be made to do work, and the quantity of it depends on the E. M. F. generated by the battery.

Electric units. For obvious reasons, it is desirable to measure the intensity and quantity of electric currents similarly as heat or other forms of energy are measured. The three chief units adopted for such measurements are named, in honor of three great pioneers in electricity, the ohm, the ampère, and the volt.

It has been stated that we differentiate between conductors and non-conductors, but even the best conductors offer resistance to the passage of an electric current. The unit of this resistance is called the *ohm,* and represents the resistance to a current in a column of mercury having a section of 1 square millimeter and a length of 106.28 centimeters, at a temperature of 0° C. For practical purposes, sets of coils, known as *resistance coils*, having a known resistance, are used for measuring electrical resistance.

An *ampère* is the unit of quantity of current, which may be determined by measuring the amount of oxygen and hydrogen liberated by the current from water within a given time.

The weight of copper deposited electrolytically by the current is used also as a means of determining its ampèrage. One ampère of current deposits 1.177 grammes of copper per hour. For practical purposes, instruments known as *ampèremeters*, or *ammeters*, are used for measuring ampèrage; use is made in these instruments of the fact that a current deflects a magnetic needle, which is made to move over a dial-face graduated in ampères.

In using electric currents for medical purposes, 1 ampère is often too strong for the tissues of the body. For this reason the unit is divided into 1000 parts, each part being designated as a milliampère.

The *volt* is the unit for electromotive force, and is the pressure required to maintain a current of 1 ampère through a resistance of 1 ohm.

The relation existing between these three units is expressed in Ohm's law: The strength of the current is equal to the E. M. F. divided by the resistance of the current.

The chief difference between frictional and galvanic electricity is that the first is of high tension but small in amount, while current electricity is of low tension but greater in amount.

Electromagnets. When a piece of insulated wire is wound in spiral form around a bar of soft iron, and an electric current is made to pass through the wire, the iron becomes a magnet for the time being, and is then called an *electromagnet.* If a piece of steel is treated in the same way, it remains a magnet even after the current is broken, or after it has been taken from the spiral.

As the strength of an electromagnet is proportional to the strength of the current and the length of wire wound around it, electromagnets of very much greater power than ordinary magnets can be made The position of the north and south poles of the magnet depends on the direction of the current, a reversion of the latter producing a reversion of the polarity in the electromagnet. Practical use is made of the electromagnet in telegraph instruments, in the telephone, the electric bell, and in many other contrivances.

Electricity generated by magnetism. Not only can magnets be made by subjecting iron to the influence of electric currents, but, *vice versa,* electric currents, termed *magneto-electric currents,* can be generated by the action of magnets on metallic wires. Indeed, whenever a magnet is brought near to, or taken away from, a wire, or is moved about in its neighborhood; or if, *vice versa,* a mass of wire is moved around a magnet—*i. e.,* whenever metallic wires are made to pass through a magnetic field—temporary electric currents are always set up in the wire. These induced currents are the result of the conversion of mechanical energy—*i. e.,* the energy required to move a wire or a magnet—into electrical energy.

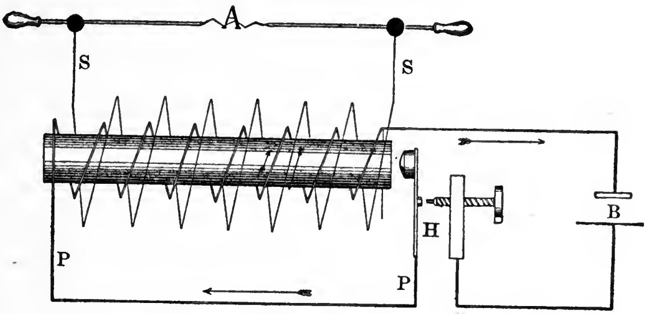
Use is made of these facts for the generation of electric currents by suitably constructed machines, known as *magneto-electric machines.* In the smaller ones a permanent horseshoe magnet is used. Between or in front of its poles revolve two coils of insulated wire with soft iron cores, known as *armatures.* During rapid revoluting the soft iron cores are magnetized while opposite one of the poles of the permanent magnet, demagnetized while equidistant from the two poles, and reversed while passing to the opposite pole. The magnetization and demagnetization of the iron cores have the same effect on the coils of wire as if a magnet were suddenly introduced into the coil and as quickly withdrawn. Thus currents will be induced in the wire, and they will run in opposite directions as the polarity of the cores changes with each half revolution. Such currents are known as *alternating currents.*

The same principle is made use of in the *dynamo-electrical machines* for generating the currents employed for motive power, electric lighting, etc. Instead of permanent magnets, powerful electromagnets are here used, and in place of an armature with two coils of wire, armatures with many coils are employed. Moreover, an arrangement known as the *commutator* is often used to change the alternating to a direct or continuous current—*i. e.,* the generated electricity is collected in such a manner that it moves in one direction continuously.

Electric motors are essentially dynamos in which the action is reversed—*i. e.,* electric currents convert iron into electromagnets, which by successive attraction and repulsion of the iron in the armature cause its rapid rotation, which motion may be communicated to other machinery.

Voltaic induction. It has been mentioned that a body charged with static electricity causes, by induction, an electric disturbance in all bodies near by. Similarly an electric current passing through one wire sets up induced currents in neighboring wires. One of the principal applications made of these induced currents is in the *induction coil,* or *Ruhmkorf coil,* shown diagrammatically in Fig. 30. It consists of a hollow cylinder covered with a coil of insulated and relatively coarse wire, P, connected with a battery, B. Over this first or primary coil is wound another, the secondary coil, S, composed of much longer and finer wire.

FIG. 30.



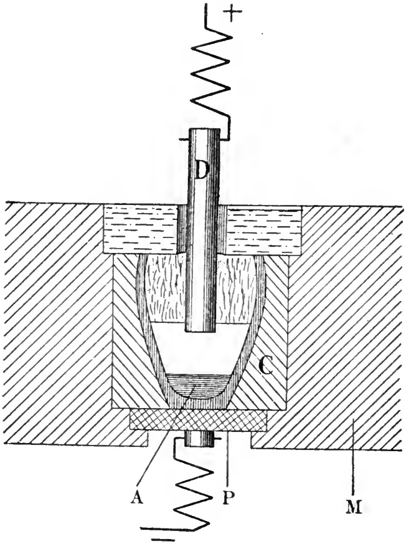
Induction coil.

While a current passes through the primary wire nothing is noticed in the secondary wire, but the instant the current is closed an instantaneous induced current is set up in the secondary wire in one direction, and on opening the circuit in the opposite direction. It follows that it requires a rapid closure and opening of the circuit to generate electricity in the secondary coil. The opening and closing of the current are accomplished by the following self-acting arrangement. In the hollow portion of the primary coil are placed bars of soft iron, which are magnetized whenever a current passes through the coil. Near one terminal of the iron bars is a movable metallic hammer, H, held by a spring in such a position that the current is closed by it. When the bars are magnetized, they raise the hammer, thereby opening the circuit; the cessation of the current causes the iron to be demagnetized and the hammer falls to its original position, closing the circuit, and this action continues as long as the current is allowed to flow. This arrangement, known as a "make and break" contrivance, generates, through the very rapid opening and closing of the primary circuit, in the secondary coil that current which is known as *secondary, induced, interrupted,* or *faradic current.*

The object of the induction coil is to generate from a battery current of low E. M. F. induced currents of very high E. M. F. The effectiveness of the induction coil increases with the length of its wire, which in large instruments is fifty miles and more. While such machines are in operation sparks several feet in length will pass between the terminals of the secondary coil at A.

Conversion of electrical energy into heat and light. Whenever a current passes through a wire (or through any other mass) it offers more or less resistance, the amount of which depends on the nature of the material and the thickness of the wire. 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.

Fig. 31.

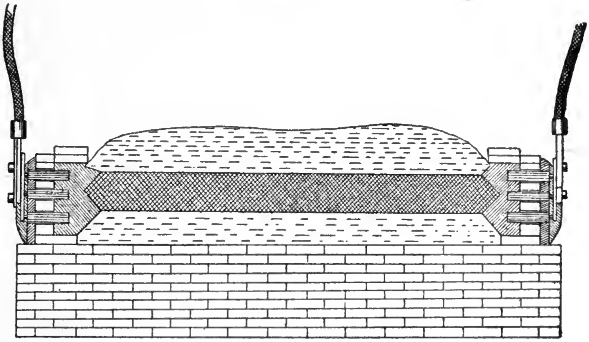


Electric furnace.

The construction of electric furnaces differs widely according to the use made of them. Fig. 31 represents the vertical section of a 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.

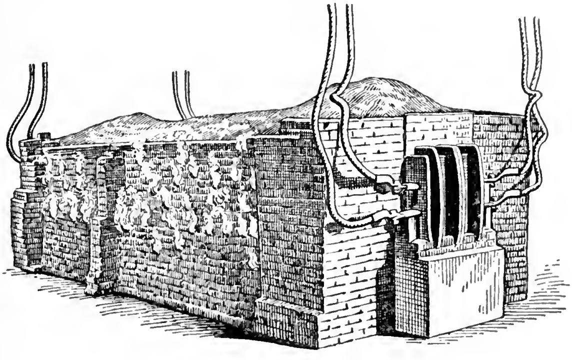
Fig. 32 gives a sectional, and Fig. 33 an exterior, view of an electric furnace used in the manufacture of carborundum. The current enters and leaves through the cables which terminate in carbon electrodes fastened in the wall. Between the electrodes is a mass of coke, which, while conducting the current, offers sufficient resistance to be heated to an extremely high temperature. (For details of the chemical action see the article on Carborundum.)

Fig. 32.



Longitudinal section of carborundum furnace.

Fig. 33.

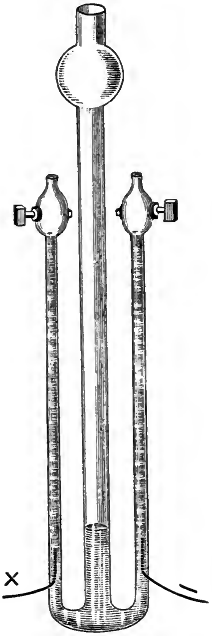


Exterior view of carborundum furnace.

The electric arc lamp and the incandescent lamp are well-known examples of the conversion of electrical energy into light. In the former lamp electricity of very high electromotive force (1000–3000 volts) passes between terminals of pencils of hard carbon, which, while infusible, burn away gradually, requiring an automatically acting contrivance to keep the two pencils at a constant distance. In the incandescent lamp a filament of carbon, fastened in an exhausted glass globe, is heated to a white heat by a current of about 50 to 120 volts.

Conversion of electrical energy into chemical action. 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. 34 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.

FIG. 34.



Electrolysis of water.

Electropositive are:	Electronegative are:
Hydrogen,	Oxygen,
Metals,	Halogens (chlorine, etc.),
Bases and basic radicals.	Acids and acid radicals.

When an electric current passes through a solution of any salt, this is split up into the base and the acid composing the salt. If the base be a metal, such as copper, it will be deposited on the electronegative 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.

Electrolysis is used also on a large scale for separating metals from ores, or from one another, and on a small scale for analytical operations; it also plays an important part in the work done by the electric furnace, in which often both the required high temperature and the decomposing influence are furnished by the electric current.

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 lightning. This spark in many cases exerts chemical action, as, for instance, when oxygen is converted into ozone, which change will be considered later.

If the discharge take 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.

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; they cannot be reflected or refracted. 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 Madam 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 farther 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 gramme 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 one gramme of radium bromide will raise the temperature of 80 grammes of water one degree C. per hour.

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, possesses remarkable penetrating power and great photographic energy; they are not deviated from their path under the influence of a magnetic field, and resemble the Röntgen rays in their action. The *beta* rays produce heat, are deviable under the influence of a magnetic field, and resemble cathode rays. The third group—*gamma* rays—is easily absorbed.

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 Röntgen 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 will 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.

When the apparently never-diminishing power of radium to give out continuously light and heat was discovered, it appeared as if our views regarding matter and energy were completely upset. A closer investigation, however, has shown that this apparently unlimited source of energy may be explained in a way conforming to our previous views.

What is supposed to take place is this: All radio-active substances send out with enormous velocity particles, called *corpuscles,* which are a thousand times smaller than a hydrogen atom. This substance which is thrown off, and which Crookes designates the *fourth state of matter,* or *radiant matter,* is called *emanation.* The phenomena of radio-activity, previously described, are due to these emanations which cause a bombardment of everything lying in their paths.

The discovery of radiant matter has modified our views regarding 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. (For the manufacture of radium compounds, see the article on Radium.)

QUESTIONS.—Name some conductors and non-conductors of electricity, and explain their behavior in connection with electrical phenomena. What is meant by positive and negative, and by static and current electricity? Describe three methods for generating electricity. Name the three principal units used in the measurement of electrical currents, and explain the methods employed. Explain the construction and action of a galvanic cell. What is a permanent magnet, and what is an electromagnet? How are they made, and what are their characteristic properties? Define the following terms: Anode, cathode, circuit, electric current, induction, and electromotive force. Describe construction of the electric furnace, and explain its action. How may electricity be used in the generation of heat, light, mechanical motion, and chemical action?

II.

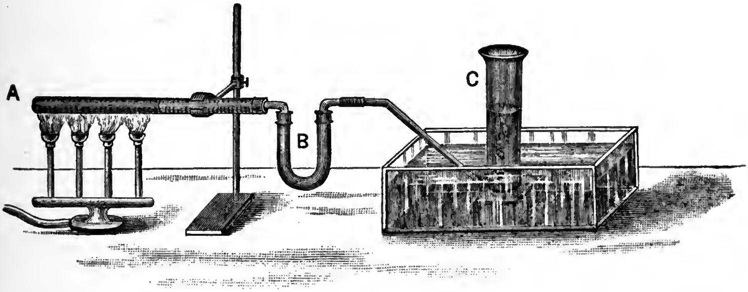
PRINCIPLES OF CHEMISTRY.

5. 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. 35.



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. 35).

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 subdivided 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 seventy-six 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.

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 electricity. It has been shown in Chapter 4 that electricity exerts under certain conditions a strong decomposing influence on many compounds. It was also stated that this process of decomposition is called *electrolysis,* while the term *electrolyte* is given to the material acted upon. This material 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.

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.

Decomposition by light. Another cause of decomposition is, in many cases, the action of light. The art of photography is based upon this kind of decomposition. Many substances, easily affected by light, have to be kept in the dark to prevent them from being decomposed.

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, 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.

6. LAWS AND THEORIES OF CHEMISTRY.[1]

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

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[1] The subject matters of chapters 6, 7, 8, and 9 are grouped together for convenience. It is not intended that they should be taken up in lectures or class work at once after chapter 5, nor in the exact order given here, but each instructor will introduce them in what, to him, seems the most logical sequence.

starch may be easily distinguished. The mixture thus produced is a *mechanical mixture of molecule clusters.*

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, one part by weight of hydrogen is taken as the standard of reference, which offers the advantage that none of the figures is less than unity. Let us illustrate by a few examples: One part of hydrogen unites with 35.18 parts of chlorine, 35.18 parts of chlorine unite with 38.82 parts of potassium, 2 × 38.82 parts of potassium unite with 15.88 parts of oxygen. But 2 × 1 parts of hydrogen also unite with 15.88 parts of oxygen. Also 15.88 parts of oxygen unite with 64.91 parts of zinc, and 64.91 parts of zinc unite with 2 × 35.18 parts of chlorine. Thus we see that the figures in these instances are reciprocally related, and the same is true for the figures assigned to all the other elements. This system of figures is called *combining weights*, and has a deep significance, which will appear clearer when the atomic theory is discussed.

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 above as combining weights, for these weights are bound to be proportional to the weight 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 the next 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 is chosen as the unit weight. The figures assigned to the other elements as atomic weights simply signify how many times heavier those atoms are than the atom of hydrogen. In other words, the atomic weights are nothing more than ratios. On the page preceding the Index is a table of the elements, with symbols and atomic weights.

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.

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 one atom of these elements. For instance: O not only signifies oxygen, but one atom or 15.88 parts by weight of oxygen; and Hg, one atom or 198.5 parts by weight of mercury.

Symbols or formulas of compounds. By suitable experiments it is possible for the chemist to determine not only the kinds of elements in a compound and their proportions, but also how many atoms are in a molecule of the substance. For the sake of economy of time and space and to give a better insight into their nature, substances are represented by formulas, which is a shorthand way of telling what would require many words. 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 formulas are formed by writing the symbols of the constituent elements side by side, and the number of atoms of each element, when more than one atom is present, is represented by a figure below and to the right of the symbol of the element; thus H_2O means that a molecule of water consists of two atoms of hydrogen and one atom of oxygen; CO_2 means that the carbon dioxide molecule consists of one atom of carbon and two atoms of oxygen. A number placed before a formula signifies so many molecules, thus $2H_2O$ means two molecules of water. As the formulas represent the size of the molecules, they are called *molecular formulas*, and the sum of the atomic weights of all the atoms composing the molecules is called the *molecular weight*, which shows how many times heavier the molecule is than an atom of hydrogen.

To establish a molecular formula requires a careful quantitative determination of the proportions of the constituents of a compound; conversely, if we know the molecular 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 molecular formula, HgO. In the molecule there is an atom of mercury weighing 198.5 times as much as an atom of hydrogen, and an atom of oxygen weighing 15.88 times as much as an atom of hydrogen. It is evident that the weights of the mercury and oxygen in a molecule are to each other as 198.5 : 15.88. What is true of one molecule must be true of any number of molecules, that is, of any quantity of oxide of mercury; hence we can conclude that in the oxide there are 198.5 parts of mercury to every 15.88 parts of oxygen, making $198.5 + 15.88 = 214.38$ parts of oxide. To calculate the percentage composition, or parts per hundred, we use the proportions,

$$214.38\ HgO : 198.5\ Hg :: 100\ HgO : x\ Hg \text{ and}$$
$$214.38\ HgO : 15.88\ O :: 100\ HgO : x\ O.$$

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:

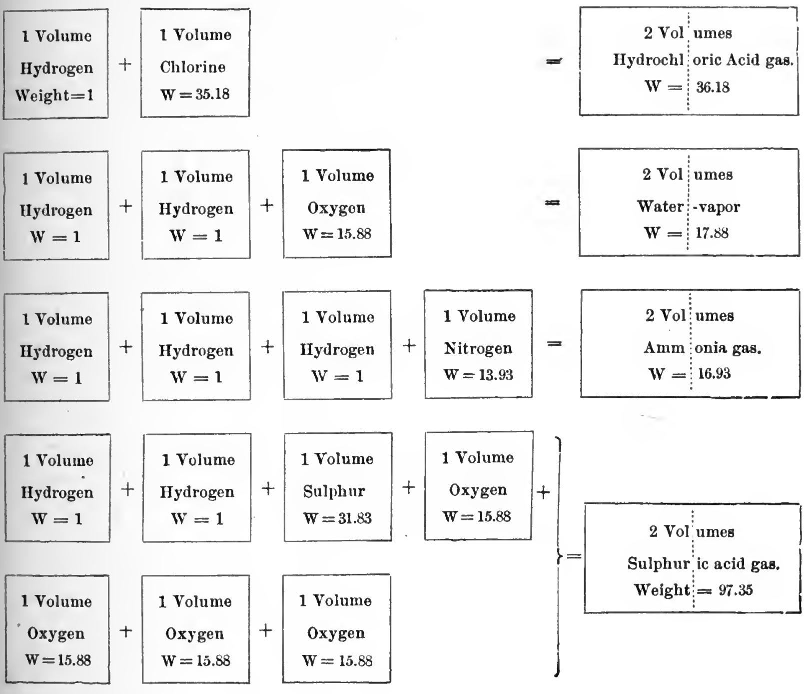
$$198.5\ Hg : 15.88\ O :: 30\ Hg : x\ O.$$
$$198.5\ Hg : 214.38\ HgO :: 30\ Hg : x\ HgO.$$

We learn from the discussion above that the elements enter into combination in quantities represented by their atomic weights, or multiples of these, to produce a quantity of compound represented by the molecular weight.

The law of chemical combination by volume, or the *Law of Gay-Lussac,* 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 atomic or molecular weights of the elements.

For instance: Equal volumes of hydrogen and chlorine combine, and the weights of these volumes are as 1:35.18, which numbers represent also the atomic weights of the two elements. Two volumes of hydrogen combine with one volume of oxygen, and the weights of the volumes are as 1 : 7.94 or 2 : 15.88, the latter being the atomic weight of oxygen.



The above diagram shows the simple relation which exists between combining volumes and atomic and molecular weights. It was, besides other factors, the discovery of this relation that led to the adoption of Avogadro's Law, which has been stated. (See Chapter I., page 30.)

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 two 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.

Theory (Law) of equivalents. Valence, or Quantivalence. When one element replaces another element in a compound, the quantities of the two elements are said to be equivalent to each other, and according to the law of equivalents the replacement of elements one by another takes place always in definite proportions. Formerly it was believed that the atoms of all elements were equivalent one with another; 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.

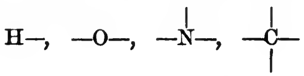
Those elements which combine with hydrogen or other univalent elements in the proportion of one atom to two atoms are bivalent, such as O, S, Se.

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.

Elementary atoms are often named according to their valence: *monads, diads, triads, tetrads, pentads, hexads, and heptads.*

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}.

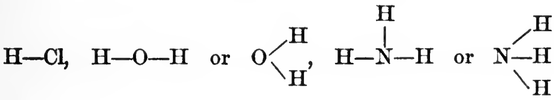
The bonds are often graphically represented by lines, thus:



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

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, and it 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.

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? 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. 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. What atom is chosen as the unit of atomic weights, and why? What are chemical symbols and what do they signify? Calculate the per cent. of oxygen and hydrogen in water, H_2O. What weight of carbon dioxide, CO_2, would result from 25 grammes of carbon? What regularity regarding volume is noticed when gases combine? Define valence. What were considered formerly as equivalent quantities, and what are such at present? Mention some univalent, bivalent, trivalent, and quadrivalent elements. What explanation is offered for variable valence?

7. DETERMINATION OF ATOMIC AND MOLECULAR WEIGHTS.[1]

Determination of atomic weights by chemical decomposition. The great difficulties originally encountered in the determination of atomic weights cannot well be described here. Consideration will be given alone to the three principal methods at present in use. These methods depend either on chemical action or on physical properties.

One of the chemical methods used for the determination of atomic weights depends upon the determination of the proportions by weight in which the element, the atomic weight of which is unknown, combines with an element the atomic weight of which is known. For instance: If in decomposing a substance we find it to contain in 72 parts by weight, 16 parts by weight of oxygen[2] and 56 parts by weight of another element, we have a right to assume the atomic weight of this second element to be 56, provided, however, that the compound is actually formed by the union of one atom of oxygen and one atom of the other element. These 56 parts by weight might, however, represent 2, 3, or more atoms. If 56 represented 2 atoms, the atomic weight would be but 28; if 4 atoms, 14.

As this mode of determination gives no clue to the number of atoms present in the molecule, the results obtained are liable to be incorrect. In fact, the atomic weights of a number of elements had originally been determined incorrectly by using the above or similar methods, and many of these old atomic weights had to be changed (generally doubled) in order to obtain the correct numbers.

Thus, in examining water, it was found that it contained 8 parts by weight of oxygen to 1 part of hydrogen, and the conclusion was drawn that the atomic weight of oxygen was 8, and that the molecule of water was formed by the union of one atom of hydrogen and one atom of oxygen. It will be demonstrated below why we assume to-day that the atomic weight of oxygen is 16, and that the molecule of water is composed of 2 atoms of hydrogen and 1 of oxygen.

Another chemical method of determining atomic weights is the replacement of hydrogen atoms in a known substance by the element the atomic weight of which is to be determined. For instance: Hydrochloric acid is composed of one atom of chlorine weighing 35.2, and one atom of hydrogen weighing 1, the molecular weight of hydrochloric acid being 36.2. If in this acid the hydrogen be replaced by some other element, for instance by sodium, we are enabled to determine the atomic weight of sodium by weighing its quantity and

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[1] The consideration of Chapter 7 should be postponed until the student has become familiar with chemical phenomena generally.

[2] For purposes of discussion, whole numbers are often used in place of exact atomic weights when these contain decimals.

that of the liberated hydrogen. Suppose that by the action of 36.2 grammes of hydrochloric acid on sodium, 1 gramme of hydrogen was replaced by 23 grammes of sodium. In that case we would say that the atomic weight of sodium is equal to 23.

The difficulty which was alluded to above exists also in this mode of determination of atomic weights, viz., not knowing whether it was actually one atom of sodium that replaced the one part of hydrogen, a doubt is left as to whether or not the determination is correct.

Determination of atomic weights by means of specific weights of gases or vapors. It has been stated before that equal volumes of gases contain, under like conditions, the same number of molecules (no matter how few or many the atoms within the molecules may be), and that the molecules of elements contain (in most cases) two atoms. These facts give in themselves the necessary data for the determination of atomic weights.

For instance: If a certain volume of hydrogen is found to weigh 2 grammes, and an equal volume of some other gaseous element is found to weigh 71 grammes, then the atomic weight of the latter element must be 35.5, because 2 and 71 represent the relative weights of the molecules of the two elements. Each molecule being composed of 2 atoms, these molecular weights have to be divided by 2 in order to find the atomic weights, which are, consequently, 1 and 35.5 respectively.

In comparing by this method oxygen with hydrogen, it is found that equal volumes of these gases weigh 32 and 2 respectively, that the atomic weight of oxygen is consequently 16, and not 8, as determined by chemical methods.

This mode of determining atomic weights may be applied to all elements which are gases or which may without decomposition be converted into gas. There are, however, elements which cannot be volatilized, and in this case it becomes necessary to determine the specific gravity of some gaseous compound of the element. The element carbon itself has never been volatilized, but we know many of its volatile compounds, and these may be used in the determination of its atomic weight.

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	7	6.59
Sodium,	0.2934	23	6.75
Sulphur,	0 2026	32	6 48
Zinc,	0 0956	65	6.22
Bromine (solid),	0.0843	79	6.66
Silver,	0.0570	107	6.10
Bismuth,	0.0308	209	6 44

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 of lithium 7 grammes, of sulphur 32 grammes, of silver 107 grammes, we have of course in these quantities equal numbers of atoms, because 7, 32, and 107 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 7 grammes of lithium 1°, which is necessary to raise either 32 grammes of sulphur or 107 grammes 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, 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.

Determination of molecular weights. From the statements made regarding the determination of atomic weights, it is evident that we may use a number of methods for determining molecular weights, these methods being to some extent analogous to the former.

Thus we have methods which are based entirely on chemical analysis or on chemical changes generally. If, for instance, the analysis of a substance shows of calcium 40 per cent., of carbon 12 per cent., and of oxygen 48 per cent., we have a right to assume that the molecule is made up of 1 atom of calcium, 1 atom of carbon, and 3 atoms of oxygen, as the atomic weights of these elements are 40, 12, and 16 approximately. The molecular weight in this case is 100, and the composition is expressed by the formula $CaCO_3$, but the molecular weight might be 200 and the correct formula $Ca_2C_2O_6$. There are actually substances which contain such multiples of atoms, as, for instance, the compounds C_2H_2 and C_6H_6, and as their percentage composition is identical, analytical methods are insufficient to indicate the number of atoms contained in these molecules.

The second method, based on Avogadro's law, is applicable to all substances which are or can be converted into gases or vapors without decomposition. 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. As we have seen, the molecule of hydrogen is known to contain two atoms, that is, its molecular weight is 2, if we call the weight of its atom 1. Hydrogen is usually chosen for comparison with other gases. Suppose it is desired to find the molecular weight of oxygen. One liter of oxygen at 0° C. and 760 mm. of pressure weighs 1.429 grammes, one liter of hydrogen under the same conditions weighs 0.08987 gramme. Hence by the proportion,

$$0.08987 : 1.429 :: 2 : x;$$
$$x = 1.429 \times 2 \div 0.08987 = 31.8,$$

that is, the molecular weight of oxygen is 31.8, or the molecule is 15.9 times heavier than the molecule of hydrogen.

If we call the density of hydrogen 1, and refer the densities of other gases to this standard, then the figures indicate how many times heavier the gases are than hydrogen under like conditions, or, what comes to the same thing, how many times heavier the molecules of the gases are than the molecule of hydrogen. Hence, a simple rule for finding molecular weight is to multiply the density of a gas on the hydrogen basis by 2.

Conversely, if we know the molecular weights of two gases, and the density of one of them, we can calculate the density of the other gas. The density of any gas is equal to the density of hydrogen multiplied by half the molecular weight of the gas.

A third method, that of Raoult, 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 32° F. (0° C.), 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

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QUESTIONS.—What are the three principal methods used for the determination of atomic weights? Why are chemical means not always sufficient to determine atomic weights? How can the specific gravity of elements in the gaseous state be used for the determination of atomic weight? Describe a method of the determination of atomic weight by chemical means. State one of the reasons why the atomic weight of oxygen has been changed from 8 to 16. What relation exists between atomic weight and specific heat? State the law of Dulong and Petit. Suppose the specific heat of an element to be 0.1138, what will its atomic weight be? Suppose the specific gravity of an elementary gas to be 14, what will its atomic weight be? Suppose 214.24 grammes of an element replace 2 grammes of hydrogen in 72.36 grammes of HCl, what will the atomic weight of the element be?

water used—then are the molecular weights of the two salts to each other as is 4 to 7.

In regard to this method of Raoult it should be stated that it is applicable only to such substances as do not act chemically upon the solvent used, and that the ratio of the lowering of the freezing-point is not the same for all substances, but only for members of the same class of substances.

8. CHEMICAL EQUATIONS. TYPES OF CHEMICAL CHANGE. REVERSIBLE ACTIONS AND CHEMICAL EQUILIBRIUM. MASS ACTION. ACIDS, BASES, SALTS. RADICAL. CONSTITUTIONAL FORMULAS.

Chemical equations. We have seen that the composition of substances can be expressed by symbols or formulas, which show at a glance the kind of elements and their proportions present in the substances. Similarly, a method of representing what takes place in a chemical change concisely and in a way that can be quickly grasped has been devised. This is done by means of chemical equations. 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, hydrochloric acid and silver nitrate mutually decompose each other and give an insoluble white substance, silver chloride and nitric acid. This may be represented thus, $HCl + AgNO_3 = AgCl + HNO_3$. 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 its 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. The unit of chemical action is the molecule, and the chemical equations are intended to show the action taking place between the molecules. Thus, in the reaction above, one molecule of hydrochloric acid decomposes one molecule of silver nitrate. We often, however, read an equation in a broader and less definite manner, thus, in the above case, we say hydrochloric acid decomposes silver nitrate and gives 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 $2H_2 + O_2 = 2H_2O$.

Every correct chemical equation is correct mathematically also—*i. e.*, the sum of the atoms as well as that of the molecular weights of the factors equals the sum of the atoms and that of the molecular weights of the products respectively. 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 molecular weights of the factors and those of the products we find equal quantities, as follows:

2Na = 45.76		Ca = 39.80		Ca = 39.80		2Na = 45.76
C = 11.91		2Cl = 70.36		C = 11.91		2Cl = 70.36
3O = 47.64				3O = 47.64		
105.31	+	110.16	=	99.35	+	116.12

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.

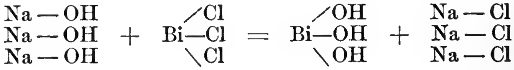
The above calculation teaches, for instance, that 105.31 parts by weight of sodium carbonate are acted upon by 110.16 parts by weight of calcium chloride, and that 99.35 parts by weight of calcium carbonate and 116.12 parts by weight of sodium chloride are formed by this action. These data may, of course, be utilized to find how much calcium chloride may be needed for the decomposition of one pound or of any other definite weight of sodium carbonate; or how much of these two substances may be required to produce one hundred pounds, or any other definite weight, of calcium carbonate.

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 when the relationship between acids, bases, and salts is understood. 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 :

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 :



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.

$Na' + H'Cl =$
$H_2'SO_4 + K'(?) =$
$Ca'' + H'Cl\,(?) =$
$Fe'' + H_2'SO_4 =$
$H'Cl + Ag'NO_3 =$
$Ca''Cl_2 + Ag'NO_3(?) =$
$Bi'''Cl_3 + Ag'NO_3(?) =$

$Cu''SO_4 + H_2'S =$
$Ba''Cl_2 + Na_2'SO_4 =$
$Na_2'CO_3 + H_2'SO_4 =$
$Bi'''(NO_3)_3 + K'OH\,(?) =$
$Al_2'''(SO_4)_3 + K'OH\,(?) =$
$Al_2'''(SO_4)_3 + Ca''(OH)_2(?) =$
$Fe_2'''Cl_6 + Ag'NO_3\,(?) =$

Types of chemical change. 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.*

$$2.\ \left.\begin{array}{l}(a)\ AB = A + B\\ (b)\ ABC = AB + C\\ (c)\ ABC = AC + BC\end{array}\right\}\textit{simple decomposition.}$$

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.

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:

$$MN + PR \rightleftarrows MR + PN.$$

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.

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 8H.$$

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:

$$Fe_3O_4 + 8H \rightleftarrows 3Fe + 4H_2O.$$

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 dissolved 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.

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[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.

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.

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:

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

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

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

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 consistency, 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 show properties which are chemically opposite to those of acids. As a general rule bases are compounds of electro-positive 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 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 hydrogen by acid radicals. In the base lead hydroxide, $Pb(OH)_2$, one of the hydrogen atoms may be replaced by the radical of nitric acid, when basic lead nitrate, $Pb\Big\langle\begin{matrix}NO_3,\\ OH\end{matrix}$ is formed.

In bismuth hydroxide, $Bi(OH)_3$, one, two, or three hydrogen atoms may be replaced by nitric acid, when the salts $Bi\Big\langle\begin{matrix}NO_3\\ (OH)_2\end{matrix}$, $Bi\Big\langle\begin{matrix}(NO_3)_2\\ OH\end{matrix}$ 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, $KNaSO_4$.

Residue, radical, or compound radical, are expressions for unsaturated groups of atoms known to enter as a whole into different compounds, but having no separate existence. For instance: The bivalent oxygen combines with two atoms of the univalent hydrogen, forming the saturated compound H_2O, water. If we take from this H_2O one atom of H, there is left the group of atoms HO (generally written OH), consisting of an atom of oxygen in which but one point of attraction is actually saturated, the second one not being provided for.

This group, OH, is a residue or radical, and is known to enter into many compounds; it is, for instance, a constituent of all the different hydroxides (formerly called hydrates), such as potassium hydroxide, KOH, calcium hydroxide, $Ca(OH)_2$, etc.

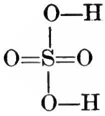
According to the number of points of attraction left unprovided for in a radical, we distinguish univalent, bivalent, trivalent, and quadrivalent radicals.

Carbon is a quadrivalent element forming with the univalent hydrogen the saturated compound CH_4. By removal of one, two, or three hydrogen atoms the radicals CH_3', CH_2'', CH''', are formed.

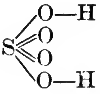
Constitutional or graphic formulas. Though it is impossible to examine the structure of a molecule by means of a microscope, yet we may obtain some information of the atomic arrangement within the molecules by a study of the formation and decomposition which they undergo under different conditions.

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:



or



Questions.—What are chemical equations and how do they serve as a basis for calculations? 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? Define an acid, and state the general properties of basic and neutral substances. By what means can they be recognized? Distinguish between mono-, di-, and tri-basic acids. What are salts and how are they formed? Define neutral, acid, and double salts. Explain the term radical or residue.

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.

9. GENERAL REMARKS REGARDING ELEMENTS.

Relative importance of different elements. Of the total number of about seventy-six 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 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.

Aluminum
Calcium
Carbon
Chlorine
Hydrogen
Iron
Magnesium
Nitrogen
Oxygen
Phosphorus
Potassium
Silicon
Sodium
Sulphur

II.

Antimony
Arsenic
Barium
Bismuth
Boron
Bromine
Cadmium
Cerium
Chromium
Cobalt
Copper
Fluorine
Gold
Iodine

Iridium
Lead
Lithium
Manganese
Mercury
Molybdenum
Nickel
Platinum
Radium
Silver
Strontium
Tin
Uranium
Zinc

III.

Argon
Beryllium (Glucinum)
Cæsium
Columbium (Niobium)
Erbium
Gadolinium
Gallium
Germanium
Helium
Indium
Krypton
Lanthanum
Neodymium
Neon
Osmium
Palladium
Praseodymium
Rhodium
Rubidium
Ruthenium
Samarium
Scandium
Selenium
Tantalum
Tellurium
Terbium
Thallium
Thorium
Thulium
Titanium
Tungsten
Vanadium
Xenon
Ytterbium
Yttrium
Zirconium

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 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 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 58 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,	35.2	Sulphur,	31.8	Lithium,	7.0	Calcium,	39.8
Bromine,	79.3	Selenium,	78.6	Sodium,	22.9	Strontium,	86.9
Iodine,	125.9	Tellurium,	126.6	Potassium,	38.8	Barium,	136.4

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:

$$\frac{35.2 + 125.9}{2} = 80.55; \ \frac{31.8 + 126.6}{2} = 79.2; \ \frac{7.0 + 38.8}{2} = 22.9; \ \frac{39.8 + 136.4}{2} = 88.1.$$

Mendelejeff's periodic law.[1] 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 128 it will be seen that all 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.

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[1] The consideration of this law should be postponed until the student has become acquainted with the larger number of important elements.

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 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 as yet missing elements, but also described

PERIODIC SYSTEM.[1]

Series.	GROUP 0.	GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.
	— —	— R_2O	— R O	— R_2O_3	R H_4 R O_2	R H_3 R_2O_5	R H_2 R O_3	R H R_2O_7	— R O_4?
1	—	H, 1	—	—	—	—	—	—	
2	He, 4	Li, 7	Be, 9	B, 11	C, 12	N, 14	O, 16	F, 19	
3	Ne, 20	Na, 23	Mg, 24	Al, 27	Si, 28	P, 31	S, 32	Cl, 35	
4	A, 39	K, 39	Ca, 40	Sc, 44	Ti, 48	V, 51	Cr, 52	Mn, 55	Fe, 56. Ni, 58. Co, 59
5	—	(Cu, 63)	Zn, 65	Ga, 70	Ge, 72	As, 75	Se, 79	Br, 79	
6	Kr, 81	Rb, 85	Sr, 87	Y, 88	Zr, 90	Cb, 94	Mo, 95	—	Ru, 101. Rb, 102. Pd, 106
7	—	Ag, 107	Cd, 112	In, 113	Sn, 118	Sb, 119	Te, 126	I, 126	
8	Xe, 128	Cs, 132	Ba, 136	La, 138	Ce, 139	Nd, 142	Tb, 159	—	— — —
9	—	—	—	—	—	Er, 165	—	—	
10	—	—	—	Yb, 172	—	Ta, 182	W, 183	—	Os, 190. Ir, 192. Pt, 193
11	—	(Au, 196)	Hg, 199	Tl, 203	Pb, 205	Bi, 207	—	—	
12	—	—	Ra, 223	—	Th, 231	—	U, 237	—	— — —

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[1] The decimals are omitted in giving the atomic weights.

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. 36). 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.

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. The explanation given for this surprising fact, that one and the same element has different properties in certain modifications, is, that either the molecules or the atoms within the molecules are arranged differently. Ozone, for instance, has three atoms of oxygen in the molecule, while the common oxygen molecule contains but two atoms.

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

FIG. 36.

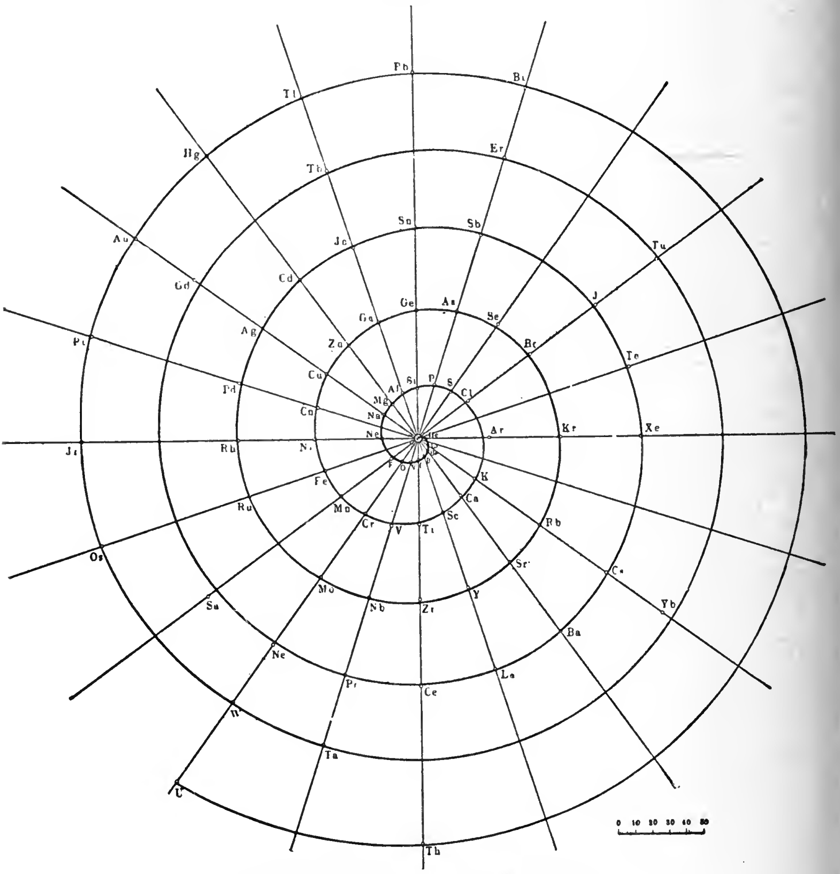

Diagram of periodic system in spiral form.

Relationship between elements and the compounds formed by their union. The properties of the compounds formed by the combination of elements are so various that it is next to impossible to give any general rule by which they may be indicated. It may be said, however, that nearly all of the gaseous compounds contain at least one gaseous element, and that solid elements, when combining with each other, generally form solid substances, rarely liquids, and never compounds showing the gaseous state at the ordinary temperature.

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.

How to study chemistry. In studying chemistry, the student is advised to impress upon his memory five points regarding every important element or compound. These points are:

1. *Occurrence in nature.* Whether in free or combined state; whether in the air, water, or solid part of the earth.
2. *Mode of preparation* by artificial means.
3. *Physical properties.* State of aggregation and influence of heat upon it; color, odor, taste, solubility, etc.
4. *Chemical properties.* Atomic and molecular weight; valence; amount of attraction toward other elements or compounds; acid, alkaline, or neutral reaction; reactions by which it may be recognized and distinguished from other substances.
5. *Application and use* made of it in every-day life, in the arts, manufactures, or medicine.

Of the most important elements and compounds, the history of their discovery, and, occasionally, some special points of interest, should be noticed also.

All students having the facility for working in a chemical laboratory are strongly advised to make all those experiments and reactions which will be mentioned in connection with the different substances to be considered in this book.

By adopting this mode of studying chemistry the student will soon acquire a fair knowledge of chemical facts, yet he might know little of the science of chemistry. In order to acquire this latter knowledge he should study not only facts, but also the relationship existing between them and between the laws governing the phenomena connected with these facts. It is by this method only that the science of chemistry can be successfully mastered.

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. What relation exists between the properties of elements and the properties of the compounds formed by their union? In which cases are the syllables mono-, di-, tri-, tetra-, and penta- used in chemical nomenclature? What use is made of the syllables *ous* and *ic*, *ite* and *ate*, in distinguishing compounds from each other? What are the principal features of the periodic law?

III.

NON-METALS AND THEIR COMBINATIONS.

THE total number of the non-metals is about eighteen; some of them, such as selenium, tellurium, argon, helium, and a few others, are of so little importance that they will be but briefly considered in this book.

Symbols, atomic weights, and derivation of names.

Boron,	B = 10.9.	From *borax*, the substance from which boron was first obtained.
Bromine,	Br = 79.36.	From the Greek *βρῶμος* (bromos), stench, in allusion to the intolerable odor.
Carbon,	C = 11.91.	From the Latin *carbo*, coal, which is chiefly carbon.
Chlorine,	Cl = 35.18.	From the Greek *χλωρός* (chloros), green, in allusion to its green color.
Fluorine,	F = 18.9.	From *fluorspar*, the mineral calcium fluoride, used as flux (*fluo*, to flow.)
Hydrogen,	H = 1.	From the Greek *ὕδωρ* (hudor), water, and *γεννάω* (gennao), to generate.
Iodine,	I = 125.9.	From the Greek *ἴον* (ion), violet, referring to the color of its vapors.
Nitrogen,	N = 13.93.	From the Greek *νίτρον* (nitron), nitre, and *γεννάω* (gennao), to generate.
Oxygen,	O = 15.88.	From the Greek *ὀξύς* (oxus), acid, and *γεννάω* (gennao), to generate.
Phosphorus,	P = 30.77.	From the Greek *φῶς* (phos), light, and *φέρειν* (pherein), to bear.
Silicon,	Si = 28.2.	From the Latin *silex*, flint, or silica, the oxide of silicon
Sulphur,	S = 31.83.	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,	11	175
Nitrogen,	—194			Sulphur,	114	400
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.

Valence.[1]

Univalent.	*Bivalent.*	*Trivalent or quinquivalent.*	*Quadrivalent.*
Hydrogen,	Oxygen,	Nitrogen,	Carbon,
Chlorine,	Sulphur.	Boron,	Silicon.
Bromine,		Phosphorus.	
Iodine,			
Fluorine.			

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[1] The valences here given are the ones generally exerted by the elements, but it will be shown later that most of the elements may exhibit a valence differing from the ones here mentioned.

10. OXYGEN.[1]

$O^{II} = 15.88.$

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 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

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[1] Many instructors prefer to postpone the discussion of the laws of combination, atomic theory, symbols, and chemical equations until after a few elements and compounds have been studied as an introduction and foundation. If such a procedure is followed by those who use this book, the equations in the chapters that may be taken up before the theoretical matters are presented which make the equations intelligible, should, of course, be omitted. They are given in each chapter for the sake of completeness and reference.

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 largely in England 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* (see page 114). When the dioxide is exhausted, the process is repeated. One kilogram of barium oxide yields about ten liters of oxygen at a single operation.

The quantity of oxygen liberated from a given quantity of a substance may be easily calculated from the atomic and molecular 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 100.)

The molecular weight of potassium chlorate is found by adding together the weights of 1 atom of potassium $= 38.86 +$ 1 atom of chlorine $= 35.18 + 3$ atoms of oxygen $= 47.64$; total $= 121.68$. Every 121.68 parts by weight of potassium chlorate liberate the weight of 3 atoms, or 47.64 parts by weight, of oxygen. If 47.64 are obtained from 121.68, 100 are obtained from 255.4.

$$47.64 : 121.68 :: 100 : x$$
$$x = 255.4.$$

In a similar manner, it will be found that 815.7 pounds of manganese dioxide are necessary to produce 100 pounds of oxygen. $MnO_2 = 54.6 + 31.76 = 86.36$. $3MnO_2 = 3 \times 86.36 = 259.08$. Every 259.08 parts furnish $2 \times 15.88 = 31.76$ parts of oxygen.

$$31.76 : 259.08 :: 100 : x$$
$$x = 815.7.$$

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 grammes in 1 liter at 0° C. and 760 mm. pressure. Hence, under these conditions, 100 grammes 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.)

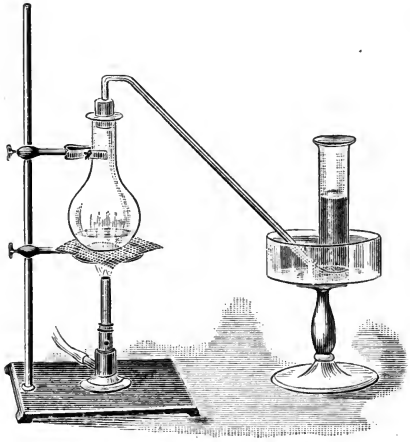
The densities of gases are generally given in books, but they can be calculated, if the molecular weights of the gases are known. The relation between densities and molecular weights of gases is discussed on page 108. The density of any gas is equal to the density of hydrogen multiplied by one-half the molecular weight of the gas; 1 liter of hydrogen at 0° C. and 760 mm. pressure weighs 0.08987 gramme, the molecular weight of oxygen is 31.76; hence 1 liter of oxygen weighs $0.08987 \times 15.88 = 1.427$ grammes.

Experiment 1. Generate oxygen by heating a small quantity (about 5 grammes) 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. 37). Collect the gas by placing over the delivery-tube large test-tubes (or other suitable vessels) 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.

FIG. 37.



Apparatus for generating oxygen.

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 $\frac{1}{15}$ of its volume.

The temperature above which a gas cannot be liquified 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 grammes.

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 is generally higher than 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.

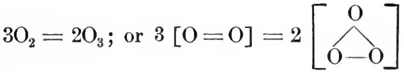
The total amount of heat evolved during the combustion of a substance is the same as that generated by the same substance when undergoing slow combustion, but the intensity depends upon the time required for the oxidation. A piece of iron may require years to combine with oxygen, and it may be burned 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.

While 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. Theoretically, we assume that ozone contains three, common oxygen but two, atoms in the molecule, which is substantiated by the fact that three volumes suffer a condensation to two volumes when converted into ozone, which would indicate that three molecules of oxygen furnish two molecules of ozone, thus:



$$3O_2 = 2O_3;\ \text{or}\ 3\,[O=O] = 2\left[\begin{array}{c} O \\ O-O \end{array}\right]$$

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 5 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 48). 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 chemical 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 grammes corresponding to the chemical symbols of the substances. For instance, the thermal equation for the formation of water is written, $2H + O = H_2O + 67{,}883$ cal., which means that when 2 grammes of hydrogen unite with 15.88 grammes of oxygen to form 17.88 grammes of water (corresponding to the symbol H_2O), 67,883 calories of heat are liberated, or enough to raise nearly 68 kilogrammes of water one degree in temperature. The thermal equation,

$$HgO = Hg + O - 30{,}370.5 \text{ cal.},$$

means that when 214.38 grammes of oxide of mercury (corresponding to HgO) are decomposed by heat into mercury and oxygen, 30,370.5 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, $2O_3 = 3O_2 + 64{,}314$ cal., states that when 95.28 grammes of ozone (corresponding to $2O_3$) decomposes into ordinary oxygen, 64,314 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.

11. HYDROGEN. WATER. HYDROGEN DIOXIDE.

$H = 1.$ $H_2O = 17.88.$ $H_2O_2 = 33.76.$

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.

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.

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 grammes 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 thermo-chemistry? What is a thermal reaction?

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:

$$K + H_2O = KOH + H;$$
$$3Fe + 4H_2O = Fe_3O_4 + 8H.$$

A very convenient way of liberating hydrogen is the decomposition of dilute hydrochloric or sulphuric acid by zinc or iron:

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

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

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:

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

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

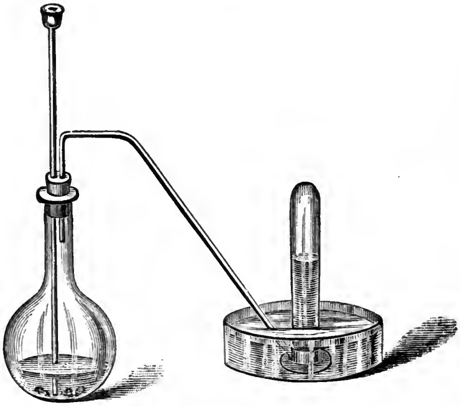
Whenever hydrogen is generated, care should be taken to expel all atmospheric air from the vessel in which the generation takes place, before the hydrogen is ignited, as otherwise an explosion may result.

Experiment 3. Place a few pieces of granulated zinc (about 10 grammes) in a flask of about 200 c.c. capacity, which is arranged as shown in Fig. 38. Cover 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.

FIG. 38.



Apparatus for generating hydrogen.

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 gramme, 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 gramme 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 gramme of zinc and 0.024 gramme of magnesium. Notice that in this case equal volumes of hydrogen are obtained. Calculate the weight of hydrogen from the cubic centimetres 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 atomic 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 gramme, or one gramme 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 lately, 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:

$$\mathrm{CuO + 2H = H_2O + Cu.}$$

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 154). 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, $H_2O = 17.88$. 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 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 hydrogen, 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 parts by weight of hydrogen to 15.88 parts, by weight, of oxygen. It has been ascertained that the molecule of water is made up of two atoms of hydrogen and one atom of oxygen, H_2O. Hence, it follows that the atomic weight of oxygen is 15.88. 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 properties, and on evaporation the dissolved solid will be re-obtained unchanged. Instances of this kind are solutions of sugar or table salt and water. (The breaking down of molecules into ions during simple solution will be considered later.)

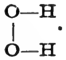
In chemical solutions there takes place a rearrangement of the atoms within the molecules, both of the solvent and of the substance dissolved. Moreover, on evaporation of the solution a substance is obtained entirely different from the one which has been dissolved. Instances of this kind are the dissolving 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 have 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 effervescence 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, or  $\begin{array}{l} O\text{—}H \\ | \\ O\text{—}H \end{array}$. This compound may be obtained in aqueous solution from several metallic dioxides which, when treated with an acid, yield a portion of their oxygen to water.

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 subtances, 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.

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.

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.

Solution of hydrogen dioxide, Aqua hydrogenii dioxidi, 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—

$$H_2O_2 = H_2O + O + 22{,}926 \text{ cal.}$$

that is, when 33.76 grammes of hydrogen dioxide corresponding to the formula, H_2O_2, decomposes, 22,926 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

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[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.

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 c.c. 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.

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 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?

12. 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 grammes 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 grammes of water dissolve 2.1 grammes of ether, while 100 grammes of ether dissolve 11 grammes 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 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 grammes 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 grammes of the substance in 100 grammes of the solvent, or in 100 c.c. of the solution, or of the grammes of solvent required to dissolve 1 gramme 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 grammes corresponding to its chemical formula (molecular weight) is dissolved in an unlimited amount of water.

When 95.35 grammes of sulphuric acid (corresponding to H_2SO_4) are thus dissolved, 38,880 calories of heat are liberated, or enough heat to raise over 38 liters of water 1° C. in temperature. When 284.11 grammes of crystallized sodium carbonate ($Na_2CO_3.10H_2O$) are dissolved, 16,038 calories are absorbed, but solution of an equivalent weight of anhydrous sodium carbonate (Na_2CO_3), or 105.31 grammes, liberates 5,598 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 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. 152). 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 molecular quantities of substances: *The molecular weights in grammes of different substances dissolved in 1000 grammes of the same solvent produce the same depression of the freeezing-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 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 molecular 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 molecular weight, and g the weight of the solvent in grammes.

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 molecular weight of sodium chloride, 58.06 grammes, dissolved in 1000 grammes 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 molecules of different substances in a given amount of solvent produces the same lowering of the freezing-point, and the molecular weights in grammes contain the same number of molecules. The fact that the depression of the freezing-point of a solution of the molecular weight in grammes of sodium chloride in 1000 grammes 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 molecule 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 molecules. This assumption of the decomposition of molecules is applied in the case 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 molecular weight in grammes of normally acting substances, dissolved in 1000 grammes 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 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. 40). 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.

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[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.

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 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:

Grammes of cane-sugar in 1000 grammes of water. . .	68.4	136.8	171	342
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 molecular weight in grammes of a substance in one 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.

13. NITROGEN.

$N^{iii} = 14$ (13.93).

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. 37, page 140. Place in the flask about 10 grammes 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

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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?

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. Nitrogen is trivalent in some compounds, quinquivalent in others.

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 at 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 80 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. The valence of nitrogen is 3 in ammonia, which represents the limit of reduction, while it is 5 in nitric acid, which is the limit of oxidation of nitrogen.

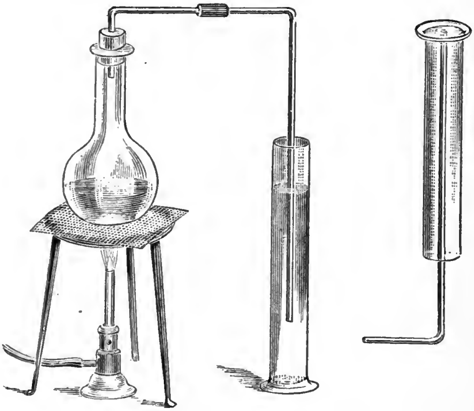
Ammonia, $NH_3 = 16.93$. This compound is constantly forming in nature by the decomposition of organic (chiefly animal) matter, such as meat, urine, blood, etc. It is also obtained during the process of destructive distillation, which is the heating of non-volatile organic substances in suitable vessels 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 grammes of each) of ammonium chloride and calcium hydroxide (slaked lime) in a flask of about 200 c.c. capacity, and arranged as in Fig. 39; cover the mixture with water and apply heat.

Fig. 39.



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:

$$NH_3 + HCl = NH_4Cl.$$

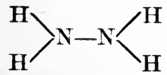
The union of water or hydrochloric acid directly with ammonia is explained by the increase of valence of the nitrogen atom from 3 to 5. In the hydroxide and all the salts, there is a group of atoms, $(NH_4)-$, which acts exactly like an atom of metal. It has, therefore, been called *ammonium.* This radical 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 $N_2H_4(HCl)_2$. The constitution of hydrazine may be represented by the formula



$$\begin{matrix} H \\ H \end{matrix}\!>\!N-N\!<\!\begin{matrix} H \\ H \end{matrix}$$

Hydroxylamine, NH_2OH. The term amine is used to designate compounds derived from ammonia by replacement of one or more hydrogen atoms by basic atoms or radicals, and it is in keeping with this terminology that the compound under consideration is known as hydroxyl-amine, while hydrazine is termed di-amine.

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

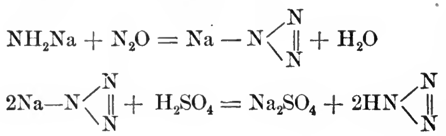
$$HNO_3 + 6H = NH_2OH + 2H_2O.$$

The compound is known only in solution; with acids it forms well-defined salts, which appear to be ammonium salts in which a hydrogen atom has been replaced by hydroxyl. 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:

$$NH_3 + Na = NH_2Na + H$$



$$NH_2Na + N_2O = Na-N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. + H_2O$$

$$2Na-N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. + H_2SO_4 = Na_2SO_4 + 2HN\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right.$$

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:

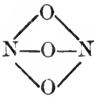
	Composition.			
	By weight.		By volume.	
	N	O	N	O
Nitrogen monoxide, N_2O	28	16	2	1
Nitric oxide, NO	28	32	2	2
Nitrogen trioxide, N_2O_3	28	48	2	3
Nitrogen tetroxide, $N_2O_4 = 2(NO_2)$	28	64	2	4
Nitrogen pentoxide, N_2O_5	28	80	2	5

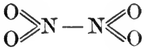
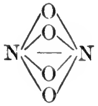
The trioxide and pentoxide are called also acid anhydrides, or nitrous and nitric anhydride respectively, because they combine with water to give nitrous and nitric acid. Conversely, when the acids are deprived of the elements of water, the respective oxides of nitrogen are obtained. The monoxide corresponds 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.

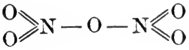
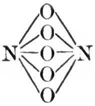
While our knowledge of the structure of the oxides of nitrogen is unsatisfactory, the following graphic formulas, in which the valence of nitrogen is assumed to be either 1, 3, or 5, have been proposed to show the manner in which the atoms may be linked together:

Nitrogen monoxide, $N — O — N$ or


Nitric oxide, $N = O$

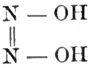
Nitrogen trioxide, $O = N — O — N = O$ or


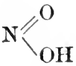
Nitrogen tetroxide,

$$\begin{matrix}O\\O\end{matrix}\!\!\gg N — N \ll\!\!\begin{matrix}O\\O\end{matrix}$$
or


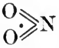
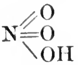
Nitrogen pentoxide,

$$\begin{matrix}O\\O\end{matrix}\!\!\gg N — O — N \ll\!\!\begin{matrix}O\\O\end{matrix}$$
or


Nitrogen tetroxide, at high temperature, has the composition NO_2, and it is possible that in NO_2, and nitric oxide, NO, the valence of nitrogen is 4 and 2 respectively. The truth is that we have not sufficient knowledge of the structure of the oxides of nitrogen to make any positive statement as to the valence of nitrogen in them.

The structure of the nitrogen acids may be represented thus:

Hyponitrous acid, $N — OH$, or possibly


Nitrous acid, $O = N — OH$, or


Nitric acid,

$\begin{matrix}O\\O\end{matrix}\!\!\gg N — OH$, or


Nitrogen tetroxide, at low temperature, has the formula N_2O_4, but at elevated temperatures this splits up into $2NO_2$, to form again N_2O_4, when the temperature is decreased. There are many other cases like this in chemistry.

Such a decomposition which proceeds at high temperatures, while at lower ones the constituents can recombine, is called *dissociation.*

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, N_2O (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, chloronitrous and chloronitric oxides.

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. 37, page 140. Place in the dry flask about 10 grammes 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.).

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 one or more atoms of 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. 38. Put about 20 grammes 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.

Hyponitrous acid, HNO, or possibly $H_2N_2O_2$, 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, = 62.57 (*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.

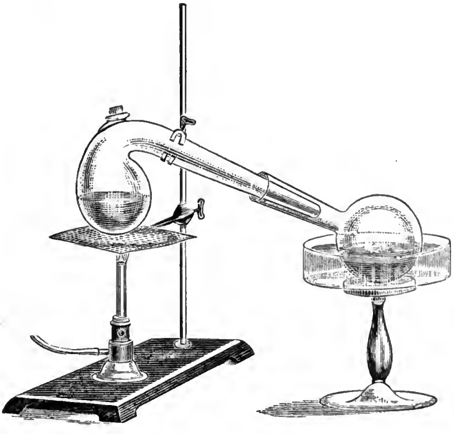
Experiment 10. Prepare an apparatus as shown in Fig. 40. Heat in a retort of about 250-c.c. capacity a mixture of about 50 grammes of potassium nitrate and nearly the same weight of sulphuric acid. Nitric acid is evolved and distils over into the receiver, which is to be kept cool during the operation 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 grammes 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 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 *diluted nitric acid* of the U. S. P. 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.

FIG. 40.



Distillation of nitric acid.

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 gramme 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.

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.

14. CARBON. SILICON. BORON.

$C^{iv} = 12\ (11.91)$. $Si^{iv} = 28.3$. $B^{iii} = 10.9$.

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 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 lamp-black it is used in printer's ink; in bone-black 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 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. 114.)

Experiment 12. Use apparatus represented in Fig. 38, page 146. Place about 20 grammes 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 grammes.

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.

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 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, but which seem to be directly poisonous. The bad effects experienced in breathing air which has become contaminated by the exhalations from the lungs, are most likely due to these unknown bodies. As we have as yet no methods of ascertaining the quantity of these poisonous substances present in exhaled air, the determination of the amount of exhaled carbon dioxide present must serve as an indicator of the fitness of an air for breathing purposes. 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.

As exhaled air contains from 3.5 to 4 per cent. of carbon dioxide, it is unfit to be breathed again. The total amount of carbon dioxide evolved by the lungs and skin of a grown person amounts to about 0.7 cubic foot per hour. Hence the necessity for a constant supply of fresh air by ventilation. This becomes the more necessary where an additional quantity of carbon dioxide is supplied by illuminating flames.

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 respiration (if we may so call it), 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.

Carbon dioxide is an acid oxide, which combines with water, forming carbonic acid:

$$CO_2 + H_2O = H_2CO_3.$$

Carbonic acid, H_2CO_3, $CO(OH)_2$, 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 substances 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 gives 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 is gas in the act of combustion. 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.

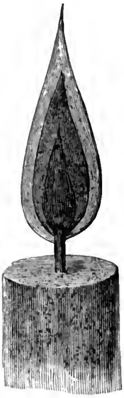
These gases are generated by destructive distillation, the heat being supplied either by a separate process (manufacture of illuminating gas by heating wood or coal in retorts), or generated during the combustion itself.

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. 41) 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.

FIG. 41.



Structure of flame.

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.

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, 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.

Silicon carbide, SiC. (*Carborundum, Carbon silicide*). This compound furnishes a typical illustration of the possibilities of the electric furnace for manufacturing purposes. Figs. 32 and 33, page 81, 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:

$$SiO_2 + 3C = 2CO + SiC.$$

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.

Boron, $B'''=10.9$, 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 nitrogen boride, BN.

Boric acid, Acidum boricum, H_3BO_3, $B(OH)_3=61.54$ (*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.

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.

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.

Sodium perborate, $NaBO_3.4H_2O$. When a mixture of 248 grammes of boric acid and 78 grammes 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.

15. 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 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 (see page 82) 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, electro-positive ions, or *cations,* because they are attracted to the negative pole or *cathode* during electrolysis, and electro-negative 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 is 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 114). 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:

$$\mathrm{HCl} \rightleftarrows \mathrm{H}^{\cdot} + \mathrm{Cl}'; \quad \mathrm{NaCl} \rightleftarrows \mathrm{Na}^{\cdot} + \mathrm{Cl}'; \quad \mathrm{NaOH} \rightleftarrows \mathrm{Na}^{\cdot} + (\mathrm{OH})'.$$

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 versâ*. 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 grammes 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:

$$\begin{array}{l} \left.\begin{array}{lll} \mathrm{KCl} & \rightleftarrows \mathrm{K}^{\cdot} & + \mathrm{Cl}' \\ \mathrm{NaNO_3} & \rightleftarrows \mathrm{NO}'_3 & + \mathrm{Na}^{\cdot} \end{array}\right\} \rightleftarrows \mathrm{NaCl}. \\ \qquad\qquad\quad \downarrow\uparrow \\ \qquad\qquad\quad \mathrm{KNO_3} \end{array}$$

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:

$$\begin{array}{l} \left.\begin{array}{lll} \mathrm{AgNO_3} & \rightleftarrows \mathrm{NO_3}' & + \mathrm{Ag}^{\cdot} \\ \mathrm{NaCl} & \rightleftarrows \mathrm{Na}^{\cdot} & + \mathrm{Cl}' \end{array}\right\} \rightleftarrows \mathrm{AgCl\ precipitate.} \\ \qquad\qquad\quad \downarrow\uparrow \\ \qquad\qquad \mathrm{NaNO_3\ soluble.} \end{array}$$

A simple equation, in which only the ions are represented, may be used:

$$\mathrm{Ag}^{\cdot} + \mathrm{NO_3}' + \mathrm{Na}^{\cdot} + \mathrm{Cl}' = \mathrm{AgCl} + \mathrm{Na}^{\cdot} + \mathrm{NO_3}'.$$

The simplest equation of all is one which shows only those ions that are actually involved in the precipitation, thus:

$$\mathrm{Ag}^{\cdot} + \mathrm{Cl}' = \mathrm{AgCl}.$$

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:

$$\begin{array}{l} \left.\begin{array}{lll} \mathrm{2NH_4Cl} & \rightleftarrows \mathrm{2Cl}' & + \mathrm{2NH_4}^{\cdot} \\ \mathrm{Ca(OH)_2} & \rightleftarrows \mathrm{Ca}^{\cdot\cdot} & + \mathrm{2(OH)}' \end{array}\right\} \rightleftarrows \mathrm{2NH_4OH} = \mathrm{2H_2O} + \mathrm{2NH_3\ (gas)\ undissociated.} \\ \qquad\qquad\quad \downarrow\uparrow \\ \qquad\qquad \mathrm{CaCl_2\ soluble.} \end{array}$$

Or, more simply,

$$\mathrm{Ca}^{\cdot\cdot} + \mathrm{2(OH)}' + \mathrm{2NH_4}^{\cdot} + \mathrm{2Cl}' = \mathrm{Ca}^{\cdot\cdot} + \mathrm{2Cl}' + \mathrm{2NH_4OH}.$$

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:

$$\left.\begin{array}{l} Na_2CO_3 \rightleftarrows 2Na^{\cdot} + CO_3^{\prime\prime} \\ H_2SO_4 \ \rightleftarrows SO_4^{\prime\prime} + 2H^{\cdot} \end{array}\right\} \rightleftarrows H_2CO_3 = H_2O + CO_2 \text{ (gas).}$$

$$\downarrow\uparrow$$

$$Na_2SO_4 \text{ soluble.}$$

Or simply

$$2Na^{\cdot} + CO_3^{\prime\prime} + 2H^{\cdot} + SO_4^{\prime\prime} = 2Na^{\cdot} + SO_4^{\prime\prime} + H_2CO_3.$$

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:

$$\left.\begin{array}{l} 2KNO_3 \rightleftarrows 2K^{\cdot} \ + 2NO_3^{\prime} \\ H_2SO_4 \ \rightleftarrows SO_4^{\prime\prime} + 2H^{\cdot} \end{array}\right\} \rightleftarrows 2HNO_3 \text{ volatile by heating.}$$

$$\downarrow\uparrow$$

$$K_2SO_4 \text{ non-volatile.}$$

Or simply

$$2K^{\cdot} + 2NO_3^{\prime} + 2H^{\cdot} + SO_4^{\prime\prime} = 2K^{\cdot} + SO_4^{\prime\prime} + 2HNO_3.$$

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. 114, 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 82. 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. 34 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 result 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. 34) 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 gramme 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 gramme 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 gramme of hydrogen, 0.0000828 gramme of oxygen, 0.0003294 gramme of copper, 0.001118 gramme of silver, etc. These quantities are proportional to the chemical equivalents, and are called in electrical science, *electro-chemical equivalents.*

An instrument constructed for determining the amount of a substance as silver or copper liberated by a current in a given time, and from this the current strength, is called a *voltameter* (see page 77). Suppose a current flowing for 1 hour through a voltameter liberates 0.59292 gramme 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 (see page 76). 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, thus:

$$\text{Conductivity} = \frac{1}{\text{resistance}}.$$

In order that results may be compared, conductivity measurements are made with electrodes 1 cm. apart. The algebraic character used to represent conductivity is λ_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
Gold
Platinum
Palladium
Silver
Mercury
Bismuth
Antimony
Copper
Arsenic
Hydrogen
Lead
Tin
Nickel

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 8. 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 solutions 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 grammes as contain the same weight of replaceable hydrogen. For example, two molecular weights of HCl are equivalent to one moleculer 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 versâ.

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.

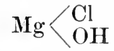
Acid salts. These may be acid, neutral, or alkaline to litmus, depending on the mode of ionization. An acid salt of a highly ionizing acid shows an acid reaction in solution, because of the presence of hydrogen ions. For example, sodium bisulphate acts thus in solution:

$$\begin{aligned} NaHSO_4 &\leftrightarrows Na^{\cdot} + HSO_4' \\ HSO_4' &\leftrightarrows H^{\cdot} + SO_4'' \end{aligned}$$

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  $Mg\langle{}^{Cl}_{OH}$ 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:

$$\left.\begin{array}{l} Na_2CO_3 \rightleftarrows 2Na^{\cdot} + CO_3'' \\ H_2O \rightleftarrows (OH)' + H^{\cdot} \end{array}\right\} \rightleftarrows HCO_3'.$$

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:

$$\begin{array}{l} CuSO_4 + 2H_2O = Cu(OH)_2 + H_2SO_4 \\ Na_2CO_3 + H_2O = NaOH + NaHCO_3 \end{array}$$

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· 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· 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:

$$\begin{array}{c} \left.\begin{array}{l} NaOH \rightleftarrows Na^{\cdot} + (OH)' \\ HNO_3 \rightleftarrows NO_3' + H^{\cdot} \end{array}\right\} \rightarrow H_2O \\ \downarrow\uparrow \\ NaNO_3 \end{array}$$

As fast as H· 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· 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 (17.88 gm.) of water, and is nearly 13,600 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.
Nitric acid	82
Hydrochloric acid	78.4
Sulphuric acid	51
Hydrofluoric acid	7
Acetic acid	0.4
Carbonic acid $\left(\frac{n}{10}\right)$	0.17
Hydrogen sulphide $\left(\frac{n}{10}\right)$	0.07
Boric acid $\left(\frac{n}{10}\right)$	0.01
Hydrocyanic acid $\left(\frac{n}{10}\right)$	0.01
Phosphoric acid $\left(\frac{n}{2}\text{ at }25°\text{ C.}\right)$	17
Potassium hydroxide	77
Sodium hydroxide	73
Calcium hydroxide, sat. sol. at 25° C.	90
Ammonium hydroxide	0.4

Electrolyte.	Per cent. dissociation.
Sodium phosphate, very dilute	83
Ammonium chloride	74
Sodium chloride	67.5
Potassium nitrate	64
Potassium acetate	64
Silver nitrate	58
Potassium sulphate	53
Sodium acetate	53
Sodium bicarbonate	52
Potassium carbonate	49
Sodium sulphate	44.5
Zinc sulphate	24
Zinc chloride	48
Copper sulphate	22
Mercuric chloride, less than	1
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.

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.

16. SULPHUR.

$S^{II} = 32$ (31.83).

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 pyrites, FeS_2, galena, PbS, cinnabar, HgS, etc.). Sulphur enters also into organic compounds, being a normal constituent of all proteids, 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 disulphide of carbon, 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 thin and 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 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 grammes of powdered sulphur, 20 grammes 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, $SO_2 = 63.59$ (*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.

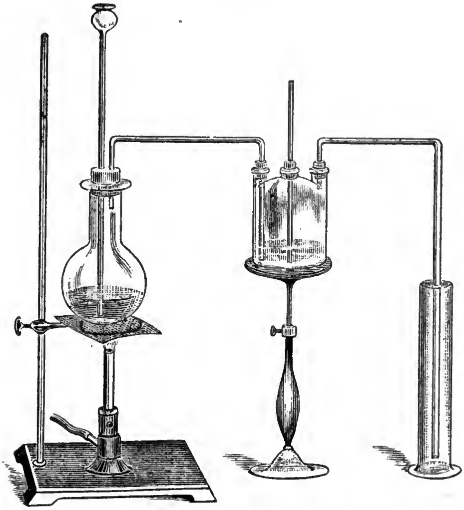
Sulphurous acid, Acidum sulphurosum, H_2SO_3, $SO_2.H.OH$. This acid, similar to carbonic acid, is not known in a pure state, but is believed to exist in aqueous solution, which decomposes into water and sulphur dioxide when attempts are made to concentrate it. One volume of cold water absorbs about 40 volumes of sulphur dioxide, equal to about 11 per cent. by weight. The official acid must contain not less than 6 per cent. by weight, equal to about 2000 volumes of gas dissolved in 100 of water. According to the U. S. P. the acid is 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.

Experiment 14. Use an apparatus as shown in Fig. 42. Place in the flask about 20 grammes 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 grammes 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.

FIG. 42.



Apparatus for making sulphurous acid.

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 195 and 201. 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, $SO_2(OH)_2 = 97.35$ (*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 pyrites 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 179.)

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 200). 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 114). These tests, like all similar ones that follow, are explained in terms of the ionic theory on pages 193 and 200.

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. 42, page 207. Place about 20 grammes 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 grammes 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 198) 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:

$$Pb(NO_3)_2 + H_2S = \underset{\text{Lead sulphide.}}{PbS} + 2HNO_3,$$

$$\text{or} \quad Pb^{\cdot\cdot} + 2(NO_3)' + 2H^{\cdot} + S'' = PbS + 2H^{\cdot} + 2(NO_3)'.$$

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:

$$FeSO_4 + (NH_4)_2S = \underset{\text{Iron sulphide.}}{FeS} + (NH_4)_2SO_4,$$

$$\text{or} \quad Fe^{\cdot\cdot} + SO_4'' + 2(NH_4)^{\cdot} + S'' = FeS + 2(NH_4)^{\cdot} + SO_4''.$$

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, Carbonei disulphidum, $CS_2 = 75.57$. 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 193) 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 constant (see page 192). 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:

$$\begin{array}{rcl}\text{FeS (slightly soluble)} \rightleftarrows \text{Fe}^{\cdot\cdot} & + & \\ 2\text{HCl} \rightleftarrows 2\text{Cl}' & + & \end{array}\left.\begin{array}{l}\text{S}''\\ 2\text{H}^{\cdot}\end{array}\right\} \rightleftarrows \text{H}_2\text{S}.$$

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:

$$\left.\begin{array}{r}\text{CuS (very slightly soluble)}\\ 2\text{HCl}\end{array}\right\}\begin{array}{l}\rightleftarrows \text{Cu}^{\cdot\cdot} \;+\\ \rightleftarrows 2\text{Cl}' \;+\end{array}\left.\begin{array}{l}\text{S}''\\ 2\text{H}^{\cdot}\end{array}\right\} \rightleftarrows \text{H}_2\text{S}.$$

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· 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.*

17. PHOSPHORUS.

$P^{iii} = 31$ (30.77).

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.

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.

The manufacture of phosphorus to-day 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 phophate 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:

$$CaH_4(PO_4)_2 + H_2SO_4 = CaSO_4 + 2(H_3PO_4).$$

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 corresponding 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 great resemblance to the metallic 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 $4 \times 30.77 = 123.08$.

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.

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.

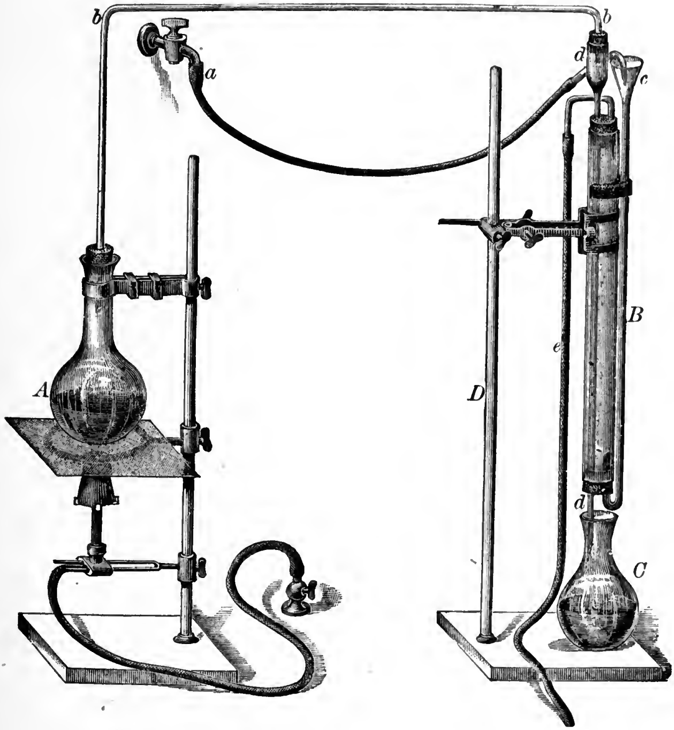
In cases of poisoning by phosphorus, efforts should be made to eliminate the poison as rapidly as possible by means of stomach-pump, emetics, or cathartics. As antidote a one-tenth per cent. solution of potassium permanganate has been used successfully; it acts by oxidizing the phosphorus, converting 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. 43) 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. The three lower oxides are obtained by slow oxidation, or by the burning of phosphorus in a limited supply of air; while the pentoxide is formed whenever phosphorus burns under ordinary conditions. The pentoxide is a white powder possessing an intense affinity for water, with which it combines to form phosphoric acid, while the trioxide with water produces phosphorous acid.

FIG. 43.



Apparatus for detection of phosphorus in cases of poisoning.

Hypophosphorous acid, Acidum hypophosphorosum, H_3PO_2, $PO.H_2.OH = 65.53$. 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, hypophosphorous 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 porcelain dish until it ignites. The salt is decomposed into a phosphate and phosphine, 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 re-formed.

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 tetra-basic 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, $PO(OH)_3 = 97.29$ (*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 gramme), 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 grammes 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:

$$\begin{aligned} NaH_2PO_4 &\rightleftarrows Na^{\cdot} + H_2PO_4{}' \\ H_2PO_4{}' &\rightleftarrows H^{\cdot} + HPO_4{}''. \end{aligned}$$

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,

$$\left.\begin{array}{l}2Na^{\cdot} + HPO_4'' \\ (OH)' + H^{\cdot}\end{array}\right\} \rightleftarrows H_2PO_4',$$

or,

$$Na_2HPO_4 + H_2O = NaOH + NaH_2PO_4,$$

Trisodium phosphate is completely hydrolyzed in solution into disodium phosphate and sodium hydroxide, $Na_3PO_4 + H_2O = Na_2HPO_4 + NaOH$.

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, $Fe_2(PO_4)_2$, thus:

$$2Na_2HPO_4 + Fe_2Cl_6 = Fe_2(PO_4)_2 + 4NaCl + 2HCl.$$

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.

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?

18. CHLORINE.

$Cl^1 = 35$ (35.18).

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 page 125). 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, may be used potassium chlorate, potassium dichromate, potassium permanganate, chromic acid, nitric acid, and many other substances.

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:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl.$$
$$MnO_2 + 2NaCl + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + 2Cl.$$

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 apparatus as in Fig. 39, page 168. Conduct operation in a fume-chamber. Place about 50 grammes 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:

$$\begin{aligned} H_2O &+ 2Cl = 2HCl + O. \\ NH_3 &+ 3Cl = 3HCl + N. \\ C_{10}H_{16} &+ 16Cl = 16HCl + 10C. \end{aligned}$$

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.

Compound solution of chlorine, Liquor chlori compositus (*Chlorine water*). Cold water absorbs about two volumes of chlorine, which is equal to 0.4 per cent. by weight. This solution is unstable because the chlorine gradually combines with hydrogen of water, while oxygen is set free. It is for this reason that the U. S. P. has substituted for ordinary chlorine water the compound solution of chlorine, which is to be freshly made when wanted. It is prepared by digesting in a large flask potassium chlorate with hydrochloric acid and then adding water to dissolve the liberated chlorine, as also some chlorinated products and the potassium chloride which are formed. The reaction, when complete, is this:

$$KClO_3 + 6HCl = KCl + 3H_2O + 6Cl.$$

Chlorine water is a greenish-yellow liquid, having the odor of chlorine.

Hydrochloric acid, Acidum hydrochloricum, $HCl = 36.18$ (*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:

$$NaCl + H_2SO_4 = HCl + NaHSO_4;$$

or

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

Experiment 18. Use apparatus as in Fig. 39, p. 168. Place about 20 grammes 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. 42, page 207, 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 117 pounds of sodium chloride?

The liberation of 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 114). 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 15. The ionic reaction is this:

$$\left.\begin{array}{l} NaCl \rightleftarrows Na^{\cdot} \quad + Cl' \\ H_2SO_4 \rightleftarrows HSO_4' + H^{\cdot} \end{array}\right\} \rightleftarrows \underset{\text{dissolved}}{HCl} \rightarrow \underset{\text{gas.}}{HCl.}$$

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 15).

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 $PbCl_2$.

$$Pb(C_2H_3O_2)_2 + 2NaCl = PbCl_2 + 2Na(C_2H_3O_2).$$
$$Pb^{\cdot\cdot} + 2(C_2H_3O_2)' + 2Na^{\cdot} + 2Cl' \rightarrow PbCl_2 + 2Na^{\cdot} + 2(C_2H_3O_2)'.$$

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:

$$2HNO_3 + 8HCl + Pt = H_2Pt.Cl_6 + 2NOCl + 4H_2O.$$

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:

$$\begin{aligned} Cl_2O + H_2O &= 2HClO. \\ 2ClO_2 + H_2O &= HClO_2 + HClO_3. \\ Cl_2O_7 + H_2O &= 2HClO_4. \end{aligned}$$

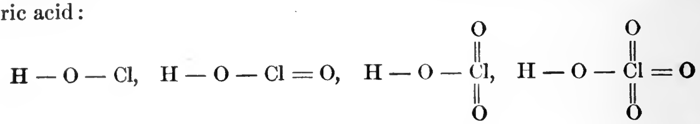
The oxide, Cl_2O_5, from which chloric acid, $HClO_3$, might be formed, is not known. The chlorine oxides, the acids, and many of their salts are distinguished by the great facility with which they decompose, frequently with violent explosion, for which reason care must be taken in the preparation and 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 reaction 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, $HClO_3$, 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 236).

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?

19. BROMINE—IODINE—FLUORINE.

Bromine, Bromum, Br = 79.36. 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 parts of water, more freely in alcohol, abundantly in ether and bisulphide 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 = 80.36. 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:

$$\begin{aligned} 2NaBr + H_2SO_4 &= 2HBr + Na_2SO_4; \\ 2HBr + H_2SO_4 &= 2Br + SO_2 + 2H_2O. \end{aligned}$$

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.

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.

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 = 125.90. 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 seaweeds 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 Chili 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 grammes of iodine and 50 grammes 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 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, $HI = 126.9$. This is a colorless gas readily soluble in water; the solution is unstable, being easily decomposed with liberation of iodine. It may be obtained by processes analogous to those mentioned for the preparation of hydrobromic acid. The action of hydrogen sulphide upon iodine in the presence of water is as follows:

$$H_2S + 2I = 2HI + S.$$

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:

$$6I + 10HNO_3 = 5N_2O_2 + 5H_2O + 3I_2O_5.$$

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.

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, Sulphuris iodidum, 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.

Fluorine, F = 18.9. 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 grammes 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, p. 186.)

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?

IV.

METALS AND THEIR COMBINATIONS.

20. GENERAL REMARKS REGARDING METALS.

Of the total number of sixty metallic elements only about one-half are of sufficient general interest and importance to deserve consideration in this book.

Derivation of names, symbols, and atomic weights.

Aluminum,	Al = 26.9.	From *alum*, a salt containing it.
Antimony, (Stibium.)	Sb = 119.3.	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 = 74.4.	From the Greek *ἀρσενικὸν* (arsenicon), the name for the native sulphide of arsenic.
Barium,	Ba = 136.4	From the Greek *βαρὺς* (barys), heavy, in allusion to the high specific gravity of barium sulphate, or heavy-spar.
Bismuth,	Bi = 206.9.	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 = 111.6.	From the Greek *καδμεία* (kadmeia) the old name for calamine (zinc carbonate), with which cadmium is frequently associated.
Calcium,	Ca = 39.8.	From the Latin *calx*, lime, the oxide of calcium.
Chromium,	Cr = 51.7.	From the Greek *χρῶμα* (chroma), color, in allusion to the beautiful colors of all its compounds.
Cobalt,	Co = 58.56.	From the German *Kobold*, which means a demon inhabiting the mines.
Copper,	Cu = 63.1.	From the Latin *cuprum*, copper, and this from the Island of Cyprus, where copper was first obtained by the ancients.
Gold, (Aurum.)	Au = 195.7.	Gold means bright yellow in several old languages. The Latin *aurum* signifies the color of fire.
Iridium,	Ir = 191.5.	From iris, rainbow, in allusion to the varying tints of its salt solutions.
Iron,	Fe = 55.5.	Iron probably means metal; the derivation of the Latin *ferrum* is not definitely known.

Lead, (Plumbum.)	Pb	= 205.35.	Both words signify something heavy.
Lithium,	Li	= 6.98.	From the Greek λίθειος (litheios), stony.
Magnesium,	Mg	= 24.18.	From Magnesia, a town in Asia Minor, where magnesium carbonate was found as a mineral.
Manganese,	Mn	= 54.6.	Probably from magnesium, with the compounds of which it was long confounded.
Mercury, (Hydrargyrum)	Hg	= 198.5.	From Mercury, the messenger of the Greek gods. Hydrargyrum means liquid silver.
Molybdenum,	Mo	= 95.3.	From the Greek μόλυβδος (molybdos), lead.
Nickel,	Ni	= 58.3.	From the old German word *nickel*, which means worthless.
Platinum,	Pt	= 193.3.	Platina is the diminutive of the Spanish word *plata*, silver.
Potassium, (Kalium.)	K	= 38.86.	From pot-ash; potassium carbonate being the chief constituent of the lye of wood-ashes. Kali is the Arabic word for ashes.
Silver, (Argentum.)	Ag	= 107.12.	Both words signify white.
Sodium, (Natrium.)	Na	= 22.88.	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	= 86.94.	From Strontian, a village in Scotland, where strontium carbonate is found.
Tin, (Stannum.)	Sn	= 118.1.	Both words most likely signify stone.
Zinc,	Zn	= 64.9.	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.		

Infusible below a red heat.	Silver	1020	1868
	Copper	1100	2012
	Gold	1200	2192
	Cast-iron	1150	2102
	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,	1807–1808	H. Davy discovered methods for the separation of these metals from their oxides.
Sodium,		
Barium,		
Calcium,		
Strontium,		
Magnesium,		
Cadmium,	1817, by Stromeyer.	
Lithium,	1817, by Arfvedson.	
Aluminum,	1828, by Wöhler.	

Valence of metals.[1]

Univalent.
Lithium,
Potassium,
Sodium,
Silver.

Bivalent.
Barium,
Calcium,
Strontium,
Magnesium,
Cadmium,
Zinc,
Copper,
Mercury.

Trivalent.
Aluminum,

Bi, tri, or sexivalent.
Chromium,
Cobalt,
Iron,
Manganese,
Nickel,
Molybdenum.

Bi- and quadrivalent.
Iridium,
Platinum,
Tin.

Tri- and quinquivalent.
Antimony,
Arsenic,
Bismuth.

Uni- or trivalent.
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.

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[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.	*Heavy metals.*
Sp. gr. from 0.6 to 4.	Sp. gr. from 6 to 22.4.
Sulphides soluble in water.	Sulphides insoluble in water.

Light metals.

Earth metals.	*Alkaline earth metals.*	*Alkali-metal.*
Al, and many rare metals.	Ba, Ca, Sr, (Mg).	K, Na, Li, (NH_4).
Oxides insoluble.	Oxides soluble; Carbonates insoluble.	Oxides, carbonates, and most salts soluble.

Heavy metals.

Arsenic group.	*Lead group.*	*Iron group.*
As, Sb, Sn, Au, Pt, Mo.	Pb, Cu, Bi, Ag, Hg, Cd.	Fe, Co, Ni, Mn, Zn, Cr.
Sulphides insoluble in dilute acids.		Sulphides soluble 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.

Metals do not combine chemically with 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 198.)

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:

$$MO + C = CO + M;$$

or

$$2MO + C = CO_2 + 2M.$$

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 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 highest 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.

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?

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).

$K^{1} = 39$ (38.86).

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 red heat. Of all metals, those of the alkalies are the only ones forming hydroxides and carbonates which are not decomposed by heat.

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.

Potassium hydroxide, Potassii hydroxidum, $KOH = 55.74$ (*Caustic potash*), may be obtained by the action of the metal on water:

$$K + H_2O = H + KOH$$

The usual process for making potassium hydroxide is to boil together a dilute solution of potassium carbonate or bicarbonate and calcium hydroxide:

$$K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2KOH.$$

Large quantities of high-grade potassium hydroxide are now manufactured directly from the chloride by electrolysis.

Experiment 20. Add gradually 5 grammes of calcium hydroxide (slaked lime) to a boiling solution of about 5 grammes 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 one liter 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.

Antidotes: dilute acids, vinegar, to form salts; or fat, oil, or milk, to form soap.

Liquor potassii hydroxidi is a 5 per cent. solution of potassium hydroxide in water.

Potassium oxide, K_2O. This compound can be obtained either by burning potassium in air and subsequent heating of the product to a high temperature, or by fusing together potassium hydroxide and metallic potassium:

$$2KOH + 2K = 2K_2O + 2H.$$

Besides this potassium monoxide, corresponding to water in its composition, two other oxides of the composition K_2O_2 (corresponding to hydrogen peroxide, H_2O_2) and K_2O_4 are known. The latter oxide is obtained by the combustion of potassium in oxygen. It is a strong oxidizing agent, and at a high temperature is decomposed into oxide and oxygen.

Potassium carbonate, Potassii carbonas, $K_2CO_3 = 137.27$, 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 pages 122 and 201.)

$$K_2CO_3 + H_2O = KHCO_3 + KOH.$$

Potassium bicarbonate, Potassii bicarbonas, $KHCO_3 = 99.41$. Obtained by passing carbon dioxide through a strong solution of potassium carbonate, when the less soluble bicarbonate forms and separates into crystals:

$$K_2CO_3 + H_2O + CO_2 = 2KHCO_3.$$

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 = 100.43 (*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 micro-organisms, 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 mixing hot concentrated solutions of sodium nitrate and potassium chloride, when, on cooling, potassium nitrate separates in crystals, because it is much less soluble in cold water than sodium nitrate is. (See page 193.)

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

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, $KClO_3$ = 121.68 (*Chlorate of potash*). This salt may be obtained by the action of chlorine on a boiling solution of potassium hydroxide, as explained on page 237.

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, Potassii sulphas, $K_2SO_4 = 173.04$. 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, $KPH_2O_2 = 103.39$, 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, $KI = 164.76$, 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 grammes 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 grammes 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, $KBr = 118.22$, 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.

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:

$$2KNO_3 + H_2PtCl_6 = K_2PtCl_6 + 2HNO_3;$$

$$\text{or} \quad 2K^{\cdot} + 2NO_3' + 2H^{\cdot} + PtCl_6'' = K_2PtCl_6 + 2H^{\cdot} + 2NO_3'.$$

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 $HC_4H_4O_6'$ ions 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]

With few exceptions, potassium compounds are white, soluble in water, and not volatile at a low red heat. Of the above tests, the

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[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.

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 grammes of potassium iodide?

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 (NATRIUM).

$Na^{i} = 23$ (22.88).

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, $NaCl = 58.06$ (*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.

Sodium hydroxide, Sodii hydroxidum, $NaOH = 39.76$ (*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 double compound of oxy-sulphide 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.

Sodium carbonate has strong alkaline properties; it is soluble in 1.6 parts of cold water, and in much less water at higher temperatures; the crystals lose water on exposure to the air, falling into a white powder; heat facilitates the expulsion of the water of crystallization, and is applied in making the *monohydrated sodium carbonate, Sodii carbonas monohydras,* $Na_2CO_3.H_2O = 123.19$, which should contain about 85 per cent. of anhydrous sodium carbonate.

Sodium bicarbonate, Sodii bicarbonas, $NaHCO_3 = 83.43$ (*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.

$$Na_2CO_3.H_2O \quad + \quad CO_2 \quad = \quad 2NaHCO_3.$$

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.

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, $Na_2SO_4 10H_2O = 319.91$ (*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. (59° F.), in 0.25 part at 34° C. (93° F.), and in 0.47 part of boiling water.

Experiment 23. Dissolve about 10 grammes 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 grammes of crystallized sodium carbonate.

Sodium sulphite, Sodii sulphis, $Na_2SO_3.7H_2O = 250.39$. Sodium bisulphite, Sodii bisulphis, $NaHSO_3 = 103.35$. 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, $Na_2S_2O_3.5H_2O = 246.46$. 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 is used under the name of "hypo" in photography to dissolve chloride, bromide, or iodide of silver.

Sodium phosphate, Sodii phosphas, $Na_2HPO_4.12H_2O = 355.61$, 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:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$

The solution is filtered and sodium carbonate added, when calcium phosphate is precipitated, phosphate of sodium, 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 phenol-phthalein.

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 grammes 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, Sodii pyrophosphas, $Na_4P_2O_7.10H_2O = 443.02$. When exsiccated sodium phosphate is heated to a low red heat it loses water, and is converted into pyrophosphate, which, dissolved in hot water and crystallized, forms the official salt. 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, Sodii nitras, $NaNO_3 = 84.45$ (*Chile saltpeter, Cubic niter*). Found in nature, and is purified by crystallization. The crystals are transparent, deliquescent, and readily soluble.

Sodium nitrite, Sodii nitris, $NaNO_2 = 68.57$, 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, $Na_2B_4O_7.10H_2O = 379.32$ (*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. 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 has an important bearing in prescription writing. On diluting the glycerin mixture strongly with water, the alkaline reaction returns.

Other sodium salts which are official are *sodium hypophosphite,* $NaPH_2O_2 + H_2O$; *bromide,* $NaBr$; *iodide,* NaI; *chlorate,* $NaClO_3$.

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 = 6.98. 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.

$NH_4^i = 18$ (17.93).

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 :

$$HgK + NH_4Cl = KCl + NH_4Hg;$$
$$NH_4Hg = NH_3 + H + Hg.$$

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:

$$NH_4^{\cdot} + OH' + H^{\cdot} + Cl' \rightarrow NH_4^{\cdot} + Cl' + H_2O.$$

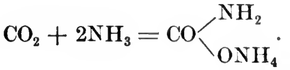
As fast as $(OH)'$ and $H^{\cdot}$ ions unite to form water, more NH_4OH dissociates and more NH_3 unites with water to form NH_4OH until the reaction is complete. All ammonium salts are highly dissociated in dilute solutions.

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 194.

Ammonium chloride, Ammonii chloridum, $NH_4Cl = 53.11$ (*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:



$$CO_2 + 2NH_3 = CO\left\langle\begin{array}{l}NH_2\\ONH_4\end{array}\right..$$

Ammonium carbonate, Ammonii carbonas, $NH_4HCO_3.NH_4NH_2CO_2 = 156.01$ (*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:

$$\begin{aligned}
H_2SO_4 + 2NH_4OH &= (NH_4)_2SO_4 + 2H_2O.\\
HNO_3 + NH_4OH &= NH_4NO_3 + H_2O.\\
H_3PO_4 + 2NH_4OH &= (NH_4)_2HPO_4 + 2H_2O.\\
H_2SO_4 + (NH_4)_2CO_3 &= (NH_4)_2SO_4 + H_2O + CO_2.
\end{aligned}$$

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:

$$\begin{aligned}
2KI + (NH_4)_2SO_4 &= 2NH_4I + K_2SO_4;\\
2KBr + (NH_4)_2SO_4 &= 2NH_4Br + K_2SO_4.
\end{aligned}$$

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 platinic chloride, 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 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

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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.

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.

$Mg^{ii} = 24.18.$

General remarks. Magnesium occupies a position intermediate between the alkali metals and the alkaline earths. To some extent it resembles also the heavy metal zinc, with which it has in common the volatility of the chloride, the solubility of the sulphate, and the isomorphism of several of its compounds with the analogously constituted compounds of zinc.

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 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. 31, page 80.

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.

Magnesium carbonate, Magnesii carbonas. Approximately: **$(MgCO_3)_4.Mg(OH)_2.5H_2O = 482.26$** (*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:

$$5MgSO_4 + 5Na_2CO_3 + 6H_2O = (MgCO_3)_4 Mg(OH)_2 5H_2O + 5Na_2SO_4 + CO_2.$$

By filtering, washing, and drying the precipitate, it is obtained in the form of a white, light powder.

Experiment 25. Dissolve 10 grammes 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 grammes of crystallized magnesium sulphate?) Notice that the dried precipitate evolves carbon dioxide when heated with acids.

Magnesium oxide, Magnesii oxidum, $MgO = 40.06$ (*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:

$$(MgCO_3)_4.Mg(OH)_2.5H_2O = 5MgO + 4CO_2 + 6H_2O.$$

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 gramme 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, $MgSO_4.7H_2O = 244.69$ (*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.

Effervescent magnesium sulphate, Magnesii sulphas effervescens, is a granular mixture of magnesium sulphate, sodium bicarbonate, tartaric and citric acids, in proper proportions. It contains what is equal to 50 per cent. of crystallized magnesium sulphate, and, like all effervescent salts, gives off carbonic acid when dissolved, which makes it more palatable.

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 discussing 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 versâ*. 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 195). 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.

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?

25. CALCIUM. STRONTIUM. BARIUM.

$Ca^{II} = 40\ (39.81)$. $Sr^{II} = 86.94$. $Ba^{II} = 136.4$.

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 mollusca, 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.

Calcium oxide, Lime, Calx, CaO = 55.68 (*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 acid among acids, and is used directly or indirectly in many branches of chemical manufacture.

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.

Freshly slacked lime, made into a thin paste with water and mixed with 3 to 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 (or perhaps oxide) which re-dissolves 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, $CaCO_3 =$ 99.35. Precipitated calcium carbonate is obtained as a white, tasteless, neutral, impalpable powder by mixing solutions of calcium chloride and sodium carbonate:

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

Experiment 28. Add to about 10 grammes 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, Calcii sulphas exsiccatus, $CaSO_4$ = 135.15 (*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.

Precipitated calcium phosphate, Calcii phosphas præcipitatus, $Ca_3(PO_4)_2$ = 307.98 (*Phosphate of lime*). By dissolving bone-ash (bone from which all organic matter has been expelled hy 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.

Calcium hypophosphite, Calcii hypophosphis, $Ca(PH_2O_2)_2 =$ 168.86. 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.)

$$8P + 6H_2O + 3[Ca(OH)_2] = 3[Ca(PH_2O_2)_2] + 2PH_3.$$

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, $CaCl_2 = 110.16$, and **Calcium bromide, Calcii bromidum, $CaBr_2 = 198.52$,** may both be obtained by dissolving calcium carbonate in hydrochloric acid or hydrobromic acid, until the acids are neutralized. Both salts are highly deliquescent.

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.

Sulphurated lime, Calx sulphurata, 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 274.)

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 116 and 193). 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, $Sr^{ii} = 86.94$. 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, $Ba^{ii} = 136.4$. 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 are poisonous; antidotes are sodium and 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.

Radium, Ra = 223.3. This element, discovered in 1899, has been mentioned in the article on radio-activity, page **85.** 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 gramme 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 radiferous barium salt (chloride or bromide) are extracted, and from

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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?

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.

Summary of analytical characters of the alkaline earth-metals.

	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.

26. ALUMINUM.

Al^{iii} 27 (26.9).

Aluminum is the representative of the metals of the earths proper; all other members of this class are found in nature in very small quantities, and are chiefly of scientific interest, with the exception of cerium, which furnishes an official preparation.

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.

Metallic aluminum may be obtained by the decomposition of aluminum chloride by metallic sodium :

$$AlCl_3 + 3Na = 3NaCl + Al.$$

It is now manufactured by the electrolysis of aluminum and sodium fluoride, or of other aluminum compounds.

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.

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.

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.

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 trivalent, and the composition of the chloride and hydroxide is therefore given as $AlCl_3$ and $Al(OH)_3$ respectively.

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*, $KAl(SO_4)_2.12H_2O = 471.02$, a white salt crystallizing in large octahedrons, soluble in 10 parts of cold and 0.3 part of boiling water; this solution has an acid reaction and a sweetish astringent taste.

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.

Dried alum, Alumen exsiccatum, $KAl(SO_4)_2 = 256.46$ (*Burnt alum*). This is common 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 hydroxide, Alumini hydroxidum, $Al(OH)_3 = 77.54$. 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 $Al^{\cdot\cdot\cdot}$, 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.

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 grammes 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 grammes 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 grammes 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, Alumini sulphas, $Al_2(SO_4)_3.16H_2O$ = 625.93. 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.

$$2Al(OH)_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 6H_2O.$$

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 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 $H_2Al_2Si_2O_8.H_2O$.

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 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 decomposed by heat, leaving a residue of oxide.

Cerium, Ce = 141. 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 either 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 rare earths.

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.

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 alum is official, how is it made, what are its properties, and what is it used for? What is dried alum, and how does it differ from common alum? How is aluminum chloride made, and how is the metal obtained from it? 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.

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.

27. IRON. (*Ferrum.*)

$Fe^{ii} = 55.5$.

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.

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 pyrites, bisulphide 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 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:

$$Fe_2O_3 + 3C = 3CO + 2Fe$$

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):

$$FeSO_4 + 2NH_4OH = (NH_4)_2SO_4 + Fe(OH)_2;$$
$$2Fe(OH)_2 + O + H_2O = Fe_2(OH)_6.$$

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, Ferri hydroxidum, $Fe(OH)_3 = 106.14$, 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 *loadstone*. 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.

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, $FeCl_2$ (*Protochloride of iron*), is obtained as a pale-green solution by dissolving iron in hydrochloric acid:

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

The anhydrous salt cannot be obtained by evaporation of the solution, as it decomposes; but it may be made by heating iron in a current of dry hydrochloric acid gas. The solution and salt absorb oxygen very readily:

$$3FeCl_2 + O = FeO + 2FeCl_3.$$

Ferric chloride, Ferri chloridum, $FeCl_3.6H_2O = 268.32$ (*Chloride, sesqui-chloride, or perchloride of iron*), 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.

Experiment 30. Dissolve by the aid of heat 1 gramme 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 $FeCl_2$, how much $FeCl_3$, and how much $FeCl_3.6H_2O$ can be obtained from 1 gramme 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 on ferric chloride this 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 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, $FeSO_4.7H_2O = 276.01$ (*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:

$$FeS_2 + 6O = FeSO_4 + SO_2.$$

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:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3[Fe_2(SO_4)_3] + 2NO + 4H_2O.$$

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, nitrogen dioxide 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, Ferri et ammonii sulphas,* $FeNH_4(SO_4)_2.12H_2O$ (*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 $5[Fe_2(SO_4)_3].Fe_2(OH)_6$.

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, $FePO_4$, may be obtained from ferric chloride solution by precipitation with an alkali phosphate. The *Soluble ferric phosphate* and the *Soluble ferric pyrophosphate* of the U. S. P., are scale compounds. (See index.)

Ferric hypophosphite, Ferri hypophosphis, $Fe(H_2PO_2)_3$ = 249.09 (*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.

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.

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.

PLATE I.

IRON. COBALT. NICKEL.

1

Ferrous sulphide, precipitated from ferrous solutions by ammonium sulphide.

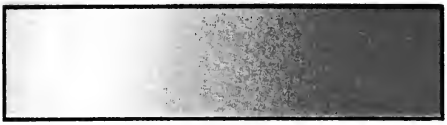
2

Ferrous hydroxide, passing into ferric hydroxide. Ferrous solutions precipitated by alkali hydroxides.

3

Ferric hydroxide, precipitated from ferric solutions by alkali hydroxides.

4



Ferrous solutions, precipitated by potassium ferrocyanide.

5

Ferric solutions, precipitated by potassium ferrocyanide, or, **Ferrous solutions** precipitated by potassium ferricyanide.

6

Ferric solutions, treated with alkali sulphocyanates.

7

Cobaltous carbonate, precipitated from cobaltous solutions by sodium carbonate.

8

Nickelous carbonate, precipitated from nickelous solutions by sodium carbonate.

A. Hoen & Co. Lith. Baltimore, Md.

28. MANGANESE—CHROMIUM—COBALT—NICKEL.

Manganese, Mn = 54.6. 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 mangan*ous* 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:

$$\begin{aligned} 2HMnO_4 &= H_2O + Mn_2O_7, \\ Mn_2O_7 &= 5O + 2MnO, \\ 2MnO + 2H_2SO_4 &= 2MnSO_4 + 2H_2O. \end{aligned}$$

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, 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, $MnO_2 = 86.36$, 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, Mangani sulphas, $MnSO_4.4H_2O = 221.47$, 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, isomorphous with the sulphates of magnesium and zinc; it is easily soluble in water.

Manganese hypophosphite, Mangani hypophosphis, $Mn(PH_2O_2)_2.H_2O = 201.54$, 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, $KMnO_4$ = 156.98. 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 grammes manganese dioxide, 2 grammes potassium hydroxide, and 1 gramme 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, $HMnO_4$, 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 200). 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. $Cr = 51.7$. Found in nature almost exclusively as chromite, or chrome-iron ore, $FeO.Cr_2O_3$, a mineral analogous in composition to magnetic iron ore, $FeO.Fe_2O_3$. The name chromium, from the Greek χρῶμα (chroma), color, was given to this metal on account of the beautiful colors of its different compounds, none of which is colorless. Chromium forms two basic oxides, *Chromous oxide*, CrO, the salts of which are, however, very unstable, and *chromic oxide* or *chromium sesquioxide*, Cr_2O_3, and an acid oxide, *chromium trioxide*, CrO_3, the combinations and reactions of which have to be studied separately. While chromium is closely allied to aluminum and iron on one side, it also shows a resemblance to sulphur, as indicated by the trioxide, CrO_3, and the acid, H_2CrO_4, which are analogous to SO_3 and H_2SO_4. Moreover, the barium and lead salts of chromic and sulphuric acids are both insoluble in water.

Metallic chromium is used in small proportion as an admixture to steel to which it imparts great hardness.

Potassium dichromate, Potassii dichromas, $K_2Cr_2O_7 = 292.28$ (*Bichromate or red chromate of potash*). This salt is by far the most important of all chromium compounds, and is 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*), 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 = 99.34 (*Chromic acid, Chromic anhydride*), 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 grammes 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*), 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:

$$\begin{array}{lclclclcl} K_2Cr_2O_7 & + & H_2SO_4 & = & K_2SO_4 & & & + & H_2Cr_2O_7, \\ H_2Cr_2O_7 & = & H_2O & + & 2CrO_3; 2CrO_3 & & & = & Cr_2O_3 + 3O, \\ Cr_2O_3 & + & 3H_2SO_4 & = & Cr_2(SO_4)_3 & & & + & 3H_2O. \end{array}$$

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 re-precipitated 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).

Cobalt and Nickel, Co = 58.56, Ni = 58.3. 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.)

29. ZINC.

$Zn^{ii} = 64.9.$

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.

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.

PLATE II.

MANGANESE. CHROMIUM.

1

Potassium permanganate solution, more or less saturated. Boraxbead colored by manganese.

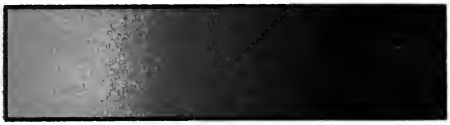
2

Manganous sulphide, precipitated from manganous solutions by ammonium sulphide.

3

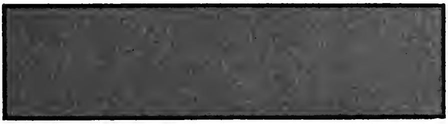
Manganous hydroxide, passing into the higher oxides. Manganous solutions precipitated by alkali hydroxides.

4



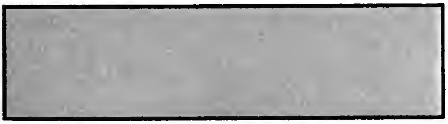
Potassium dichromate solution deoxidized by reducing agents.

5



Chromic hydroxide, precipitated from chromic solutions by alkali hydroxides.

6



Lead chromate, precipitated from soluble chromates by lead acetate.

7

Silver chromate, precipitated from neutral chromates by silver nitrate.

8

Mercurous chromate, precipitated from neutral chromates by mercurous solutions.

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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.

As has been pointed out in Chapter 24, zinc bears a close chemical relationship to magnesium, and both these metals resemble cadmium in their chemical properties. In fact, the three elements magnesium, zinc, and cadmium form a natural group similar to that of the alkali metals or the alkaline earth metals.

Zinc oxide, Zinci oxidum, $ZnO = 80.78$ (*Flores zinci, Zinc-white*), 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:

$$3[Zn(OH)_2].2ZnCO_3 = 5ZnO + 2CO_2 + 3H_2O.$$

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, $ZnCl_2 = 135.26$. 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, Zinci bromidum, $ZnBr_2 = 223.62$. Obtained analogously to the chloride by dissolving zinc in hydrobromic acid; it is a white powder, resembling the chloride in its properties.

Zinc iodide, Zinci iodidum, $ZnI_2 = 316.7$. 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.

$$5ZnSO_4 + 5Na_2CO_3 + 3H_2O = 3CO_2 + 5Na_2SO_4 + 2(ZnCO_3).3Zn(OH)_2.$$

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 grammes 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, $ZnSO_4.7H_2O = 285.4$ (*White vitriol*), is obtained by dissolving zinc in dilute sulphuric acid:

$$H_2SO_4 + xH_2O + Zn = ZnSO_4 + xH_2O + 2H.$$

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 15.

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.

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 have 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 whose sulphide is white.)

If the zinc salt is not pure, the sulphide may appear more or less gray instead of white:

$$ZnSO_4 + (NH_4)_2S = (NH_4)_2SO_4 + ZnS.$$

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.

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, $Cd = 111.6$. 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.

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, $Pb^{ii} = 205.35$ (*Plumbum*). This metal 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

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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?

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 gramme 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 198). 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 = 221.23 (*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:

$$2PbSO_4 + 2H_2O \underset{\text{charging} \rightarrow}{\overset{\leftarrow \text{ discharging.}}{\rightleftarrows}} Pb + 2H_2SO_4 + PbO_2.$$

Lead nitrate, Plumbi nitras, $Pb(NO_3)_2 = 328.49$. 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, $PbCO_3$, 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, Plumbi iodidum, $PbI_2 = 457.15$. 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, mangesium 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, page 317.)

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, $Cu^{ii} = 63.1$ (*Cuprum*). Found in nature sometimes in the metallic state—generally, however, combined with sulphur or oxygen. The commonest copper-ore is *Copper pyrites,* 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	...	...
Babbit-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. Cuprous salts of oxygen acids do not exist. 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:

$$CuSO_4 + 2KI = CuI + I + K_2SO_4.$$

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):

$$\begin{aligned} CuSO_4 + 2KOH &= K_2SO_4 + Cu(OH)_2; \\ Cu(OH)_2 &= H_2O + CuO. \end{aligned}$$

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.)

$$\begin{aligned} CuO + Cu &= Cu_2O; \\ 2CuO + C &= Cu_2O + CO. \end{aligned}$$

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 grammes 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, $CuSO_4.5HO_2 = 247.85$ (*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 pyrites, 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 grammes of fine copper wire 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 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 $Cu(NH_3)_4^{\prime\prime}$, 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.)

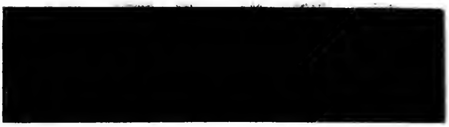
3. Add ammonia water: a bluish precipitate of cupric hydroxide is formed which readily dissolves in an excess of the reagent, forming a deep azure-blue solution containing an ammonio-copper compound. (See explanation above.) (Plate III., 3.)

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.

PLATE III.

COPPER. LEAD. BISMUTH.

1

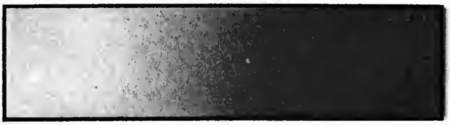


Cupric sulphide or **lead sulphide,** precipitated from solutions of copper or lead by hydrogen sulphide.

2

Cupric hydroxide passing into **cupric oxide.** Cupric solutions precipitated by potassium hydroxide and boiling.

3



Cupric solutions treated with ammonia water.

4

Cupric carbonate, precipitated from cupric solutions by sodium carbonate.

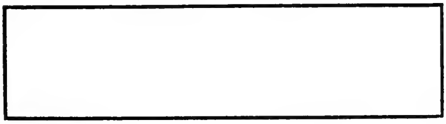
5

Cupric ferrocyanide, precipitated from cupric solutions by potassium ferrocyanide.

6

Lead iodide, precipitated from lead solutions by soluble iodides.

7



Lead solutions with soluble chlorides, sulphates or carbonates. **Bismuth solutions** with alkali hydroxides or carbonates.

8

Bismuth sulphide, precipitated from bismuth solutions by hydrogen sulphide.

A Hoen & Co Lith Baltimore, Md

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 319.)

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

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, $Bi^{iii} = 206.9$. Found in nature chiefly in the metallic state, disseminated, in veins, through various rocks. 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.

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:

$$Bi(OH)_3 = Bi\begin{cases} O \\ OH \end{cases} + H_2O.$$

Bismuth subnitrate, Bismuthi subnitras, $BiONO_3.H_2O$? (*Oxynitrate of bismuth*). By dissolving metallic bismuth in nitric acid, a solution of bismuth nitrate is obtained, nitrogen dioxide 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 gramme 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 this solution of normal bismuth nitrate into 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 $(BiO)_2CO_3.H_2O$ (?) (*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.

31. SILVER—MERCURY.

Silver, Ag = 107.12 (*Argentum*). This metal is found sometimes in the metallic state, but generally as a sulphide, which is nearly always in combination with large quantities of lead sulphide, such ore being known as *argentiferous galena.* The lead manufactured from this ore contains the silver, and is separated from it by roasting the alloy in a current of air, whereby lead is oxidized and converted into litharge, while pure silver is left.

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?

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.

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, $AgNO_3 = 168.69$. 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.*

When fused with twice its weight of potassium nitrate and formed into similar rods, it forms the *mitigated* or *diluted silver nitrate* (*mitigated caustic*) of the U. S. P.

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 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, $Ag_2O = 230.12$. 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 an 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. Solution of alkali hydroxides precipitates 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 319.)

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 193.)

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 = 198.5 (*Quicksilver*). 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 the metal with 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 radicle. 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, $HgO = 214.38$. 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, Hydrargyrum chloridum mite, HgCl = 233.68 (*Calomel, Mild chloride of mercury, 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, $HgCl_2$ = 268.86 (*Corrosive chloride of mercury, 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.

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, $HgI = 324.4$ (*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, $HgI_2 = 450.3$ (*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 oxy-sulphate*). 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 gramme) 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 nitro-hydrochloric 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 = 249.61 (*White precipitate, Mercuric-ammonium 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 mercuric-ammonium 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 mercuric-ammonium 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.

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:

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4;$$
$$2HgCl + SnCl_2 = 2Hg + SnCl_4.$$

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.	....

PLATE IV.

MERCURY. SILVER.

1

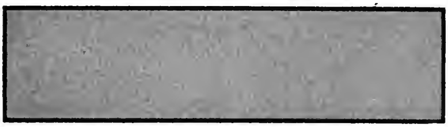

Mercuric sulphide, precipitated fro mercuric solutions by hydrogen sulphid

2


Mercuric sulphide, Cinnabar.

3


Yellow mercuric oxide, precipitat from mercuric solutions by potassium h droxide.

4


Red mercuric oxide, obtained heating mercuric nitrate.

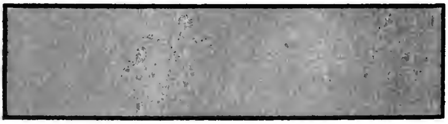
5


Mercurous oxide, precipitated fro mercurous solutions by potassium hydro ide.

Silver sulphide, precipitated fro silver solutions by hydrogen sulphide.

6


Mercuric iodide, precipitated fro mercuric solutions by alkali iodides.

7


Mercurous iodide, precipitated fro mercurous solutions by alkali iodides.

8


Mercuric solutions with ammoniu hydroxide. **Mercurous solutions** wit soluble chlorides. **Silver solutions** wit soluble chlorides.

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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 319.)

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.

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.

32. ARSENIC.

$As = 74.4.$

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.

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 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.

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 arsenio-sulphide 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:

$$As_2O_3 + 3C = 3CO + 2As.$$

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 amospheric 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, $As_2O_3 = 196.44$ (*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 semi-transparent masses which frequently show a stratified appearance; recently sublimed arsenous oxide exists as the amorphous semi-transparent 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 *met-arsenous 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 potassii 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 met-arsenite.

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 pyroarsenate, 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, $Na_2HAsO_4.7H_2O$ = 309.84 (*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 pyroarsenate 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:

$$\begin{aligned} As_2O_3 + 12H &= 2AsH_3 + 3H_2O. \\ As_2O_5 + 16H &= 2AsH_3 + 5H_2O. \\ AsCl_3 + 6H &= AsH_3 + 3HCl. \end{aligned}$$

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 deposit of metallic 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 metallic 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 metallic 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 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 sulph-arsenate:

$$2(NH_4)_3AsS_4 + 6HCl = 2H_3AsS_4 + 6NH_4Cl.$$
$$2H_3AsS_4 = 3H_2S + As_2S_5.$$

The tri- and pentasulphide of arsenic have acid properties, similar to the corresponding oxides. They unite with alkali sulphides to form soluble meta-sulph-arsenites and sulph-arsenates:

$$As_2S_3 + (NH_4)_2S = 2NH_4AsS_2.$$
$$As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3AsS_4.$$

When the trisulphide is dissolved in a solution of a polysulphide (yellow ammonium sulphide), a sulph-arsenate 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 met-arsenite and meta-sulph-arsenite, and arsenate and sulph-arsenate respectively.

Arsenous iodide, Arseni iodidum, AsI_3 = 454.5 (*Iodide of arsenic*), 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 gramme 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 precipitate 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 an 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

PLATE V

ARSENIC. ANTIMONY. TIN.

1

Arsenous sulphide, precipitated fr
arsenous solutions by hydrogen sulphi

2

Cupric arsenite, precipitated fr
arsenous solutions by cupric-ammoniu
sulphate.

3

Silver arsenite, precipitated fr
arsenous solutions by silver nitrate.

4

Silver arsenate, precipitated fro
arsenic solutions by silver nitrate.

5

Antimonous sulphide, precipitat
from solutions of antimony by hydrog
sulphide.

6

Native or **crystallized antimono**
sulphide.

7

Stannous sulphide, precipitated fr
stannous solutions by hydrogen sulphi

8

Stannic sulphide, precipitated fr
stannic solutions by hydrogen sulphide.

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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 arseno-molybdate 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.

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 metallic ring in the upper part of the contraction. (Fig. 44.)

Fig. 44.

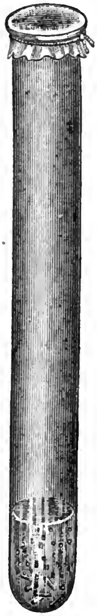
7. Heat arsenous or arsenic oxide upon a piece of charcoal by means of a blow-pipe: a characteristic odor of garlic is perceptible.

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 saturated solution of stannous chloride in concentrated hydrochloric acid, and heat in boiling water for 15 minutes; a brown color or precipitate is formed, due to separation of the arsenic. Antimony does not respond to this test.

FIG. 45.



10. *Gutzeit's test.* Place a small piece (about 1 gramme) 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. 45.) 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:

$$AsH_3 + 6AgNO_3 = 3HNO_3 + Ag_3As.(AgNO_3)_3.$$

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, U. S. P. This is employed in nearly all instances in the U. S. P. where traces of arsenic are 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 grammes 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 $\frac{1}{500}$ per cent. solution of arsenic trioxide, which need not be submitted to the reduction with sulphur dioxide. Antimony gives a dark coloration.

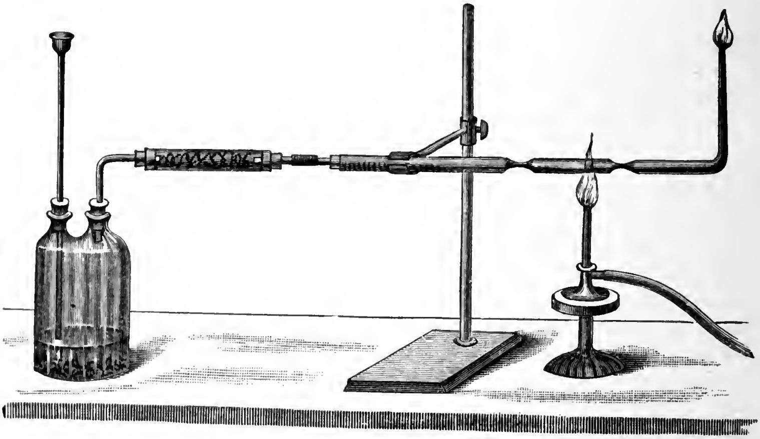
11. *Fleitmann's test.* This is similar to the Gutzeit's test, the chief difference being that hydrogen is evolved in alkaline solution, which has the advantage that the presence of antimony does not interfere, because this metal does not form antimonetted hydrogen in alkaline solutions.

Place about 1 gramme 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. 46) 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 ¼ inch, drawn out at intervals of about 3 inches, so as to reduce its diameter to ⅛ 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 30 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. 46.



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 metallic arsenic. (See explanation above in connection with arsenetted hydrogen.)

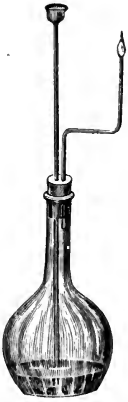
The glass tube heated, as above mentioned, at one of its wide parts, will show a bluish-black metallic mirror at the constriction beyond.

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. 47 represents a simpler form of Marsh's apparatus, which generally will answer for students' tests.

Fig. 47.



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 = 119.3 (*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

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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.

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, forming met-antimonates 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 gramme 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 nitro-hydrochloric 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 antimony*). 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, semi-transparent 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 grammes 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 oxy-chloride 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 gramme 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, have 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 = 118.8 (*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 (*Stannic acid*), **H_2SnO_3**, 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):

$$SnCl_4 + 4H_2S = 4HCl + SnS_2.$$

The precipitate is soluble in ammonium sulphide.

3. Sodium or potassium hydroxide added to a stannous salt produces a white precipitate of stannous hydroxide, $Sn(OH)_2$. 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 = 195.7 (*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 nitro-hydrochloric 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 nitro-hydrochloric 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 = 193.3. 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*), 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 Röntgen 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 = 191.5. 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 = 95.3. 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.

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.	....	....	....	....

V.

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. 48.)
2. Bunsen lamp with flexible tube (Fig. 48) or (where without gas-supply) spirit-lamp and alcohol.

3. Test-tube stand and one dozen assorted test-tubes. (Fig. 49.)
4. Three beakers from 100 to 150 c.c. capacity. (Fig. 50, A.)
5. Two flasks of 100 to 150 c.c. capacity. (Fig. 50, B.)

Fig. 48.

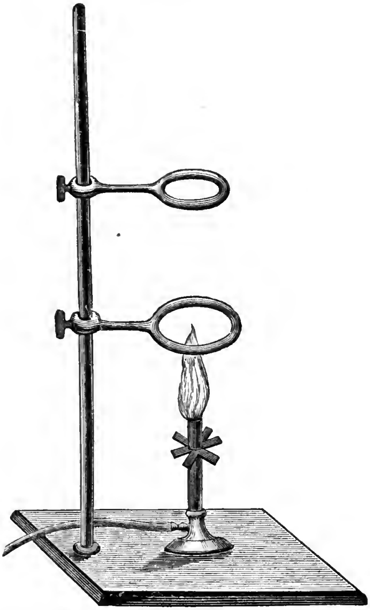


Fig. 49.

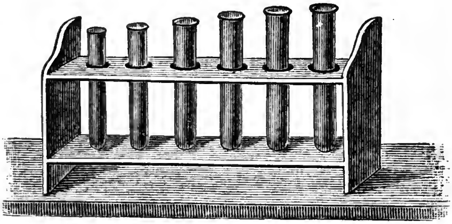
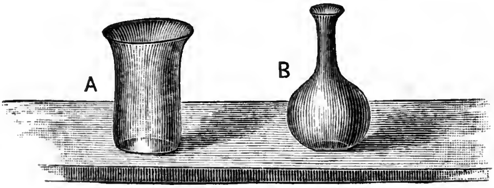


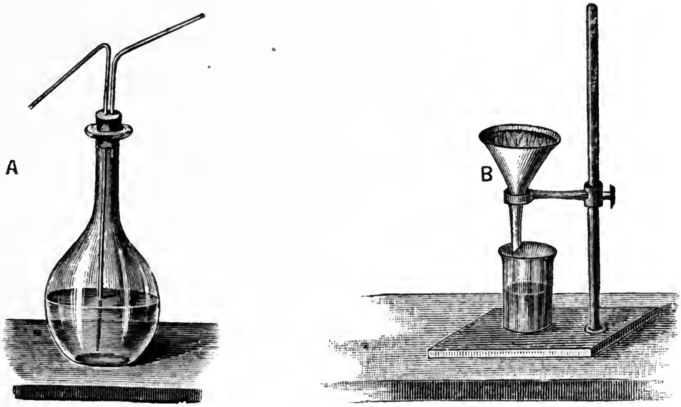
Fig. 50.



6. Wash-bottle of about 400 c.c. capacity. (Fig. 51, A.)
7. Three small glass funnels, about one and a half to two inches in diameter. (Fig. 51, B.)

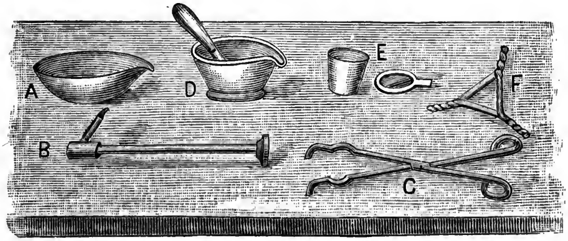
8. A few pieces of glass tubing about ten inches long, and some India-rubber tubing to fit the glass tubing.
9. Three glass rods.

Fig. 51.



10. Three small porcelain evaporating dishes, about two inches in diameter. (Fig. 52, A.)
11. Blowpipe. (Fig. 52, B.)
12. Crucible tongs. (Fig. 52, C.)

Fig. 52.



13. Round and triangular file
14. Wire gauze, about six inches square, or sand tray.
15. One 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. 52, D.)
22. Small porcelain crucible.
23. Small platinum crucible. (Fig. 52, E.)
24. Wire triangle to support the crucible. (Fig. 52, 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 grammes of cobaltous nitrate, $Co(NO_3)_2.6H_2O$, and 10 grammes 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 grammes of potassium iodide are dissolved in hot water, and to this is added a hot solution, made by dissolving 2.5 grammes of mercuric chloride in 10 c.c. of water. To the turbid red mixture is added a solution made by dissolving 16

grammes 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 notebook, 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 in so far 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 gramme. 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.)

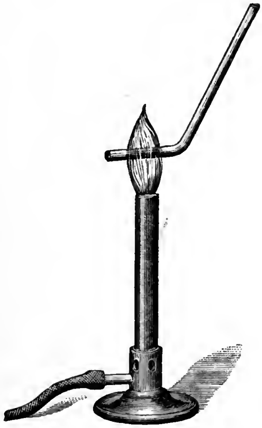
3. Heating on platinum foil or in a dry glass tube, open at both ends. (If the substance to be examined be a liquid, it should be evaporated in a small porcelain dish to see whether a solid residue be left or not. If a residue be left, it should be treated like a solid.) The heating of a small quantity 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 381.)

FIG. 53.



Heating of solids in bent glass tube.

FIG. 54.

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. 53, 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. 54). 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. 55.)

Fig. 55.

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. 56), the other end is bent so as to form a small 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.

Fig. 56.

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 bead 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 re-obtained 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 nitro-hydrochloric 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 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.

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. *Easily volatilized* are: All compounds of **ammonium** and **mercury,** some of **arsenic,** some of **antimony,** etc. (Heat in a glass tube as directed on page 377.) *Fusible* are: Most of the salts of the **alkalies,** and some of those of the **alkaline earths,** many metals, etc. *Infusible* are: Salts of the **earths,** and most salts of the **alkaline earths** and **heavy metals,** most **silicates,** etc. *Assume a darker color:* Many **oxides of the heavy metals** and **their salts** (oxides of zinc, antimony, lead, etc.). *Evolve water:* Many **salts containing water of crystallization,** some **hydroxides,** etc. *Decrepitate:* Some **salts,** sodium chloride, for instance.
Heat the solid substance on charcoal.	*Deflagrate:* **Nitrates, chlorates, iodates, bromates,** etc. 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.** Give *bright metallic grains without incrustation:* Compounds of **gold, silver, copper, tin.** Give *bright metallic grains with incrustation:* Compounds of **lead, bismuth, antimony.** 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.** *Violet* flame, compounds of **potassium.** *Crimson* flame, compounds of **lithium** or **strontium.** *Orange* flame, compounds of **calcium** *Yellowish-green* flame, compounds of **barium** or **molybdenum.** *Green* flame, compounds of **copper, phosphoric** or **boric acids.** *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.** *Blue* bead, compounds of **cobalt** or **copper** in the oxidizing flame. *Red* bead, compounds of **copper** in the reducing flame. *Violet* bead, compounds of **manganese.** *Yellow* to *brown* bead, compounds of **iron.** *Colorless* bead, compounds of the **light metals** and those of the **arsenic group**; also **silver, bismuth, lead,** etc.

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 344, 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 *ammonium 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

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?

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.

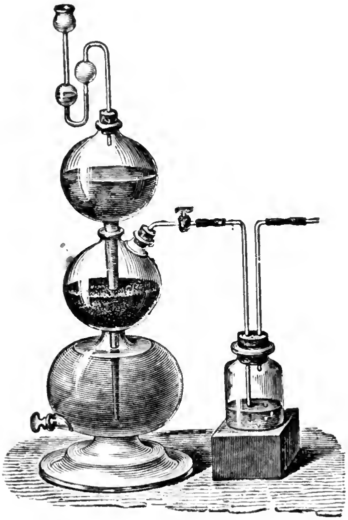
Acidifying the solution. Hydrogen sulphide has to be added to the *acidified* solution for two reasons, viz.: In a neutral or alkaline solution some metals of the arsenic group (which are to be precipitated) would not be precipitated by hydrogen sulphide; some of the metals of the iron group (which are 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 387.

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.

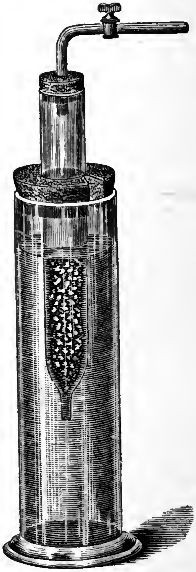
Addition of hydrogen sulphide. This reagent is employed either in the gaseous state (by passing it through the heated solution) or as hydrogen sulphide water. The latter reagent answers in those cases where but one metal is present; if, however, metals of the arsenic and lead groups are to be separated from metals of other groups, the gas must be used.

Fig. 57



Apparatus for generating hydrogen sulphide.

Fig. 58.



Apparatus for generating hydrogen sulphide.

For generating hydrogen sulphide the directions given on page 214 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. 57 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. 58. 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. A precipitate may be caused by other substances than those mentioned. See page 342.	**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.**
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 389.

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.

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 fil-

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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? 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?

trate, 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.

TABLE IV.—Treatment of that portion of the hydrogen sulphide precipitate which is insoluble in ammonium sulphide.

<table>
<tr><td colspan="4">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.</td></tr>
<tr><td rowspan="3">Residue may consist of:
Mercuric sulphide, which is black and easily dissolves in nitrohydrochloric acid, which solution, after sufficient evaporation, is tested by potassium iodide, etc.
Lead sulphate is white, pulverulent, and soluble in ammonium tartrate.
Sulphur is yellow and combustible.</td><td colspan="3">Filtrate may contain the **nitrates of lead, copper, bismuth,** and **cadmium.** Add to the solution a few drops of dilute sulphuric acid.</td></tr>
<tr><td rowspan="2">Precipitated is **lead,** as white lead sulphate which is soluble in ammonium tartrate with excess of ammonium hydroxide.</td><td colspan="2">Solution may contain **copper, bismuth,** and **cadmium.** Supersaturate with ammonium hydroxide.</td></tr>
<tr><td>Precipitated is white **bismuth** hydroxide. Dissolve in hydrochloric acid and apply tests for bismuth.</td><td>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.**</td></tr>
</table>

TABLE V.—Treatment of the hydrogen sulphide precipitate which is soluble in ammonium sulphide.

<table>
<tr><td colspan="2">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.</td></tr>
<tr><td>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.
A dark-colored residue may indicate gold or platinum, for which use special tests.</td><td>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.</td></tr>
</table>

TABLE VI.—Treatment of the precipitate formed by ammonium hydroxide and ammonium sulphide.

<table>
<tr><td colspan="4">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.</td></tr>
<tr><td colspan="2">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.</td><td colspan="2">The solution may contain zinc, manganese, cobalt, and nickel. Acidulate the ammonia solution with acetic acid, and add hydrogen sulphide.</td></tr>
<tr><td>Precipitated is ferric hydroxide, reddish-brown. Dissolve in dilute hydrochloric acid, and add <i>potassium ferrocyanide.</i> A blue precipitate indicates iron.

Precipitate may also contain the <i>phosphates of the alkaline earths or magnesium.</i> 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 <i>calcium.</i>
<i>Barium and strontium</i> are indicated by the addition of calcium sulphate, and distinguished by flame reaction.
Test for phosphoric acid by ammonium molybdate.</td><td>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 <i>chromium,</i> or <i>aluminum</i> and <i>chromium.</i> 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 <i>aluminum.</i> To filtrate add barium chloride; a yellow precipitate indicates <i>chromium.</i></td><td>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.</td><td>Solution may contain manganese, which is verified by adding ammonium hydroxide and sulphide, which produce a flesh-colored precipitate.</td></tr>
</table>

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[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

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[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 indica-

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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?

tions 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.

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 re-precipitating 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 re-precipitated.

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.

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). **Phosphoric acid** (molybdate of ammonium test). **Boric acid** (green flame after moistening with sulphuric acid). **Arsenic acid,** **Silicic acid,** **Molybdic acid,** **Phosphorous acid,** **Arsenous acid,** } Special tests.	**Hydrochloric acid** (silver test). **Carbonic acid** (the gas is generated also by diluted acids in the cold, and renders lime-water turbid). **Nitric acid** (the vapors turn red on the addition of ferrous sulphate). **Sulphurous acid** (odor). **Hydrogen sulphide** (odor). **Hydrofluoric acid** (corrodes glass). **Acetic acid** (odor of acetic ether on the addition of alcohol). **Many organic acids** are decomposed with liberation of colorless gases.	**Hydriodic acid** (violet vapors of iodine). **Hydrobromic acid** (brown vapors of bromine). **Bromic acid** (brown vapors; deflagration on charcoal). **Chloric acid** (the greenish-yellow gas explodes readily). **Nitric acid** (vapors more red on adding ferrous sulphate). **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.**
All the above precipitates are soluble in hydrochloric and most other acids, with the exception of barium sulphate.					**Chloric acid.** **Hypochlorous acid.** **Acetic acid.**

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	a	w	a	w	a	...
Arsenite . . .	...	w	a	a	...	...	a	...	a	a	a	a	a	a	a	a	a	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	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 inflammable 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 1. Odor of SO_2—test for sulphite (alkaline). Odor of SO_2 + precipitate of sulphur—test for thiosulphate (neutral). 2. Odor of H_2S—test for a sulphide (alkaline). 3. Odor of HCN*—test for cyanide (alkaline). 4. Odor of HCN and a cryst. deposit, often bluish—test for ferro- or ferricyanide. 5. Odor of HCN + ppt. of sulphur—test for a sulphocyanate.	*b.* Colored fumes: 1. Brownish—test for bromide. 2. Violet—test for iodide. 3. Greenish-yellow—test for chlorate. (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.	*c.* Colored fumes. 1. Reddish—test for nitrite (alkaline). 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.
d. A *strongly acid*, combustible mass—test for free H_3PO_2: a *neutral* combustible mass, indicates a salt of H_3PO_2 (hypophosphorous acid).	**Caution.*—Take care in smelling vapors of HCN, as they are poisonous.	*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.
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*.		
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*.		

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: *Note.*—If Pb, Hg(ous), Ag, are indicated by the preliminary examination, omit treatment with HCl, but use HNO_3.	*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:*
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— *a.* Mercuric sulphide, HgS, black or red, and volatile on foil by heat. *b.* Gold. *c.* Mercurous chloride, HgCl. (Slowly soluble in HNO_3. See *B*, *c*.) *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— 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. 2. Test for phosphate by molybdate solution. 3. Test for borate by alcohol flame. 4. Arsenate and arsenite are detected in analysis for metals: make further tests to distinguish the two. 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 $AgNO_3$. (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— *a.* Sulphate of Ba, Sr, Pb. These must be fused with Na_2CO_3. *b.* Lead chloride, $PbCl_2$ ($PbBr_2$, PbI_2) (if not removed by much hot water.) *c.* Chloride, bromide, iodide, or cyanide of silver, AgCl, AgBr, AgI, AgCN. Test solubility in NH_4OH and $Na_2S_2O_3$. (AgCN with HCl forms insoluble AgCl and leaves HCN in solution recognized by odor.) *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,

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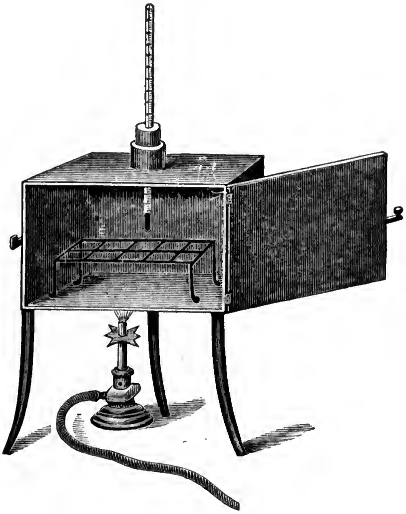
Questions.—Why is sulphuric acid added to a solid substance when it is to be examined for acids? Mention some acids which cause the liberation of colorless, and some which cause the liberation of colored gases when the salts of these acids are heated with sulphuric acid. Mention an acid which is precipitated 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?

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 gramme) 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's-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. 59, in which a constant temperature of about 100° C. (212° F.) is maintained. The dried filter is then taken from the funnel and its contents are transferred to a platinum (or porcelain) crucible, which has been previously

FIG. 59.



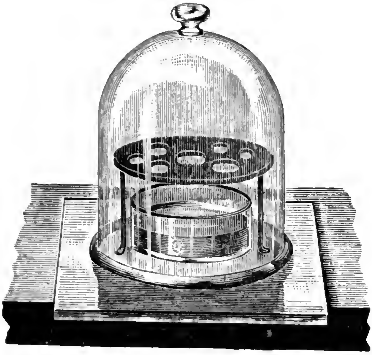
Drying-oven.

weighed and stands on a piece of glazed, colored paper in order to collect any particle of the dried precipitate which 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 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 kept dry by means of concentrated sulphuric acid. Fig. 60 shows a convenient form of desiccator.

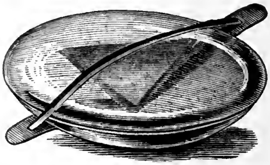
The empty crucibles should be weighed under the same conditions —*i. e.*, after having been heated and cooled in a desiccator.

Fig. 60.



Desiccator.

Fig. 61.



Watch-glasses for weighing filters.

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.

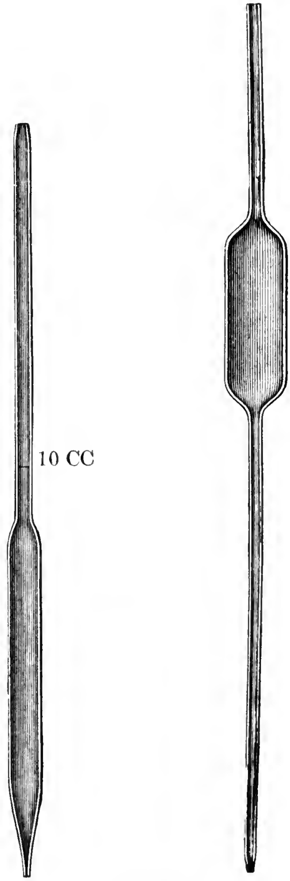
The weighing of dried filters is best accomplished by placing them between two watch-glasses held together by means of a brass or nickel clamp, as shown in Fig. 61.

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.

Fig. 62.

Liter flask.

Fig. 63.

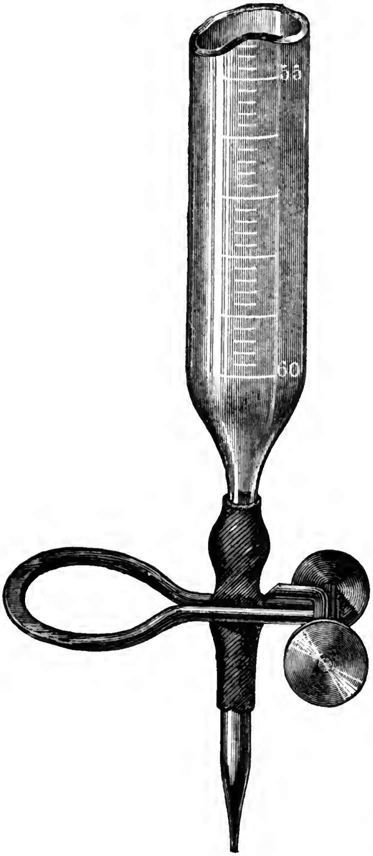


Pipettes.

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.

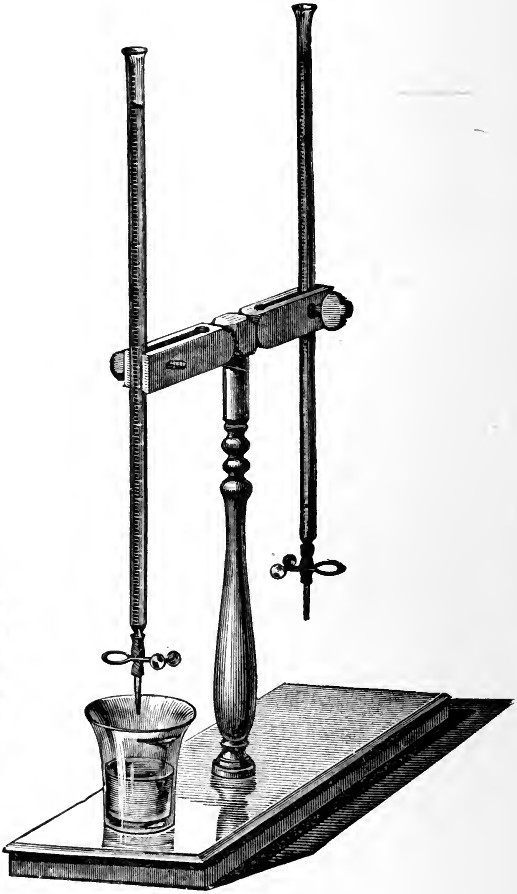
The special apparatus required for volumetric analysis consists of a few flasks, some pipettes, burettes, and a burette-holder. The flasks should have a mark on the neck, indicating a capacity of 100, 250, 500, and 1000 c.c. respectively. (See Fig. 62.)

FIG. 64.



Mohr's burette and clamp.

FIG. 65.

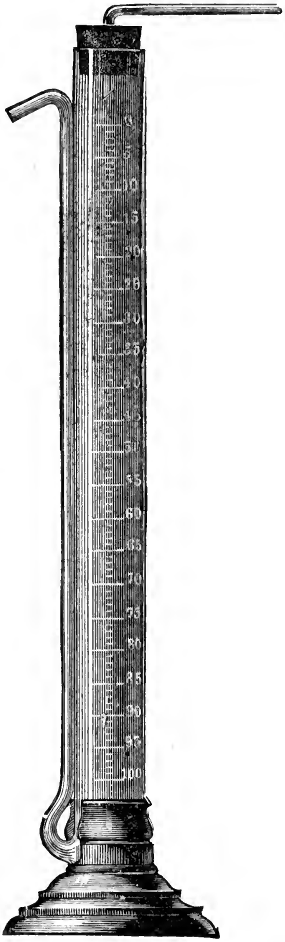


Mohr's burette and holder.

Of pipettes (Fig. 63) are mostly used those having a capacity of 5, 10, 25, and 50 cubic centimeters.

Of burettes many different forms are used; in most cases Mohr's burette (Figs. 64 and 65) 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. 66) is generally used.

FIG. 66.



Gay Lussac's burette.

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 one gm. of hydrogen, or the weight of one atom of hydrogen expressed in grammes, or the chemical equivalent of one gm. of hydrogen, contained 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 grammes.

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:

$$\underset{36.18}{HCl} + \underset{55.74}{KOH} = KCl + H_2O.$$

$$2HCl + Ba(OH)_2 = BaCl_2 + 2H_2O.$$

or

$$\underset{36.18}{HCl} + \underset{\frac{170.16}{2}}{\frac{Ba(OH)_2}{2}} = \frac{BaCl_2}{2} + H_2O.$$

$$\underset{55.74}{KOH} + \underset{\frac{97.35}{2}}{\frac{H_2SO_4}{2}} = \frac{K_2SO_4}{2} + H_2O.$$

The above equations show that 36.18 gramme of HCl are equivalent to 55.74 gramme of KOH, but these are the quantities taken for a liter of normal solution respectively, 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 48.675 grammes 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 grammes, 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: Carbonate 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. Of indicators, a few drops are in most cases sufficient for the purpose. (See colored Plate VII.)

Litmus solution. This is made by exhausting coarsely powdered litmus with boiling alcohol, which removes a red coloring matter, erythrolitmin. 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 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 gramme of phenolphthalein is dissolved in 50 c.c. of alcohol and water added to make 100 c.c. The colorless solution is colored deep purplish-red by alkali hydrates or carbonates, but not by bicarbonates; acids render the red solution colorless. The solution is not suitable as an indicator for ammonia. Carbonates must be titrated in boiling solution to drive off carbon dioxide.

Methyl-orange solution. 1 gramme of methyl-orange (also known as helianthin, tropæolin D, or Poirier's orange 3 P), the sodium or ammonium salt of dimethylamido-azobenzol-sulphonic 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 hydrates, carbonates, or bicarbonates. Carbonic acid does not affect it, but mineral acids change its color to crimson. It should be used in cold solutions.

Hæmatoxylin solution. 0.2 gramme 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 gramme 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.

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, may be mentioned those 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 in a definite volume of 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.

It is for this reason that the basis in preparing a volumetric normal acid solution is oxalic acid, a substance which can be readily obtained in a pure crystallized condition.

Normal acid solution. Crystallized oxalic acid has the composition $H_2C_2O_4.2H_2O$ and a molecular weight of 125.1. Being dibasic, only half of its weight is taken for the normal solution, which is made by placing 62.55 grammes 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 phenolphthalein 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 48.675 grammes of H_2SO_4, and normal hydrochloric acid 36.18 grammes 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.

Other methods of determining the exact standard of normal acids depend upon the precipitation of 10 c.c. of the sulphuric acid solution by barium chloride, or of 10 c.c. of the hydrochloric acid solution by silver nitrate, and weighing the precipitated barium sulphate or silver chloride. Ten c.c. of normal sulphuric acid give 1.1587 grammes of barium sulphate, and 10 c.c. of normal hydrochloric acid 1.423 grammes of silver chloride.

A third method depends on the formation of, and the weighing as, an ammonium salt. Ten c.c. of either acid are neutralized (or slightly supersaturated) with ammonia water. The solution is evaporated in a previously weighed platinum dish over a water-bath, the dry salt is repeatedly moistened with alcohol, and finally dried in an air-bath at a temperature of 105° C. (221° F.) for about half an hour. Ten c.c. of normal sulphuric acid give of ammonium sulphate 0.65605 gramme, and 10 c.c. of normal hydrochloric acid of ammonium chloride 0.5311 gramme.

Normal alkali solution. A normal solution of sodium carbonate may be made by dissolving 52.655 grammes (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 grammes of potassium hydroxide or 60 grammes 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 solution of litmus or phenolphthalein, 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 186.78 it follows that this weight in grammes will neutralize one liter of normal alkali solution. The Pharmacopœia directs to dissolve 9.339 grammes of potassium bitartrate in boiling water and titrating with a portion of the caustic alkali solution, the remainder of which is then diluted until 50 c.c. are required 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 of the two indicators mentioned 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.

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:

$$\underset{36.18}{\mathrm{HCl}} + \underset{55.74}{\mathrm{KOH}} = \mathrm{KCl} + \mathrm{H_2O},$$

from which we see that

36.18 gm. HCl = 55.74 gm. KOH = 1000 c.c. normal KOH,
or, 0.03618 gm. HCl = 1 " "

Again,

$$\underset{2 \times 55.74}{\mathrm{2KOH}} + \underset{97.35}{\mathrm{H_2SO_4}} = \mathrm{K_2SO_4} + \mathrm{2H_2O}.$$

97.35 gm. H_2SO_4 = 2 × 55.74 gm. KOH = 2000 c.c. normal KOH.
48.675 " " = 55.74 " " = 1000 " "
0.048675 " " = 1 " "

Phosphoric acid presents a peculiar case. When tropæolin is used as an indicator the change in color takes place when this reaction is completed:

$$\underset{97.29}{\mathrm{H_3PO_4}} + \underset{55.74}{\mathrm{KOH}} = \mathrm{KH_2PO_4} + \mathrm{H_2O}.$$

Hence,

97.29 gm. H_3PO_4 = 55.74 gm. KOH = 1000 c.c. normal KOH.
0.09729 " " = 1 " "

With phenolphthalein, the indicator changes color when the subjoined reaction is completed:

$$\mathrm{H_3PO_4} + \mathrm{2KOH} = \mathrm{K_2HPO_4} + \mathrm{2H_2O}.$$

Hence,

97.29 gm. H_3PO_4 = 2 × 55.74 gr. KOH = 2000 c.c. normal KOH.
or 0.04864 " " = 1 " "

The calculation for the amount of acid or alkali is made in this way. Suppose we weigh off 10 grammes 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 0.04867 gramme H_2SO_4 for neutralization, hence 20 c.c. normal KOH require 0.04867 × 20 = 0.9735 gramme H_2SO_4. That is, in the 10 grammes dilute acid weighed off there are 0.9735 gramme H_2SO_4, or in 100 grammes there are 9.735 grammes, or 9.73 per cent. This instance will serve as a type for all calculations of percentages.

Use of empirical solutions. The primary advantage in using normal, decinormal, 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, decinormal, 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 decinormal 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, caustic and alkaline 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:

	Gramme.
Ammonia, NH_3	0.01693
Ammonium carbonate, $(NH_4)_2CO_3$	0.04770
Ammonium carbonate (U. S. P.), $NH_4HCO_3.NH_4NH_2CO_2$	0.05200
Lead acetate, crystallized $Pb(C_2H_3O_2)_2.3H_2O$ [1]	0.18807
Lead subacetate, $Pb_2O(C_2H_3O_2)_2$ [1]	0.13593
Lithium benzoate, $LiC_7H_5O_2$ [2]	0.12711
Lithium carbonate, Li_2CO_3	0.03675
Lithium citrate, $Li_3C_6H_5O_7$ [2]	0.06952
Lithium salicylate, $LiC_7H_5O_3$ [2]	0.14299
Potassium acetate, $KC_2H_3O_2$ [2]	0.09744
Potassium bicarbonate, $KHCO_3$	0.09941
Potassium bitartrate, $KHC_4H_4O_6$ [2]	0.18678
Potassium carbonate, K_2CO_3	0.06863
Potassium citrate, crystallized, $K_3C_6H_5O_7\ H_2O$ [2]	0.10736
Potassium hydroxide, KOH	0.05574
Potassium permanganate, $KMnO_4$ [3]	0.03139
Potassium sodium tartrate, $KNaC_4H_4O_6.4H_2O$ [2]	0.14009
Potassium tartrate, $2K_2C_4H_4O_6.H_2O$ [2]	0.11679
Sodium acetate, $NaC_2H_3O_2.3H_2O$ [2]	0.13510
Sodium benzoate, $NaC_7H_5O_2$ [2]	0.14301
Sodium bicarbonate, $NaHCO_3$	0.08343
Sodium borate, crystallized, $Na_2B_4O_7.10H_2O$	0.18966
Sodium carbonate, monohydrate, $Na_2CO_3.H_2O$	0.06159
Sodium carbonate, Na_2CO_3	0.05265
Sodium hydroxide, $NaOH$	0.03976
Sodium salicylate, $Na(C_7H_5O_3)$[2]	0.15889

One c.c. of normal sodium carbonate, potassium hydroxide, or sodium hydroxide, is the equivalent of:

---

[1] With sulphuric acid and methyl-orange. [2] After ignition. [3] With oxalic acid only.

Acetic acid, $HC_2H_3O_2$	0.05958
Boric acid, H_3BO_3	0.06154
Citric acid, crystallized, $H_3C_6H_5O_7.H_2O$	0.06950
Hydrobromic acid, HBr	0.08036
Hydrochloric acid, HCl	0.03618
Hydriodic acid, HI	0.12690
Hypophosphorous acid, HPH_2O_2	0.06553
Lactic acid, $HC_3H_5O_3$	0.08937
Nitric acid, HNO_3	0.06257
Oxalic acid, crystallized, $H_2C_2O_4.2H_2O$	0.06255
Phosphoric acid, H_3PO_4 (to form K_2HPO_4; with phenol-phthalein)	0.04864
Phosphoric acid, H_3PO_4 (to form KH_2PO_4; with methyl-orange)	0.09729
Potassium dichromate, $K_2Cr_2O_7$ (with phenol-phthalein)	0.14614
Sulphuric acid, H_2SO_4	0.04867
Tartaric acid, $H_2C_4H_4O_6$	0.07446

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 grammes of oxygen, for

$$H_2 + O = H_2O, \text{ or } H + \frac{O}{2} = HO_{\frac{1}{2}}.$$

The substances generally used in oxidimetry are potassium permanganate and potassium dichromate.

Potassium permanganate, $KMnO_4$, 156.98, is chiefly used for normal or decinormal 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 grammes, or 31.396 gm. 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 grammes 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 gramme of potassium permanganate.

To determine the strength of the solution draw off 10 c.c. of deci-normal oxalic acid solution into a beaker, add 1 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 permanganate, while stirring constantly, until a faint pink color is produced, which remains permanent for one-half minute. Note the number of cubic centimetres 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 gramme of potassium iodide in 10 c.c. of dilute sulphuric acid, 20 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 solution, metallic iron may be used, and the operation should be conducted as follows: 0.2 gramme of pure, thin iron wire is dissolved in about 20 c.c. of dilute sulphuric acid (1 acid, 5 water) by the aid of heat, and in a flask arranged as in Fig. 67. The flask is provided, by means of a perforated cork, with a piece of glass tubing, to which is attached a piece of rubber tubing in which is cut a vertical slit about one inch long and which is closed at the upper end by a piece of glass rod; gas or steam generated in the flask may escape, while atmospheric air cannot enter, the ferrous solution being thus protected from oxidation.

The iron solution, obtained from the 0.2 gramme of iron, is cooled and diluted with about 300 c.c. of water, and then deci-normal potassium permanganate solution is added with constant stirring until the solution is tinged pinkish.

As 1 c.c. of deci-normal permanganate solution corresponds to 0.00555 gramme of metallic iron, the 0.2 gramme of iron wire used will consume 36.03 c.c. of the solution.

Fig. 67.

Flask for dissolving iron for volumetric determination.

Permanganate is often used in determinations of iron and iron compounds. Many of the latter contain iron in the ferric state, which must be converted into ferrous compounds before titration. This conversion is accomplished by heating the solution of a weighed quantity of the ferric compound with nascent hydrogen—*i. e.*, with metallic zinc and dilute sulphuric acid—in a flask arranged as the one spoken of above, and shown in Fig. 67.

A very much quicker reduction of the ferric into a ferrous compound may be accomplished by adding very slowly with constant stirring a saturated solution of sodium sulphite to the boiling, acidified iron solution contained in the flask until the liquid becomes colorless. All excess of sulphur dioxide is expelled before titrating, by boiling the solution (which should contain a sufficient quantity of sulphuric acid to decompose all sodium sulphite) for about ten minutes in a flask, arranged as the one mentioned above.

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:

$$MNO_2 + O = MNO_3, \text{ where } M = \text{metal.}$$

$$MNO_2 = 1 \text{ atom } O = \text{quantity liberated by 2 liters } \frac{N}{1} KMnO_4,$$

$$\frac{MNO_2}{2} = \tfrac{1}{2} \quad \text{``} \quad = 1 \text{ liter } \frac{N}{1} KMnO_4,$$

$$\frac{MNO_2}{2 \times 10} = 1 \text{ liter } \frac{N}{10} \quad \text{``}$$

$$\frac{MNO_2}{2 \times 10 \times 1000} = 1 \text{ c.c. } \frac{N}{10} \quad \text{``}$$

In this manner all other equivalents are found. The reactions between permanganate and ferrous salts, and hydrogen dioxide respectively, are expressed in these equations:

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$
$$H_2O_2 + O = H_2O + 2O.$$

One c.c. of deci-normal potassium permanganate, containing of this salt 0.0031396 gramme, is the equivalent of:

	Gramme.
Ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_26H_2O$	0.038934
Ferrous carbonate, $FeCO_3$	0.011505
Ferrous oxide, FeO	0.007138
Ferrous sulphate, $FeSO_4$	0.015085
Ferrous sulphate, crystallized, $FeSO_4.7H_2O$	0.027601
Ferrous sulphate, dried, $2FeSO_4 + 3H_2O$	0.017767
Hydrogen dioxide, H_2O_2	0.001688
Iron, in ferrous compounds, Fe	0.005550
Oxalic acid, crystallized, $H_2C_2O_4.2H_2O$	0.006255
Oxygen, O	0.000794
Potassium nitrite, KNO_2	0.004227
Sodium nitrite, $NaNO_2$	0.003428

Potassium dichromate, $K_2Cr_2O_7 = 292.28$. 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 $K_2Cr_2O_7$ (48.7133 grammes) is taken in the liter, and one-tenth this quantity, equal to 4.8713 grammes 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, is used starch solution, which is colored blue by minute portions of free iodine.

Starch solution is made by mixing 1 gramme 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 grammes 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 normal 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, which is caused to act upon potassium iodide, the liberated iodine being titrated.

Deci-normal iodine solution. Iodine being a univalent element, the weight of its atom, 125.90, in grammes, is used to make one liter of normal solution. Deci-normal solution is generally employed, and is made by dissolving 12.590 grammes of pure iodine in a solution of 18 grammes of potassium iodide in about 300 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 decinormal, by dissolving about 14 grammes of iodine instead of 12.59 grammes 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. Arsenous oxide and sodium bicarbonate are dissolved in water, and this solution, containing sodium met-arsenite, is titrated with iodine solution, when sodium met-arsenate and sodium iodide are formed:

$$NaAsO_2 + 2I + 2NaHCO_3 = NaAsO_3 + 2NaI + H_2O + 2CO_2.$$

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 grammes.

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:

$$\begin{aligned} H_2S + \quad 2I &= 2HI \quad + S. \\ H_2SO_3 + 2I + H_2O &= H_2SO_4 + 2HI. \\ Na_2SO_3 + 2I + H_2O &= Na_2SO_4 + 2HI. \end{aligned}$$

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:

$$\begin{gathered} 2KSbOC_4H_4O_6 + H_2O + 4I + 4NaHCO_3 = \\ 2HSbO_3 + 2KHC_4H_4O_6 + 4NaI + 4CO_2 + H_2O. \end{gathered}$$

One c.c. of deci-normal iodine solution, containing of iodine 0.01259 gramme, is the equivalent of:

	Gramme.
Antimony and potassium tartrate, $2KSbOC_4H_4O_6.H_2O$	0.016495
Arsenous oxide, As_2O_3	0.004911
Hydrogen sulphide, H_2S	0.001691
Potassium sulphite, crystallized, $K_2SO_3.2H_2O$	0.009648
Sodium bisulphite, $NaHSO_3$	0.005168
Sodium hyposulphite (thiosulphate), $Na_2S_2O_3.5H_2O$	0.024646
Sodium sulphite, crystallized, $Na_2SO_3.7H_2O$	0.012520
Sulphur dioxide, SO_2	0.003180

Sodium thiosulphate (Hyposulphite). From the equation:

$$\underset{2 \times 246.46}{2Na_2S_2O_3.5H_2O} + \underset{2 \times 125.9}{2I} = Na_2S_4O_6 + 10H_2O + 2NaI.$$

we see that 246.46 grammes of crystallized sodium thiosulphate are equivalent to—*i. e.*, will exactly decolorize—125.90 grammes of iodine; hence, to make a $\frac{N}{1}$ solution of this compound, 246.46 grammes must be taken in a liter, and for a $\frac{N}{10}$ solution 24.646 grammes are used. If the salt should not be absolutely pure, a somewhat larger quantity (30 grammes) 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 decinormal 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 grammes of the ordinary thiosulphate are dissolved and made up to 1000 c.c. To a solution of about 1 gramme of potassium iodide in 10 c.c. of dilute sulphuric acid in a flask, 20 c.c. of decinormal potassium dichromate solution are slowly added from a burette, and the solution shaken after each addition. The flask is then covered with a watch-glass and allowed to stand 5 minutes, after which about 250 c.c. of pure water are added, 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 obtained pure, and the decinormal solution easily made by weighing the exact quantity needed. The solution, moreover, is perfectly stable.

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.

One c.c. of deci-normal solution of sodium thiosulphate, containing of the crystallized salt 0.024646 gramme, is the equivalent of:

	Gramme.
Bromine, Br	0.007936
Chlorine, Cl	0.003518
Chromium trioxide, CrO_3	0.003311
Iodine, I	0.012590
Iron, Fe, in ferric salts	0.005550

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 (7.936 grammes 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 3.2 grammes of potassium bromate and 50 grammes of potassium bromide in 900 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 gramme 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, 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 one case only, viz., for the volumetric determination of 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 93.36, and as it reacts with 6 atoms of bromine, one-sixth of 93.36, or 15.56 grammes of phenol correspond to 1 liter of normal, and 1.556 grammes to deci-normal bromine solution—*i. e.*, 1 c.c. of deci-normal bromine solution corresponds to 0.001556 gramme of phenol. The U. S. P. directs the assay to be made as follows: Dissolve 1.556 grammes of the specimen in water to make 1 liter. Transfer 25 c.c. of this solution (0.0389 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 gramme 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.

Deci-normal solution of silver. The pure, dry crystallized silver nitrate, $AgNO_3 = 168.69$, is used for this solution, which is made by dissolving 16.869 grammes 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 5.806 grammes 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 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, the number of c.c. of the standard silver solution employed will indicate exactly one-half of the equivalent amount of cyanide present in the solution.

One c.c. of deci-normal silver nitrate solution, containing 0.016869 gramme of $AgNO_3$, is the equivalent of:

	Gramme.
Ammonium bromide, NH_4Br	0.009729
Ammonium chloride, NH_4Cl	0.005311
Ammonium iodide, NH_4I	0.014383
Calcium bromide, $CaBr_2$	0.009926
Ferrous bromide, $FeBr_2$	0.010711
Ferrous iodide, FeI_2	0.015365
Hydriodic acid, HI	0.012690
Hydrobromic acid, HBr	0.008036
Hydrochloric acid, HCl	0.003618
Hydrocyanic acid, HCN, to first formation of precipitate	0.005368
Hydrocyanic acid, HCN, with indicator	0.002684
Lithium bromide, $LiBr$	0.008634
Potassium bromide, KBr	0.011822
Potassium chloride, KCl	0.007404
Potassium cyanide, KCN, to first formation of precipitate	0.012940
Potassium cyanide, KCN, with indicator	0.006470
Potassium iodide, KI	0.016476
Potassium sulphocyanate, $KCNS$	0.009653
Sodium bromide, $NaBr$	0.010224
Sodium chloride, $NaCl$	0.005806
Sodium iodide, NaI	0.014878
Strontium bromide, $SrBr_2.6H_2O$	0.017647
Strontium iodide, $SrI_2.6H_2O$	0.022301
Zinc bromide, $ZnBr_2$	0.011181
Zinc chloride, $ZnCl_2$	0.006763
Zinc iodide, ZnI_2	0.015835

Deci-normal solution of sodium chloride is made by dissolving 5.806 grammes 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 0.005806 gramme of NaCl, is the equivalent of:

	Gramme
Silver, Ag	0.010712
Silver nitrate, $AgNO_3$	0.016869
Silver oxide, Ag_2O	0.011506

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:

$$KCNS + AgNO_3 = AgCNS + KNO_3.$$

As indicator is used ferric alum, 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, 10 grammes, which is about 3 per cent. more than the quantity required, 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.

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.

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 gramme. 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 gramme.

It has been shown on pages 26 and 45 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:

$$66 \text{ c.c.} : [54.6^\circ + 273^\circ] :: x : [0^\circ + 273^\circ],$$

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:

$$V = \frac{66 \times 750 \times 273}{760 \times (273^\circ + 54.6)} = 54.28.$$

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 177.

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 228) 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.

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

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.

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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 grammes of crystallized sodium carbonate require 14 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 grammes 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 volumetrically by solutions of iodine and sodium thiosulphate? Explain the mode in which the determinations by these agents are accomplished. Suppose 1 gramme 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.

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.

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 no wise 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 one 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 gramme 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 quantity 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 0.068 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 gramme of the salt in 10 c.c. of water. Since 0.1 c.c. of $\frac{N}{10}$ sulphuric acid is capable of neutralizing 0.000686 gramme 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.

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?

VI.

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 Wöhler discovered that an aqueous solution of ammonium cyanate, 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, millions) 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 150,000, 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 also be 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.

[1] Non-volatile organic substances are decomposed by heat with generation of volatile products.

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 substances, 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 38.86 parts by weight of potassium, and 125.9 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 characteristic 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.)

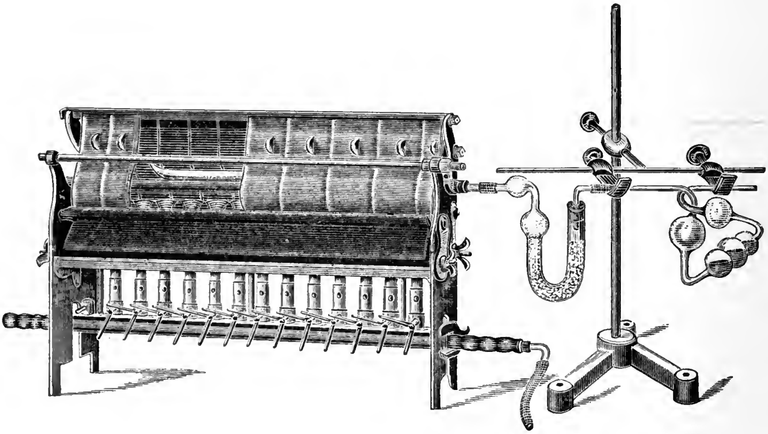
The presence of *hydrogen* can be proven by allowing the gaseous products of the combustion to pass through a cool glass tube, when drops of water will be deposited.

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 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. 68 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 operation, 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.

Fig. 68.



Gas-furnace for organic analysis.

For instance: 0.81 gramme of a substance having been analyzed, furnishes, of carbon dioxide 1.32 gramme, and of water 0.45 gramme. As every 44 parts by weight of carbon dioxide contain 12 parts by weight of carbon, the above 1.32 gramme contains of carbon 0.36 gramme, or 44.444 per cent. As every 17.88 parts of water contain 2 parts of hydrogen, the above 0.45 gramme consequently contains 0.0503 gramme, 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:

$$\frac{44.444}{11.91} = 3.731$$

$$\frac{6.213}{1} = 6.213$$

$$\frac{49.343}{15.88} = 3.107$$

The figures 3.731, 6.213, and 3.107 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, 0.6213 is the greatest divisor, which gives the following results:

$$\frac{3.731}{0.6213} = 6.005; \quad \frac{6.213}{0.6213} = 10; \quad \frac{3.107}{0.6213} = 5.$$

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 specific weight of the gaseous compound, taking hydrogen as the unit. 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, when compared with hydrogen (according to the law of Avogadro), be equal to 6.455, because a molecule of hydrogen weighs 2 and a molecule of the compound CH weighs 12.91.

Suppose, however, the density of the gaseous substance is found to be 38.73, then the molecular formula would be expressed by C_6H_6, because its molecular weight $(6 \times 11.91 + 6 \times 1)$ is equal to 77.46, which weight, when compared with the molecular weight of hydrogen $= 2$, gives the proportions 77.46 : 2, or 38.73 : 1.

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.

41. CONSTITUTION, DECOMPOSITION, AND CLASSIFICATION OF ORGANIC COMPOUNDS.

Radicals or residues. The nature of a radical or residue has been stated already in Chapter 8, 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.*

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?

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.

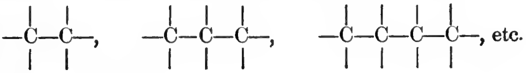
If one atom of hydrogen be removed from the saturated hydrocarbon methane, CH_4, the univalent residue methyl, CH_3, is left, which is capable of combining with univalent elements, as in methyl chloride, CH_3Cl, or, with univalent residues, as in methyl hydroxide, CH_3OH.

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.

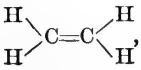
The linkage of carbon atoms may be represented thus:



$$-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-, \quad -\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-, \quad -\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-, \text{ etc.}$$

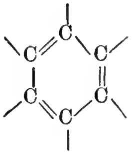
The above carbon chains have 6, 8, and 10 available affinities, respectively, which may be saturated by the greatest variety of atoms or radicals. The chain combination of carbon, above indicated by the first three members of a series, may, as far as is known, be continued indefinitely. This fact, in 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.

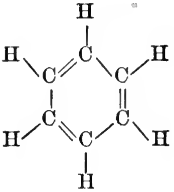
It is not always the case that the atoms when forming a chain are united by one affinity only, as above, but they may be united by two or three affinities, as indicated by the compounds C_2H_4 and C_2H_2, the graphic formulas of which may be represented by



$H-C\equiv C-H.$

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:

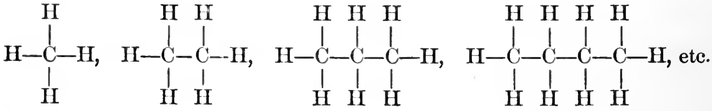




A chain has also been termed a skeleton, because it is that part of an organic compound around which the other elements or radicals arrange themselves, filling up, as it were, the unsaturated affinities.

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.



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H, \\ & | & \\ & H & \end{array}\quad \begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C & -H, \\ & | & | & \\ & H & H & \end{array}\quad \begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C & -H, \\ & | & | & | & \\ & H & H & H & \end{array}\quad \begin{array}{cccccc} & H & H & H & H & \\ & | & | & | & | & \\ H- & C- & C- & C- & C & -H, \text{ etc.} \\ & | & | & | & | & \\ & H & H & H & H & \end{array}$$

Many homologous series of various organic compounds are known, as, for instance:

$C H_3 Cl$,	$C H_4 O$,	$C H_2 O_2$.
$C_2H_5 Cl$,	$C_2H_6 O$,	$C_2H_4 O_2$.
$C_3H_7 Cl$,	$C_3H_8 O$,	$C_3H_6 O_2$.
$C_4H_9 Cl$,	$C_4H_{10}O$,	$C_4H_8 O_2$.
$C_5H_{11}Cl$,	$C_5H_{12}O$,	$C_5H_{10}O_2$.
etc.	etc.	etc.

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:

$$\underset{\text{Potassium.}}{K} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Potassium}\\\text{hydroxide.}}}{KOH} + \underset{\text{Hydrogen.}}{H}.$$

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Chlorine.}}{2Cl} = \underset{\substack{\text{Monochloracetic}\\\text{acid.}}}{C_2H_3ClO_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl}.$$

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Nitro-benzene.}}{C_6H_5NO_2} + \underset{\text{Water.}}{H_2O}.$$

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.

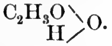
Isomerism. Two or more substances may have the same elements in the same proportion by weight (or the same centesimal composition), and yet be different bodies, showing different properties. Such substances are called isomeric bodies. Three kinds of isomerism are distinguished, viz., metamerism, polymerism, 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.

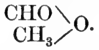
For instance: Acetic acid and methyl formate both have the composition $C_2H_4O_2$, but the arrangement of the atoms (or the structure) is very different, as shown by the formulas:

Acetic acid.



$$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right>O.$$

Methyl formate.



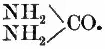
$$\left.\begin{matrix}CHO\\CH_3\end{matrix}\right>O.$$

As another instance may be mentioned the compound CN_2H_4O, which represents either ammonium cyanate or urea:

Ammonium cyanate.

$$\left.\begin{matrix}NH_4\\CN\end{matrix}\right>O.$$

Urea.



$$\left.\begin{matrix}NH_2\\NH_2\end{matrix}\right>CO.$$

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 almost invariably.

Besides the slow oxidation or decay which all dead organic matter undergoes in the presence of moisture, there is another kind of slow oxidation, called respiration, which takes place in the living animal; this process will be more fully considered in the physiological part of this book.

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 micro-organisms 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 micro-organism, 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 micro-organisms 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-fulfilment 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 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:

$$\underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Bromine.}}{2Br} = \underset{\text{Ethylene bromide.}}{C_2H_4Br_2}.$$

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} + \underset{\text{Chlorine.}}{2Cl} = \underset{\text{Aldehyde.}}{C_2H_4O} + \underset{\text{Hydrochloric acid.}}{2HCl}.$$

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Chlorine.}}{2Cl} = \underset{\substack{\text{Monochloracetic}\\ \text{acid.}}}{C_2H_3ClO_2} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{HCl}.$$

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:

$$\underset{\text{Ethyl chloride.}}{C_2H_5Cl} + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Potassium chloride.}}{KCl} + \underset{\text{Ethyl alcohol.}}{C_2H_5OH.}$$

Salts are formed:

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Sodium hydroxide.}}{NaOH} = \underset{\text{Sodium acetate.}}{NaC_2H_3O_2} + \underset{\text{Water.}}{H_2O.}$$

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:

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Potassium acetate.}}{KC_2H_3O_2} + \underset{\text{Hydrogen.}}{4H.}$$

From compounds containing nitrogen, ammonia is evolved:

$$\underset{\text{Acetamide.}}{NH_2C_2H_3O} + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Potassium acetate.}}{KC_2H_3O_2} + \underset{\text{Ammonia.}}{NH_3.}$$

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.

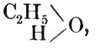
2. *Alcohols.* These are hydrocarbon radicals in combination with hydroxyl, OH. For instance, ethyl alcohol, $C_2H^{i}_5OH$, glycerin, $C_3H^{iii}_5(OH)_3$, etc.

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:

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O,} \qquad \underset{\text{Aldehyde.}}{CH_3.COH,} \qquad \underset{\text{Acetic acid.}}{C_2H_4O_2,}$$

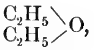
4. *Organic acids.* Hydrocarbon radicals in combination with carboxyl, a radical having the composition CO_2H, or compounds formed by replacement of hydrogen in hydrocarbons by carboxyl. Instances: Acetic acid, CH_3CO_2H; pyrotartaric acid, $C_3H_6(CO_2H)_2$.

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:



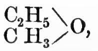
$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\rangle O,$$

Ethyl alcohol.



$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O,$$

Ethyl ether.

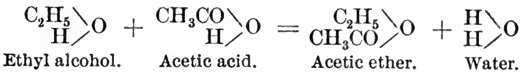


$$\left.\begin{matrix}C_2H_5\\C\,H_3\end{matrix}\right\rangle O,$$

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:



$$\underset{\text{Ethyl alcohol.}}{\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\rangle O} + \underset{\text{Acetic acid.}}{\left.\begin{matrix}CH_3CO\\H\end{matrix}\right\rangle O} = \underset{\text{Acetic ether.}}{\left.\begin{matrix}C_2H_5\\CH_3CO\end{matrix}\right\rangle O} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\rangle O}$$

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

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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.

into two large classes, each one embodying all the derivatives of one of the two hydrocarbons named. The derivatives of methane are 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.

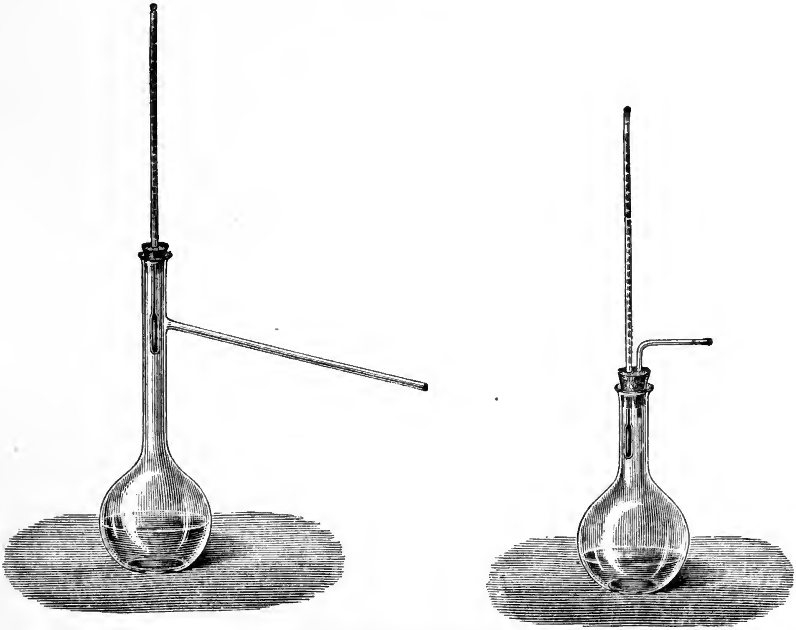
Other hydrocarbons are found in nature as products of the decomposition of organic matter. Thus methane, CH_4, is generally formed during the decay of organic matter in the presence of moisture; the higher members of the methane series are found in crude coal-oil.

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.

FIG. 69.



Flasks arranged for fractional distillation.

For fractional distillation of small quantities of liquids as well as for the determination of boiling-points, flasks arranged like those shown in Fig. 69 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.

In regard to chemical properties, it may be said that 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.
Meth*ane* series or paraffins,	C_nH_{2n+2}	CH_4
Eth*ene* series or olefins,	C_nH_{2n}	C_2H_4
Eth*ine* 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:

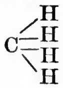
		B. P.	Sp. gr.
Methane or methyl hydride,	$C\ H_4$	gases.	
Ethane or ethyl hydride,	$C_2\ H_6$		
Propane or propyl hydride,	$C_3\ H_8$		
Butane or butyl hydride,	$C_4\ H_{10}$	1° C.	
Pentane or amyl hydride,	$C_5\ H_{12}$	38	0.628
Hexane or hexyl hydride,	$C_6\ H_{14}$	70	0.669
Heptane or heptyl hydride,	$C_7\ H_{16}$	99	0.690
Octane or octyl hydride,	$C_8\ H_{18}$	125	0.726
Nonane or nonyl hydride,	$C_9\ H_{20}$	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.

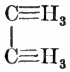
The paraffins are saturated hydrocarbons, the constitution of which has been already explained; they are incapable of uniting directly with monatomic elements or residues, but they easily yield substitution-derivatives when subjected to the action of chlorine or bromine, hydrogen in all cases being given 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.

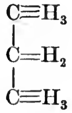
No isomeric hydrocarbons of the first three members of the paraffin series are known, which fact is in accordance with our present theories. Assuming that the quadrivalent carbon atoms exert their full valence, and that they are held together by one bond only, we can arrange the atoms in the compounds, CH_4, C_2H_6, and C_3H_8, not otherwise than thus:



$$C{<}\begin{array}{l}H\\H\\H\\H\end{array}$$

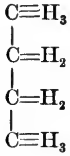


$$\begin{array}{l}C\equiv H_3\\|\\C\equiv H_3\end{array}$$

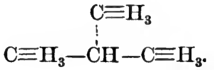


$$\begin{array}{l}C\equiv H_3\\|\\C=H_2\\|\\C\equiv H_3\end{array}$$

In the next compound, butane, C_4H_{10}, we have two possibilities explaining the structure of the molecule, namely, these:



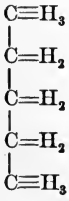
$$\begin{array}{l}C\equiv H_3\\|\\C=H_2\\|\\C=H_2\\|\\C\equiv H_3\end{array}$$



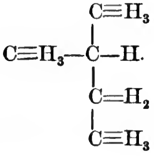
$$\begin{array}{c}C\equiv H_3\\|\\C\equiv H_3-CH-C\equiv H_3.\end{array}$$

Both these compounds are known, and termed normal butane and isobutane, respectively.

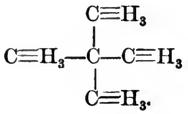
The next member, pentane, C_5H_{12}, shows three possibilities of constitution, thus:



$$\begin{array}{l}C\equiv H_3\\|\\C=H_2\\|\\C=H_2\\|\\C=H_2\\|\\C\equiv H_3\end{array}$$



$$\begin{array}{rl}&C\equiv H_3\\&|\\C\equiv H_3-&C-H.\\&|\\&C=H_2\\&|\\&C\equiv H_3\end{array}$$



$$\begin{array}{rcl}&C\equiv H_3&\\&|&\\C\equiv H_3-&C&-C\equiv H_3\\&|&\\&C\equiv H_3.&\end{array}$$

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 14, 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. Methane is of special interest, because it is the compound from which thousands of other substances are derived. 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.

Experiment 51. Use apparatus shown in Fig. 35, page 87, omitting the bent tube B. Mix in a mortar 20 grammes of sodium acetate with 20 grammes of potassium (or sodium) hydroxide and 30 grammes 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. The decomposition takes place thus:

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

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?

Ethane, C_2H_6, is a constituent of natural gas and of crude petroleum. It can be obtained from methane by first replacing in it a hydrogen atom by iodine, when iodo-methane, or methyl-iodide, CH_3I, is formed, 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:

$$\underset{\text{Zinc methyl.}}{Zn(CH_3)_2} + \underset{\text{Methyl iodide.}}{2CH_3I} = \underset{\text{Zinc iodide.}}{ZnI_2} + \underset{\text{Ethane.}}{2C_2H_6},$$

$$Zn(CH_3)_2 + \underset{\text{Ethyl iodide.}}{2C_2H_5I} = ZnI_2 + \underset{\text{Propane.}}{2C_3H_8}.$$

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 togther 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

				B. P.
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	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 apparatus shown in Fig. 35, page 87. 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, 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.

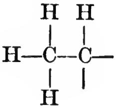
Unsaturated hydrocarbons. The terms saturated and unsaturated compounds are used for inorganic and organic substances. A compound is said to be unsaturated when it has the power to enter directly into combination with elements or compounds. Thus, carbon monoxide and phosphorus trichloride are unsaturated, as they combine directly with a number of substances; for instance, with chlorine, thus:

$$CO + 2Cl = COCl_2,$$
$$PCl_3 + 2Cl = PCl_5.$$

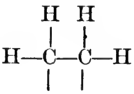
The hydrocarbons of the methane series are saturated; they cannot be made to enter directly into combination with other substances, because there are no bonds left unprovided for.

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 465, 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:

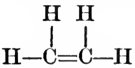


$$\begin{matrix} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ \mathrm{H}- & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & \\ & \mathrm{H} & & & \end{matrix}$$



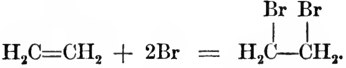
$$\begin{matrix} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ \mathrm{H}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{H} \\ & | & & | & \end{matrix}$$

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



$$\begin{matrix} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ \mathrm{H}- & \mathrm{C} & = & \mathrm{C} & -\mathrm{H} \end{matrix} \qquad \text{or} \qquad H_2C{=}CH_2.$$

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:



$$H_2C{=}CH_2 + 2Br = \begin{matrix} & \mathrm{Br} & & \mathrm{Br} \\ & | & & | \\ \mathrm{H_2} & \mathrm{C} & - & \mathrm{CH_2}. \end{matrix}$$

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:

$$HC{\equiv}CH + 4Br = Br_2HC{-}CHBr_2.$$
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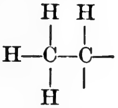
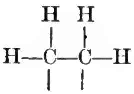
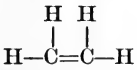


$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{|}{C}}-}$$



$$\mathrm{H-\overset{H}{\underset{|}{C}}-\overset{H}{\underset{|}{C}}-H}$$

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



$$\mathrm{H-\overset{H}{C}=\overset{H}{C}-H}$$

or $H_2C=CH_2$.

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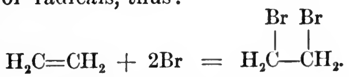


$$H_2C=CH_2 + 2Br = H_2\overset{Br}{C}-\overset{Br}{C}H_2.$$

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*), 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:

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O.$$

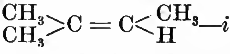
This reaction shows the possibility of preparing an unsaturated compound of the ethylene series from a saturated hydrocarbon; and as the method is applicable to compounds of other classes it furnishes the means to pass from any saturated compound to the corresponding unsaturated compound of the ethylene series.

The second method for preparing ethylene depends on the dehydrating action of sulphuric acid on ethyl alcohol:

$$C_2H_5OH \quad - \quad H_2O \quad = \quad C_2H_4.$$

Ethylene combines directly with an equal volume of chlorine forming ethylene dichloride, $C_2H_4Cl_2$, an oily liquid, whence the name olefiant gas.

Amylene, C_5H_{10}. Of the three isomeric hydrocarbons of the composition C_5H_{10}, two have been used medicinally. It is especially the amylene of the composition



$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C = C<\!\begin{matrix}CH_3\\H\end{matrix}$

—*i. e., trimethyl-ethylene*—which has been introduced as an anæsthetic under the name of *pental.* It is formed from tertiary amyl alcohol (amylene hydrate) by the action of dehydrating agents. It is a colorless, very volatile liquid, insoluble in water, but miscible in all proportions with chloroform, ether, and alcohol. It has a penetrating odor, reminding of mustard oil.

Acetylene, C_2H_2, 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.

Methyl chloride, CH_3Cl (*Monochlor-methane*), is readily obtainable by the action of hydrochloric acid on methyl alcohol:

$$CH_3OH + HCl = CH_3Cl + H_2O.$$

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:

$$CH.Cl_3 + ICl = CCl_4 + HI.$$

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, Chloroformum, $CHCl_3 = 118.45$ (*Trichlor-methane*), 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:

$$\underset{\text{Alcohol.}}{4C_2H_6O} + \underset{\substack{\text{Calcium}\\\text{hypochlorite.}}}{8Ca(ClO)_2} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\substack{\text{Calcium}\\\text{formate.}}}{3[Ca(CHO_2)_2]} + \underset{\substack{\text{Calcium}\\\text{chloride.}}}{5CaCl_2} + \underset{\text{Water.}}{8H_2O}.$$

Chloroform is now made extensively by the action of bleaching-powder upon acetone; the reaction takes place thus:

$$\underset{\text{Acetone.}}{2CO(CH_3)_2} + \underset{\substack{\text{Calcium}\\\text{hypochlorite.}}}{3Ca(ClO)_2} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\substack{\text{Calcium}\\\text{hydroxide.}}}{2Ca(OH)_2} + \underset{\substack{\text{Calcium}\\\text{acetate.}}}{Ca(C_2H_3O_2)_2}$$

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 one-half to one per cent.), allowed to be present by the U. S. P., causes the specific gravity to be about 1.48; 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 gramme 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*), 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, $CHI_3 = 390.61$ (*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 occcurs 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 grammes 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 gramme of iodine. A yellow crystalline deposit of iodoform separates.

Ethyl chloride, Æthylis chloridum, $C_2H_5Cl = 64$ (*Chlor-ethane*), 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, $As_2O_3 + 4CH_3COOK = K_2CO_3 + 2CO_2 + [(CH_3)_2As]_2O$. 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.

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.

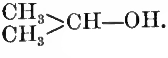
Constitution of alcohols.—The old term "alcohol" originally indicated but one substance (ethyl alcohol), but it is now applied to a large group of substances which may be looked upon as being derived from hydrocarbons by replacement of one, two, or more hydrogen atoms by hydroxyl, OH. In other words, alcohols are hydrocarbon radicals in combination with hydroxyl.

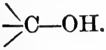
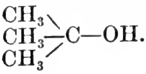
If hydroxyl replaces but one atom of hydrogen in a hydrocarbon, the alcohol is termed monatomic; diatomic and triatomic alcohols are formed by replacement of two or three hydrogen atoms respectively. (Diatomic alcohols are also termed *glycols.*) As an instance of a diatomic alcohol may be mentioned 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.

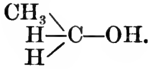
Normal alcohols are those with a straight carbon chain derived from normal hydrocarbons. Alcohols are also divided, according to the linkage between the hydroxyl groups and a carbon atom, into primary, secondary, and tertiary alcohols.

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  $-\!\!>C—OH$. For instance, tertiary butyl alcohol,  $\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!-\!\!>C—OH$. 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.



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.
	$R^{i}\text{—}OH$	$R^{ii}\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$	$R^{iii}\text{—}\begin{matrix}/OH\\OH\\ \backslash OH\end{matrix}$
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:

$$K + O\left\langle\begin{matrix}H\\H\end{matrix}\right. = H + O\left\langle\begin{matrix}K\\H\end{matrix}\right.,$$

$$K + O\left\langle\begin{matrix}H\\CH_3\end{matrix}\right. = H + O\left\langle\begin{matrix}K\\CH_3\end{matrix}\right..$$

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:

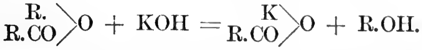
$$K.OH + HCl = KCl + H_2O,$$

$$CH_3.OH + HCl = CH_3Cl + H_2O.$$

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:



$$\left.\begin{matrix}\text{R.}\\ \text{R.CO}\end{matrix}\right\rangle O + KOH = \left.\begin{matrix}\text{K}\\ \text{R.CO}\end{matrix}\right\rangle O + R.OH.$$

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:

$$\underset{\text{Ethane.}}{C_2H_6} + 2Cl = \underset{\text{Ethyl chloride.}}{C_2H_5Cl} + HCl.$$

$$\underset{\substack{\text{Ethyl}\\ \text{chloride.}}}{C_2H_5Cl} + \underset{\substack{\text{Potassium}\\ \text{hydroxide.}}}{KOH} = \underset{\substack{\text{Potassium}\\ \text{chloride.}}}{KCl} + \underset{\substack{\text{Ethyl}\\ \text{alcohol.}}}{C_2H_5OH}.$$

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:

$$\underset{\text{Ethyl amine.}}{C_2H_5NH_2} + \underset{\substack{\text{Nitrous}\\ \text{acid.}}}{NOOH} = \underset{\substack{\text{Ethyl}\\ \text{alcohol.}}}{C_2H_5OH} + 2N + H_2O.$$

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 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	$C\ H_3\ OH$	67° C.	
Ethyl "	$C_2\ H_5\ OH$	78	
Propyl "	$C_3\ H_7\ OH$	97	
Butyl "	$C_4\ H_9\ OH$	115	
Amyl "	$C_5\ H_{11}OH$	132	
Hexyl "	$C_6\ H_{13}OH$	150	
Heptyl "	$C_7\ H_{15}OH$	168	
Octyl "	$C_8\ H_{17}OH$	186	
Nonyl "	$C_9\ H_{19}OH$	204	
Cetyl "	$C_{16}H_{33}OH$	50	Fusing-point.
Ceryl "	$C_{27}H_{55}OH$	79	
Melissyl "	$C_{30}H_{61}OH$	85	

Methyl alcohol, CH_3OH (*Methyl hydroxide, Carbinol, Wood-spirit, Wood-naphtha*). Methyl alcohol is one of the many products obtained by the destructive distillation of wood. When pure it is a thin colorless liquid, similar in odor and taste to ethyl alcohol, and is often substituted for the latter for various purposes in the arts and manufactures.

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.

Ethyl alcohol, $C_2H_5OH = 45.7$ (*Common alcohol, Ethyl hydroxide, Spirit*), 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 grammes 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.

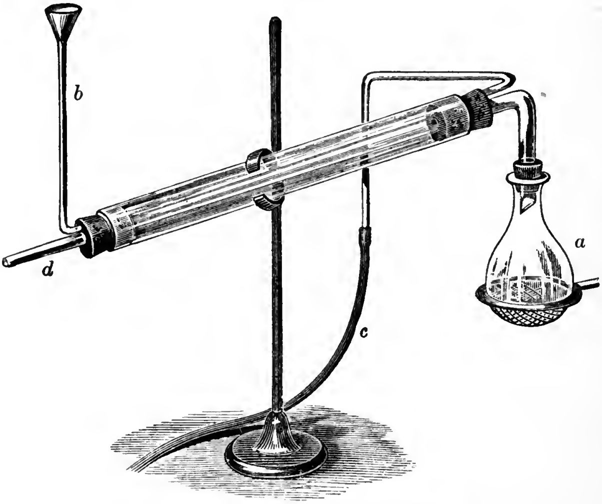
After fermentation ceases connect the flask with a condenser and distil over 50 to 100 c.c. of the liquid. Verify in the distilled portion the presence of alcohol by applying the tests mentioned below. For condensation of the distilling vapors a Liebig's condenser, represented in Fig. 70, may be used.

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 alcohol thus obtained, and containing not more than 1 per cent. of water, is known as *pure*, *absolute*, or *real alcohol* (*alcohol absolutum*). 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 fluid extracts.

Fig. 70.



Liebig's condenser with distilling-flask.

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 fifteen 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, $C_3H_5(OH)_3 = 91.37$ (*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 $CH_2OH.CHOH.CH_2OH$.

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, tannic acid, and a few others.

Boroglycerin is made by heating a mixture of boric acid and glycerin, when an ether 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 tri-nitro-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 250° C. (482° F.).

Spirit of glyceryl trinitrate, Spiritus glycerylis nitratis (*Spirit of glonoin*) is an alcoholic solution of nitro-glycerin, containing of this substance 1 per cent.

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.*

Glycerin-phosphoric 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 (see Index).

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.)

Glycerin-phosphoric 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 glycerin-phosphoric acid in the cold. The calcium, potassium, sodium, lithium, iron, and quinine salts of the acid have been introduced into medicine.

Calcium glycerin-phosphate, $C_3H_5(OH)_2CaPO_4 + H_2O$, is a white crystalline powder, soluble in 20 parts of water, but less soluble in hot water. It is neutral to litmus, but the commercial product is sometimes acid. It loses its water of crystallization at or above 130° C.

Sodium glycerin-phosphate, $C_3H_5(OH)_2.Na_2PO_4 + H_2O$, is obtained by neutralizing glycerin-phosphoric acid. It occurs in the market as a 50 per cent. solution of a clear, light yellow color.

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:

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} - 2H = \underset{\text{Acetic aldehyde.}}{C_2H_4O}.$$

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

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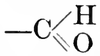
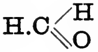
QUESTIONS.—What is the general constitution of alcohols, and what is the difference between monatomic, diatomic, and triatomic alcohols? How do alcohols occur in nature? By what processes may alcohols be formed artificially, and how may they be separated from their combinations? State the general properties 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?

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,  $CH_3.C{<}^{H}_{O}$. It is the group  $—C{<}^{H}_{O}$ 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.

Formic aldehyde, CH_2O or  $H.C{<}^{H}_{O}$ (*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. Another process is by heating paraformaldehyde, which yields formaldehyde in a pure condition.

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.

Formic aldehyde may be recognized by *Schiff's reaction:* A solution of fuchsin (rosanilin chloride) decolorized or nearly so with sulphurous acid turns pink or violet when brought in contact with any aldehyde solution. For the examination of air, suspended filter-paper, moistened with the decolorized fuchsin solution, may be used.

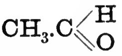
Paraformaldehyde, $C_3H_6O_3$ or $(CH_2O)_3$ (*Formalin*). On slow evaporation of a solution of formaldehyde in methyl alcohol polymerization takes place, and paraformaldehyde separates in colorless crystals which are insoluble in water. On heating the compound, which is now found in the market in the form of tablets, it splits up into three molecules of 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 grammes 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, hexamethylene tetramin, $(CH_2)_6N_4$, being formed.

Acetic aldehyde, C_2H_4O or  $CH_3.C\begin{matrix}\diagup H\\ \diagdown\!\!\diagdown O\end{matrix}$ (*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 grammes 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 grammes of pure alcohol into aldehyde?

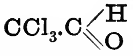
Aldehyde is a neutral, colorless liquid, having a strong and characteristic odor; it mixes with water and alcohol in all proportions and boils at 21° C. (69.8° F.). The most characteristic chemical property of aldehyde is its tendency to combine *directly* with a great number of substances; thus it combines 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:

$$C_2H_4O \ + \ 6Cl \ = \ C_2HCl_3O \ + \ 3HCl$$

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, $CCl_3.CH(OH)_2 = 164.12$. 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:

$$\underset{\text{Chloral.}}{C_2HCl_3O} + \underset{\substack{\text{Potassium}\\\text{hydroxide.}}}{KHO} = \underset{\substack{\text{Potassium}\\\text{formate.}}}{KCHO_2} + \underset{\text{Chloroform.}}{CHCl_3.}$$

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.

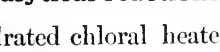
Analytical reactions for chloral.

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.



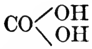
Acrylic aldehyde, $CH_2 = CH.C\begin{smallmatrix}\diagup H\\ \diagdown O\end{smallmatrix}$ (*Acrolein*), may be obtained by the careful oxidation of allyl alcohol, or by the dehydrating action of potassium acid sulphate on glycerin:

$$C_3H_8O_3 - 2H_2O = C_3H_4O.$$

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.

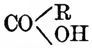
Acrolein is a highly volatile liquid, boiling at 52.4° C. It has a characteristic, penetrating odor and its vapors act on the eyes, causing the secretion of tears. Acrolein shows in its chemical behavior its aldehydic nature. It takes up oxygen forming *acrylic acid;* combines with hydrogen forming allyl alcohol; combines directly with hydrochloric acid, ammonia, etc.

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:



$$CO\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}$$

Carbonic acid.



$$CO\begin{matrix}\diagup R\\ \diagdown OH\end{matrix}$$

Organic acid.

$$CO\begin{matrix}\diagup R\\ \diagdown H\end{matrix}$$

Aldehyde.

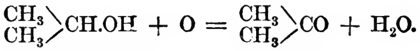
$$CO\begin{matrix}\diagup R\\ \diagdown R\end{matrix}$$

Ketone.

While aldehydes are obtained by the oxidation of primary alcohols, ketones are the first product of the oxidation of secondary alcohols. For instance:

$$C_2H_5.CH_2.OH + O = C_2H_5.COH + H_2O.$$

Primary propyl alcohol. Propionic aldehyde.

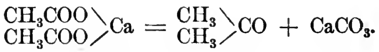


$$\begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}CH.OH + O = \begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}CO + H_2O.$$

Secondary propyl alcohol. Dimethyl ketone.

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, $CH_3.CO.CH_3 = 57.61$ (*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:



$$\begin{matrix}CH_3COO\diagdown\\ CH_3COO\diagup\end{matrix}Ca = \begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}CO + CaCO_3.$$

Calcium acetate. Acetone.

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.

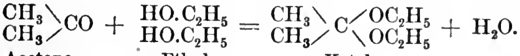
Sulphur derivatives. A comparison of such inorganic compounds as H_2S, CS_2, NH_4SH, with H_2O, CO_2, NH_4OH, shows that sulphur often replaces oxygen. Correspondingly, sulphur frequently replaces oxygen in organic compounds. When this replacement takes place in alcohols compounds are formed, called *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 proteids.

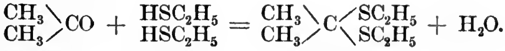
When mercaptans are treated with oxidizing agents three atoms of oxygen are taken up and compounds are formed which are called sulphonic acids, thus:

$$\underset{\text{Ethyl mercaptan.}}{C_2H_5SH} + 3O = \underset{\text{Ethyl sulphonic acid.}}{C_2H_5.SO_2OH.}$$

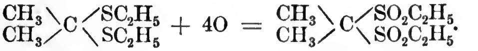
Sulphonic acids correspond to sulphurous acid in which a hydrogen atom has been replaced by a hydrocarbon radical.

Ketones form condensation products with both alcohols and mercaptans, thus:


Acetone. Ethyl alcohol. Ketol.


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:

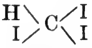

Mercaptol. Diethylsulphon-dimethyl-methane.

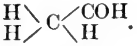
This compound is used medicinally under the name of sulphonal.

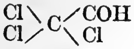
The relations between methane and some of its derivatives, which have been considered in this chapter, may be shown graphically thus:

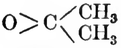

Methane.

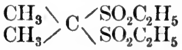

Chloroform.


Iodoform.

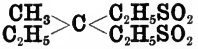
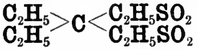

Aldehyde.


Chloral.


Acetone.

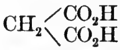
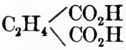

Sulphonal.

Sulphonmethane, Sulphonmethanum, Sulphonal, $(CH_3)_2C$-$(C_2H_5SO_2)_2 = 226.55$ (*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,  $\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}C_2H_5SO_2\\C_2H_5SO_2\end{matrix}$ (*Diethylsulphon-methyl-ethyl-methane*), and **Tetronal,**  $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>C<\begin{matrix}C_2H_5SO_2\\C_2H_5SO_2\end{matrix}$ (*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.

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	$CH_3 \cdot CO_2H$	 $CH_2\begin{matrix}\diagup CO_2H\\\diagdown CO_2H\end{matrix}$.
Methane.	Acetic acid.	Malonic acid.
C_2H_6	$C_2H_5\ CO_2H$	 $C_2H_4\begin{matrix}\diagup CO_2H\\\diagdown CO_2H\end{matrix}$.
Ethane.	Propionic acid.	Succinic acid.

As stated before, organic acids may also be considered as carbonic

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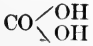
Questions.—What is an aldehyde, and what are its relations to alcohols and acids? Give composition, mode of manufacture, and properties of formaldehyde. Explain the action of chlorine upon alcohol. Give the composition and properties of chloral and hydrated chloral. What decomposition takes place when 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.

acid in which one of the hydroxyl groups has been replaced by a hydrocarbon radical, thus:

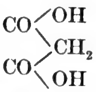


$CO\begin{smallmatrix}\diagup OH\\ \diagdown OH\end{smallmatrix}$

Carbonic acid.

$CO\begin{smallmatrix}\diagup CH_3\\ \diagdown OH\end{smallmatrix}$

Acetic acid.



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 *acid 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 radicals and acid radicals may also be stated, by saying that the first contain carbon and hydrogen only, while acid radicals contain carbon, hydrogen, and oxygen.

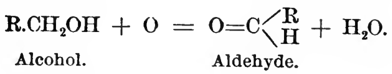
In a similar manner, as there are homologous series of alcohols corresponding to the various series of hydrocarbons, there are also homologous series of organic acids running parallel with the corresponding series of hydrocarbons or alcohols.

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.

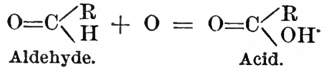
Some organic acids are also found as products of the decomposition of organic matters in nature.

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:

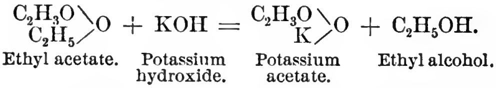


$$\underset{\text{Alcohol.}}{R.CH_2OH} + O = \underset{\text{Aldehyde.}}{O{=}C\left\langle\begin{matrix}R\\H\end{matrix}\right.} + H_2O.$$



$$\underset{\text{Aldehyde.}}{O{=}C\left\langle\begin{matrix}R\\H\end{matrix}\right.} + O = \underset{\text{Acid.}}{O{=}C\left\langle\begin{matrix}R\\OH\end{matrix}\right.}$$

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:



$$\underset{\text{Ethyl acetate.}}{\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\rangle O} + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Potassium acetate.}}{\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\rangle O} + \underset{\text{Ethyl alcohol.}}{C_2H_5OH.}$$

$$\underset{\text{Potassium acetate.}}{2C_2H_3KO_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Acetic acid.}}{2C_2H_4O_2} + \underset{\text{Potassium sulphate.}}{K_2SO_4.}$$

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, 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 acid 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 acid 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 $NO_2.OH$
Nitric acid.

$C_2H_4O_2$ or $C_2H_3O.OH$.
Acetic acid.

$$\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right>O$$
Nitric anhydride.

$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right>O.$$
Acetic andydride.

It is evident from the above that, while acids are hydroxides of acid radicals, the anhydrides are oxides. They are often formed by abstracting water from two molecules of an acid, thus:

$$\left.\begin{matrix}C_2H_3O.OH\\C_2H_3O.OH\end{matrix}\right\} = \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right>O + H_2O.$$

Amino-acids are compounds obtained from acids by replacement of a hydrogen atom of the acid 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,	$H\ CO_2H$	+ 4° C.	100° C.	Red ants and some plants, etc.
Acetic acid,	CH_3CO_2H	+17	118	Vegetable and animal fluids.
Propionic acid,	$C_2H_5CO_2H$	—21	140	Sweat, fluids of the stomach, etc.
Butyric acid,	$C_3H_7CO_2H$	—20	162	Butter.
Valeric acid,	$C_4H_9CO_2H$	—16	185	Valerian root.
Caproic acid,	$C_5H_{11}CO_2H$	— 2	205	Butter.
Œnanthylic acid,	$C_6H_{13}CO_2H$	—10	224	Castor oil.
Caprylic acid,	$C_7H_{15}CO_2H$	+14	236	Butter; cocoanut oil.
Pelargonic acid,	$C_8H_{17}CO_2H$	18	254	Leaves of geranium.
Capric acid,	$C_9H_{19}CO_2H$	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.	Scarcely 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 $CHO.OH$. 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:

$$KOH + CO = \underset{\text{Potassium formate.}}{KCHO_2},$$

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:

$$CH_2O_2 + O = CO_2 + H_2O.$$

Acetic acid, $H.C_2H_3O_2$, or $C_2H_3O.OH$, or $CH_3.CO_2H = 59.58$. 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 grammes of sodium acetate contained in a small flask which is connected with a Liebig's condenser, 40 grammes 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; to-day 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 take 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.)

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 6 to 15 hours. Milk of magnesia should be given as an antidote with a view of neutralizing 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, $KC_2H_3O_2 = 97.44$. Sodium acetate, Sodii acetas, $NaC_2H_3O_2.3H_2O = 135.1$. Zinc acetate, Zinci acetas, $Zn\,(C_2H_3O_2)_2.2H_2O = 217.82$. 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, $NH_4C_2H_3O_2$, 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, $Pb(C_2H_3O_2)_2 3H_2O = 376.15$ (*Sugar of lead*), 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 crystallization; 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.

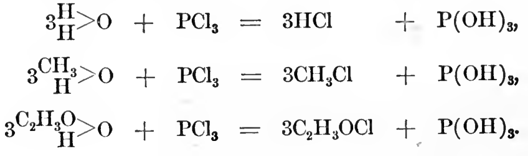
By boiling verdigris with arsenous oxide, *cupric aceto-arsenite,* $3CuAs_2O_4 + Cu(C_2H_3O_2)_2$, is formed, which is the chief constituent of *emerald green* or *Schweinfurt green,* a substance often used as a coloring matter. *Paris green* is of a similar composition, but less pure.

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:

$$\begin{array}{lcllcl}
CH_3.COOH & + & 2Cl & = & CH_2Cl.COOH & + & HCl, \\
CH_2Cl.COOH & + & 2Cl & = & CHCl_2.COOH & + & HCl, \\
CHCl_2.COOH & + & 2Cl & = & CCl_3.COOH & + & HCl.
\end{array}$$

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:



$$\begin{array}{lclclcl}
3\begin{matrix}H\\H\end{matrix}\!>O & + & PCl_3 & = & 3HCl & + & P(OH)_3, \\
3\begin{matrix}CH_3\\H\end{matrix}\!>O & + & PCl_3 & = & 3CH_3Cl & + & P(OH)_3, \\
3\begin{matrix}C_2H_3O\\H\end{matrix}\!>O & + & PCl_3 & = & 3C_2H_3OCl & + & P(OH)_3.
\end{array}$$

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, $CCl_3.CO_2H$ = 162.12. 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.

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 acetates. 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, $HC_{18}H_{35}O_2 = 282.14$. 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, $HC_{18}H_{33}O_2 = 280.14$. 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 *oleates of mercury, quinine, veratrine, atropine,* and *cocaine* are obtained by dissolving the yellow mercuric oxide, quinine, veratrine, atropine, or cocaine in oleic acid.

Dissociation of formic acid and its homologues. In Chapter 15 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.

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 acid 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?

tion. This fact indicates that the iron is held in a complex ion, $\mathrm{Fe(C_2O_4)_2''}$, 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, $\mathrm{K_3Fe(C_2O_4)_3}$, gives a green solution, and the iron is probably held in a complex ion, $\mathrm{Fe(C_2O_4)_3'''}$. It is rapidly reduced by sunlight, thus,

$$\mathrm{2K_3Fe(C_2O_4)_3 = 2K_2Fe(C_2O_4)_2 + K_2C_2O_4 + 2CO_2},$$

and, therefore, is useful in making platinotypes in photography.

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 hydroxy-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:

$$\mathrm{CH_3Br + H_2O = CH_3OH + HBr},$$

$$\mathrm{CH_2}<\begin{matrix}\mathrm{Br}\\\mathrm{CO_2H}\end{matrix} + \mathrm{H_2O} = \mathrm{CH_2}<\begin{matrix}\mathrm{OH}\\\mathrm{CO_2H}\end{matrix} + \mathrm{HBr}.$$

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, $OH.CO_2H$.
Acetic acid, $CH_3.CO_2.H$.	Hydroxy-acetic acid, $CH_2.OH.CO_2H$.
Propionic acid, $C_2H_5.CO_2H$.	Hydroxy-propionic acid, $C_2H_4.OH.CO_2H$.
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.

Monohydroxy-monobasic acids.

Glycolic acid, $CH_2.OH.CO_2H$ (*Hydroxy-acetic 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:

$$C_2H_4(OH)_2 + 2O = CH_2.OH.CO_2H + H_2O.$$

Glycolic acid is a white deliquescent, crystalline substance, easily soluble in water, alcohol, and ether.

Lactic acid, Acidum lacticum, $C_2H_4.OH.CO_2H = 89.37$ (*Hydroxy-propionic 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:

$$\underset{\text{Sugar.}}{C_6H_{12}O_6} = \underset{\text{Lactic acid.}}{2(HC_3H_5O_3)}.$$

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.

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 micro-organism.

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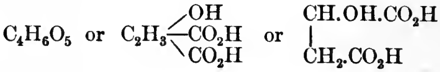
c. *Lævolactic acid* is lævorotatory, and is obtained from cane sugar by fermentation by a special micro-organism.

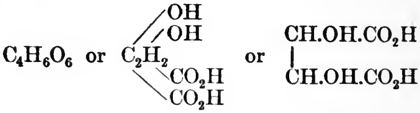
Dibasic and tribasic hydroxy-acids.

Mono-hydroxy-succinic acid, or malic acid =



$$C_4H_6O_5 \text{ or } C_2H_3\begin{cases}OH\\CO_2H\\CO_2H\end{cases} \text{ or } \begin{array}{l}CH.OH.CO_2H\\|\\CH_2.CO_2H\end{array}$$

Di-hydroxy-succinic acid, or tartaric acid =



$$C_4H_6O_6 \text{ or } C_2H_2\begin{cases}OH\\OH\\CO_2H\\CO_2H\end{cases} \text{ or } \begin{array}{l}CH.OH.CO_2H\\|\\CH.OH.CO_2H\end{array}$$

Malic acid, $H_2C_4H_4O_5$, occurs in the juices of many fruits, as apples, currants, cherries, etc. It may be extracted from these fruits or prepared synthetically.

Tartaric acid, Acidum tartaricum, $H_2C_4H_4O_6$ = 148.92. 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:

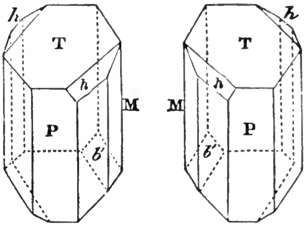
$$\underset{\text{Calcium tartrate.}}{CaC_4H_4O_6} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Tartaric acid.}}{H_2C_4H_4O_6} + \underset{\text{Calcium sulphate.}}{CaSO_4}.$$

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 135° C. (275° F.).

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.

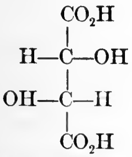
Pasteur first observed that the spontaneous evaporation of a solution of ammonium sodium racemate yields two kinds of stereo-isomeric crystals. These crystals (Fig. 71) are rectangular prisms P, M, T, having the lateral edges replaced by the faces *b′*, and the intersection of these faces with the face 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 71.



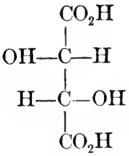
Isomeric salts of tartaric acid.

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:



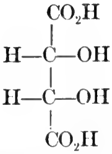
$$\begin{array}{c}\mathrm{CO_2H}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{OH{-}C{-}H}\\ |\\ \mathrm{CO_2H}\end{array}$$

Dextrotartaric acid.



$$\begin{array}{c}\mathrm{CO_2H}\\ |\\ \mathrm{OH{-}C{-}H}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{CO_2H}\end{array}$$

Lævotartaric acid.



$$\begin{array}{c}\mathrm{CO_2H}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{CO_2H}\end{array}$$

Mesotartaric acid.

Racemic acid results from the combination of dextrotartaric and lævotartaric acids.

In a tenth-normal solution of tartaric acid at 25° C., 8.2 per cent. of the acid is dissociated into $H^{\cdot}$ 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 gramme 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 gramme of silver nitrate in 100 c.c. of boiling water, add 0.166 gramme 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. $KHC_4H_4O_6 = 186.78$ (*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, $KNaC_4H_4O_6.4H_2O$=280.18 (*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 grammes of potassium acid tartrate to a hot solution of 20 grammes 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 grammes of potassium acid tartrate into Rochelle salt?

Seidlitz powders (*Compound effervescing powders*) consist of a mixture of 7.75 grammes (120 grains) of Rochelle salt with 2.58 grammes (40 grains) of sodium bicarbonate (wrapped in blue paper), and 2.25 grammes (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, $2(KSbO.C_4H_4O_6).H_2O$=659.8 (*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.

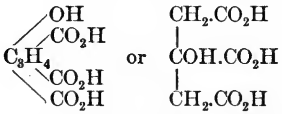
Action of certain organic acids upon certain metallic oxides. The solution of a ferric salt (or certain other metallic salts) is precipitated by alkali hydroxides, a salt of the alkali and ferric hydroxide being formed. When a sufficient quantity of either tartaric, citric, oxalic, or various other organic 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, which are the *scale compounds* of the U. S. P.

Instead of obtaining these compounds, as stated above, by adding the organic acids (or their salts) to the inorganic salts, they are more generally obtained by dissolving the freshly precipitated metallic hydroxide in the organic acid.

The true chemical constitution of many of these scale compounds has not as yet been determined with certainty.

Of official scale compounds containing tartaric acid may be mentioned the *iron and ammonium tartrate*, and the *iron and potassium tartrate*. The first compound is obtained by dissolving freshly precipitated ferric hydroxide in a solution of ammonium acid tartrate; the second, by dissolving ferric hydroxide in potassium acid tartrate. The clear solutions, after having been sufficiently evaporated, are dried, as mentioned above, on glass plates.

Citric acid, Acidum citricum, $H_3C_6H_5O_7.H_2O = 208.5$. Citric acid is a tribasic acid containing three atoms of hydrogen replaceable by metals; its constitution may be expressed by the graphic formulas:



$$\begin{array}{c} CH_2.CO_2H \\ | \\ COH.CO_2H \\ | \\ CH_2.CO_2H \end{array}$$

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 and decomposing by sulphuric acid the calcium citrate thus formed. (100 parts of lemons yield about 5 parts of the acid.) It forms colorless crystals, easily soluble in water.

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 gramme 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 *effervescent potassium citrate, lithium citrate, and magnesium sulphate* are granulated mixtures, all containing citric acid, tartaric acid, and sodium bicarbonate, mixed respectively with potassium citrate, lithium citrate, and magnesium sulphate.

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, Ferri citras. 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 or quinine, strychnine, sodium phosphate, or sodium pyrophosphate, 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, iron and strychnine citrate, soluble ferric phosphate,* and *soluble ferric pyrophosphate.*

47. ETHERS AND ESTERS.

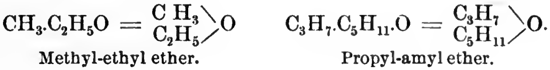
Constitution. It has been shown that alcohols are hydrocarbon residues in combination with hydroxyl, OH, and that acids are hydrocarbon residues in combination with carboxyl, CO.OH; it has further been shown that carboxyl may be considered as being composed of CO, and hydroxyl, OH, and that the term acid 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 $\begin{matrix}\mathrm{R}\\\mathrm{H}\end{matrix}\!>\mathrm{O}$, and of an acid, R.CO.OH, or $\begin{matrix}\mathrm{R.CO}\\\mathrm{H}\end{matrix}\!>\mathrm{O}$.

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:

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?

Hydroxides.	*Oxides.*	*Acids.*	*Salts.*
$KOH = \left.\begin{matrix}K\\H\end{matrix}\right\rangle O$ Potassium hydroxide.	$K_2O = \left.\begin{matrix}K\\K\end{matrix}\right\rangle O$ Potassium oxide.	$HNO_3 = \left.\begin{matrix}NO_2\\H\end{matrix}\right\rangle O$ Nitric acid.	$KNO_3 = \left.\begin{matrix}NO_2\\K\end{matrix}\right\rangle O$ Potassium nitrate.
$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\rangle O$ Ethyl alcohol.	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O$ Ethyl ether.	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\rangle O$ Acetic acid.	$\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\rangle O$ Ethyl acetate, or acetic ether.
$\begin{matrix}R\\H\end{matrix}{>}O$ Alcohol.	$\begin{matrix}R\\R\end{matrix}{>}O$ Ether.	$\begin{matrix}R.CO\\H\end{matrix}{>}O$ Acid.	$\begin{matrix}R.CO\\R\end{matrix}{>}O.$ 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:



$$CH_3.C_2H_5O = \left.\begin{matrix}C\,H_3\\C_2H_5\end{matrix}\right\rangle O \qquad C_3H_7.C_5H_{11}.O = \left.\begin{matrix}C_3H_7\\C_5H_{11}\end{matrix}\right\rangle O.$$

Methyl-ethyl ether. 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. For instance:

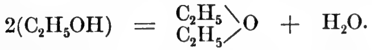
$$\left.\begin{matrix}C_2H_5\\Na\end{matrix}\right\rangle O + C_2H_5I = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O + NaI.$$

Sodium ethylate. Ethyl iodide. Ethyl ether. Sodium iodide.

$$\left.\begin{matrix}C_2N_5\\Na\end{matrix}\right\rangle O + CH_3I = \left.\begin{matrix}C_2H_5\\C\,H_3\end{matrix}\right\rangle O + NaI.$$

Sodium ethylate. Methyl iodide. Ethyl-methyl ether. Sodium iodide.

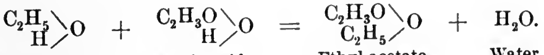
Ethers are also formed by the action of sulphuric acid upon alcohols; the sulphuric acid removing water in this case, thus:



$$2(C_2H_5OH) = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O + H_2O.$$

Ethyl alcohol. Ethyl ether. Water.

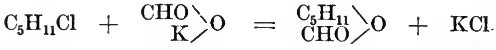
Esters are formed by the combination of acids with alcohols and elimination of water. (Presence of sulphuric acid facilitates this action.)



$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\rangle O + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\rangle O = \left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\rangle O + H_2O.$$

Ethyl alcohol. Acetic acid. Ethyl acetate. Water.

They are also formed by the action of hydrocarbon chlorides (or iodides) on salts. For instance:



$$C_5H_{11}Cl + \left.\begin{matrix}CHO\\K\end{matrix}\right>O = \left.\begin{matrix}C_5H_{11}\\CHO\end{matrix}\right>O + KCl.$$

Amyl chloride. Potassium formate. Amyl formate. Potassium chloride.

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 further 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.

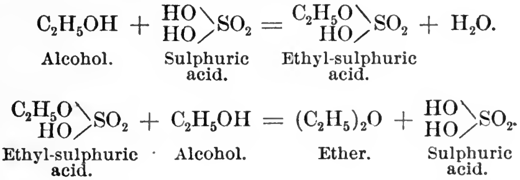
Ethyl ether, Æther, $(C_2H_5)_2O = 73.52$ (*Ether, sulphuric ether, Ethyl oxide*). The name of the whole group of ethers is derived from this (ethyl-) ether, in the same way that common (ethyl-) alcohol has given its name to the group of alcohols. The name sulphuric ether was given at a time when its 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 grammes of alcohol with 180 grammes 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:



$$\underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\text{Sulphuric acid.}}{\left.\begin{matrix}HO\\HO\end{matrix}\right\rangle SO_2} = \underset{\text{Ethyl-sulphuric acid.}}{\left.\begin{matrix}C_2H_5O\\HO\end{matrix}\right\rangle SO_2} + H_2O.$$

$$\underset{\text{Ethyl-sulphuric acid.}}{\left.\begin{matrix}C_2H_5O\\HO\end{matrix}\right\rangle SO_2} + \underset{\text{Alcohol.}}{C_2H_5OH} = \underset{\text{Ether.}}{(C_2H_5)_2O} + \underset{\text{Sulphuric acid.}}{\left.\begin{matrix}HO\\HO\end{matrix}\right\rangle SO_2}.$$

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 of ethyl-ether 96 per cent. and of alcohol 4 per cent. 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.

Spiritus ætheris and *Spiritus ætheris compositus* are mixtures of about one part of ether and two parts of alcohol, 3 per cent. of certain ethereal oils being added to the second preparation.

Methyl ether, $(CH_3)_2O$, 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, $CH_3.C_2H_5.O$, 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.

Acetic ether, Æther aceticus, $C_2H_5C_2H_3O_2 = 87.4$ (*Ethyl acetate*). 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 grammes of pure alcohol and 100 grammes of concentrated sulphuric acid 60 grammes of sodium acetate. Introduce this mixture into a boiling-flask, connect it with a Liebig's condenser and distil about 50 c.c. Redistil the liquid from a flask, as represented in Fig. 69, page 463, and collect the portion which passes over at a temperature of 77° C. (170° F.); it is nearly pure ethyl acetate.

Acetic ether 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 7 parts of water. Specific gravity 0.894. Boiling-point about 72° C. (161° F.).

Ethyl nitrite, $C_2H_5NO_2 = 74.51$ (*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.)

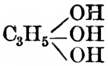
Spirit of nitrous ether, Spiritus ætheris nitrosi, Sweet spirit of niter. This is a mixture of about 4 parts of ethyl nitrite with 96 parts of alcohol. It is a clear, mobile, volatile, and inflammable liquid, of a pale straw color inclining slightly to green, a fragrant, ethereal odor, and a sharp, burning taste. It is neutral, or but very slightly acid to litmus paper but evolves no carbon dioxide with potassium bicarbonate.

Amyl nitrite, Amylis nitris, $C_5H_{11}NO_2 = 116.24$. 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 of this ether about 80 per cent., 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.

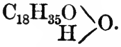
Fats and fat oils. All true fats are esters of the triatomic alcohol glycerin, in which the three replaceable hydrogen atoms of the hydroxyl are replaced by three univalent radicals of the higher members of the fatty acids. For instance:

Glycerin = $C_3H_5.(OH)_3$ or



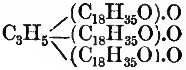
$$C_3H_5\begin{cases}OH\\OH\\OH\end{cases}$$

Stearic acid = $C_{18}H_{35}O.OH$ or



$$\left.\begin{matrix}C_{18}H_{35}O\\H\end{matrix}\right\rangle O.$$

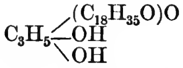
Stearin or tristearin = $C_3H_5.(C_{18}H_{35}O)_3.O_3$ or



$$C_3H_5\begin{cases}(C_{18}H_{35}O).O\\(C_{18}H_{35}O).O\\(C_{18}H_{35}O).O\end{cases}$$

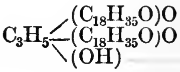
While all natural fats are glycerin in which the three hydrogen atoms are replaced, we may by artificial means introduce but one or two acid radicals, thus forming:

Monostearin =



$$C_3H_5\begin{cases}(C_{18}H_{35}O)O\\OH\\OH\end{cases}$$

Distearin =



$$C_3H_5\begin{cases}(C_{18}H_{35}O)O\\(C_{18}H_{35}O)O\\(OH)\end{cases}$$

Fats are often termed *glycerides;* stearin being, for instance, the glyceride of stearic acid.

The principal fats consist of mixtures of palmitin, $C_3H_5.(C_{16}H_{31}O)_3.O_3$, stearin, $C_3H_5.(C_{18}H_{35}O)_3.O_3$, and olein, $C_3H_5.(C_{18}H_{33}O)_3.O_3$. 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 are of importance: *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 physiologists, 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.

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:

$$\underset{\text{(olive oil).}}{\underset{\text{Oleate of glyceryl}}{C_3H_5(C_{18}H_{33}O_2)_3}} + \underset{\text{hydroxide.}}{\underset{\text{Sodium}}{3NaOH}} = \underset{\text{(hard soap).}}{\underset{\text{Sodium oleate}}{3NaC_{18}H_{33}O_2}} + \underset{\text{Glycerin.}}{C_3H_5(OH)_3}.$$

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 grammes of potassium hydroxide in 100 c.c. of alcohol. Melt 50 grammes 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 grammes 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 grammes 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 c.c. 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 a 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.

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?

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, to-day 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 synthetical 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.

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.)

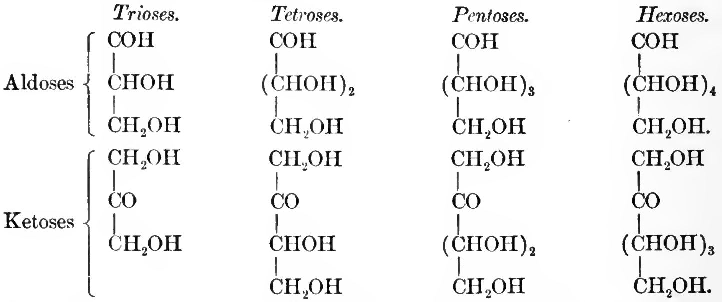
2. *Disaccharides, or complex sugars.* These are sugars which, on taking up 1 molecule of water, split up into two simple sugars. (Cane-sugar, maltose, lactose, etc.)

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 substances 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:



$$\begin{array}{lllll} & \textit{Trioses.} & \textit{Tetroses.} & \textit{Pentoses.} & \textit{Hexoses.} \\ \text{Aldoses}\left\{\begin{array}{l} \\ \\ \\ \\ \end{array}\right. & \begin{array}{l} \text{COH} \\ | \\ \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array} & \begin{array}{l} \text{COH} \\ | \\ (\text{CHOH})_2 \\ | \\ \text{CH}_2\text{OH} \end{array} & \begin{array}{l} \text{COH} \\ | \\ (\text{CHOH})_3 \\ | \\ \text{CH}_2\text{OH} \end{array} & \begin{array}{l} \text{COH} \\ | \\ (\text{CHOH})_4 \\ | \\ \text{CH}_2\text{OH.} \end{array} \\ \text{Ketoses}\left\{\begin{array}{l} \\ \\ \\ \\ \\ \\ \end{array}\right. & \begin{array}{l} \text{CH}_2\text{OH} \\ | \\ \text{CO} \\ | \\ \text{CH}_2\text{OH} \\ \\ \\ \end{array} & \begin{array}{l} \text{CH}_2\text{OH} \\ | \\ \text{CO} \\ | \\ \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array} & \begin{array}{l} \text{CH}_2\text{OH} \\ | \\ \text{CO} \\ | \\ (\text{CHOH})_2 \\ | \\ \text{CH}_2\text{OH} \end{array} & \begin{array}{l} \text{CH}_2\text{OH} \\ | \\ \text{CO} \\ | \\ (\text{CHOH})_3 \\ | \\ \text{CH}_2\text{OH.} \end{array} \end{array}$$

Glucose is an aldose-hexose, while fructose is a ketose-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 grammes of starch and 25 grammes 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.

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*), 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, but does not ferment 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 benzol derivative, viz., hexahydroxy-benzol, $C_6H_6(OH)_6$.

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* and by not forming osazones. 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, $C_{12}H_{22}O_{11} = 339.6$ (*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. 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 one 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, $C_{12}H_{22}O_{11}$, 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, $C_{12}H_{22}O_{11} + H_2O = 357.48$ (*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.

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.

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 Schweizer's reagent, a very efficient preparation of which is obtained as follows: 2 grammes 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 gramme 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 Schweizer'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 grammes of 10 per cent. borated cotton should contain 2.5 grammes of boric acid, or 10 grammes of 5 per cent. carbolated cotton should contain 0.5 gramme of pure carbolic acid.

Pyroxylin, Pyroxylinum, chiefly *cellulose tetra-nitrate,* $C_{12}H_{16}O_6(NO_3)_4$. (*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. *Styptic collodion* contains tannin. 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, resorcin, 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 grammes 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 gramme 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 exclusively in animals; 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.

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 amygdalin, 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.

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.

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:

$$\underset{\text{Nitrite.}}{R{-}O{-}NO,} \qquad \underset{\text{Nitro compound.}}{R{-}NO_2,}$$

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 derivatives 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:

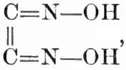
$$R_3.CH + HNO_2 = \underset{\text{Nitroso compound.}}{R_3.C.NO} + H_2O.$$

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, $C_2N_2O_2H_2$,  $\begin{array}{l} C{=}N{-}OH \\ \| \\ C{=}N{-}OH \end{array}$, 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.

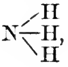
Amines may also be formed by the action of nascent hydrogen upon the cyanides of the alcohol radicals:

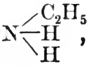
$$\underset{\text{Methyl cyanide.}}{CH_3CN} + 4H = \underset{\text{Ethyl amine.}}{NH_2.C_2H_5.}$$

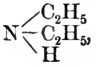
They are also formed by the action of nascent hydrogen upon nitro-compounds; the manufacture of aniline depends on this decomposition:

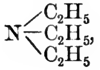
$$\underset{\text{Nitro-benzene.}}{C_6H_5NO_2} + \underset{\text{Hydrogen.}}{6H} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Phenylamine, or aniline.}}{NH_2\,C_6H_5.}$$

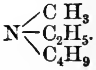
Occurrence of organic bases in nature. The various organic basic substances found in nature are either amines or amides. But a small number of organic bases is found in the animal system, urea being the most important one. In plants organic bases are frequently met with, and are grouped together under 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,	$N(C_2H_5)H_2$,	$N(C_2H_5)_2H$,	$N(C_2H_5)_3$,	$NCH_3.C_2H_5.C_4H_9$.
Ammonia.	Ethylamine.	Diethylamine.	Triethylamine.	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:

$$NH_3 + HCl = NH_4Cl;$$

$$\underset{\text{Triethylamine.}}{N(C_2H_5)_3} + HCl = \underset{\text{Triethylamine chloride.}}{N(C_2H_5)_3HCl.}$$

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:

$$\underset{\text{Methyl amine.}}{CH_3NH_2} + \underset{\text{Nitrous acid.}}{HONO} = CH_3NH_3ONO = \underset{\text{Methyl alcohol.}}{CH_3OH} + H_2O + 2N.$$

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 alkalics, giving rise to the formation of iso-nitriles, substances having a most disagreeable odor. (See tests for chloroform.) The reaction is this:

$$\underset{\text{Ethyl amine.}}{C_2H_5NH_2} + \underset{\text{Chloroform.}}{CHCl_3} = \underset{\text{Ethyl isonitrile.}}{C_2H_5NC} + 3HCl.$$

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*), is a white, crystalline substance, used medicinally on account of its solvent action on uric acid.

Hexamethylenamine, Hexamethylenamina, $(CH_2)_6N_4 = 139.18$ (*Hexamethylene tetramine, Urotropin*). This compound results from the action of ammonia on formaldehyde:

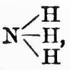
$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

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.

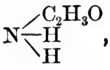
Some derivatives of hexamethylenamine have been introduced under special names, such as salicylate (saliform), bromethylate (bromalin, bromoformin), tannate (tannopin or tannon), iodoform (iodoformin).

Amides are substances derived from ammonia by replacement of hydrogen atoms by acid radicals. Thus:



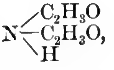
$N\begin{matrix}H\\H,\\H\end{matrix}$

Ammonia.



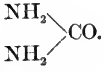
$N\begin{matrix}C_2H_3O\\H\\H\end{matrix}$,

Acetamide.



$N\begin{matrix}C_2H_3O\\C_2H_3O,\\H\end{matrix}$

Diacetamide.



$\begin{matrix}NH_2\\NH_2\end{matrix}CO.$

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 introduction of an acid radicle into ammonia may be accomplished by one of three generally applicable methods:

1. By heating the ammonium salt of organic acids,

$$\underset{}{CH_3.COONH_4} = \underset{\text{Acetamide.}}{CH_3.CONH_2} + H_2O.$$

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*, *Chloralformamidum* (*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 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.

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, 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 f water this salt is converted into urea:

$$NH_4.NH_2.CO_2 = (NH_2)_2CO + H_2O.$$

Amino-formic acid or carbamic acid, $NH_2.COOH$, 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 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, $CO.OC_2H_5.NH_2 = 88.42$. Obtained by the action of alcohol on urea or on one of its salts:

$$CO<\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix} + HOC_2H_5 = CO<\begin{smallmatrix}OC_2H_5\\NH_2\end{smallmatrix} + NH_3.$$

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, $C_6H_4<\begin{smallmatrix}CO_2CH_3\\NH.COOC_2H_5\end{smallmatrix}$, colorless, sparingly soluble crystals; *thermodin*, or phenacetin-urethane,  $C_6H_4<\begin{smallmatrix}OC_2H_5\\ \end{smallmatrix}N<\begin{smallmatrix}COCH_3\\COOC_2H_5\end{smallmatrix}$, colorless, very sparingly soluble needles; *hedonal*, or methylpropylcarbinol-urethane, $NH_2.COOCH<\begin{smallmatrix}CH_3\\C_3H_7\end{smallmatrix}$, 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 are considered in the subsequent chapters on Physiological Chemistry, but may be briefly mentioned here.

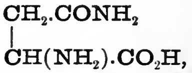
Sarcosine, Methyl-glycocoll, $CH_3NH.CH_2CO_2H$, a product of the decomposition of creatine, which is found in flesh, and of caffeine, and may be obtained by boiling these compounds with a solution of barium hydroxide. It is much like glycocoll in properties.

Cystine, $(SC(CH_3)NH_2CO_2H.)_2$, a derivative of α-amino-propionic acid, sometimes found in the sediment of urine (see Index).

Leucine, α-amino-caproic acid, $CH_3.(CH_2)_3.CH(NH_2).CO_2H$, 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 (see Index).

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,  $\begin{array}{l} CH_2.CONH_2 \\ | \\ CH(NH_2).CO_2H, \end{array}$ 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,  $(HN)C\begin{array}{l} \diagup NH_2 \\ \diagdown NCH_3.CH_2.CO_2H, \end{array}$ 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,

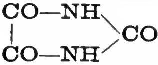
Creatinine,  $(HN)C\begin{array}{l} \diagup NH-CO \\ \qquad\quad\;\; | \\ \diagdown NCH_3-CH_2, \end{array}$ which forms prisms, readily soluble in water. It is a strong base. It is a constant constituent of urine. Creatine and creatinine are discussed at greater length further on (see Index).

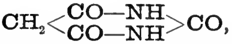
Urea, Carbamide, $CO(NH_2)_2$, is the amide of carbonic acid. It occurs in the urine and blood of all mammals, particularly of carnivorous animals. It has been made by various synthetic methods, but is most easily obtained from urine (see Index). It crystallizes in rhombic prisms, melting at 132° C., easily soluble in water and alcohol. When boiled with dilute acids or alkalies, it yields carbon dioxide and ammonia, thus:

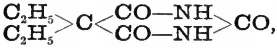
$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3.$$

Urea unites with acids, thus: urea hydrochloride, $CO(NH_2)_2.HCl$; urea nitrate, $CO(NH_2)_2.HNO_3$, 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.

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,  $\left.\begin{matrix}CO-NH\\ |\\ CO-NH\end{matrix}\right\rangle CO$, 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,  $CH_2\left\langle\begin{matrix}CO-NH\\ CO-NH\end{matrix}\right\rangle CO$, 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,  $\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\!\!>C\left\langle\begin{matrix}CO-NH\\ CO-NH\end{matrix}\right\rangle CO$, 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:

$$4NH_3 \quad + \quad 3C \quad = \quad 2(NH_4CN) \quad + \quad CH_4.$$

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:

$$Hg(CN)_2 = Hg + 2CN.$$

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, $HCN = 26.84$ (*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:

$$\underset{\text{Chloroform.}}{CHCl_3} + NH_3 = \underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Hydrochloric acid.}}{3HCl.}$$

By heating ammonium formate to 200° C. (392° F.):

$$\underset{\text{Ammonium formate.}}{NH_4CHO_2} = \underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Water.}}{2H_2O.}$$

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 grammes 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 grammes 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 two 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 grammes of silver cyanide by 15.54 c.c. of diluted hydrochloric acid, mixed with 44.10 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:

$$\left.\begin{array}{lll}KCN \rightleftarrows K^{\cdot} & + & CN' \\ HOH \rightleftarrows (OH)' & + & H^{\cdot}\end{array}\right\} \rightleftarrows HCN.$$

The action is due to the extremely weak dissociating power of hydrocyanic acid (see Chapter 15).

For peculiarities of mercury cyanide see chapter on Mercury.

Potassium cyanide, Potassii cyanidum, $KCN = 64.7$. 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:

$$\underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{K_4Fe(CN)_6} + \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} = \underset{\substack{\text{Potassium}\\\text{cyanide.}}}{5KCN} + \underset{\substack{\text{Potassium}\\\text{cyanate.}}}{KCNO} + \underset{\text{Iron.}}{Fe} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2}.$$

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, U. S. P., should contain at least 95 per cent. of potassium cyanide; it 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 but is unstable, decomposition soon taking place with the formation of potassium formate and ammonia, along with other products:

$$KCN + 2H_2O = CHKO_2 + NH_3.$$

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 cyanides 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.

Silver cyanide, Argenti cyanidum, $AgCN = 132.96$. A white powder, obtained by precipitating a solution of potassium cyanide with silver nitrate. It is insoluble in water, slowly soluble in ammonia water, sodium thiosulphate, and potassium cyanide; when heated it evolves cyanogen, metallic silver being left.

Mercuric cyanide, $Hg(CN)_2$. A white crystalline salt, obtained by dissolving mercurous 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 ten 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 atmos-

phere. 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 cyanide 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 *sulpho-cyanates*. 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-cynogen 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. 549.)

Potassium ferrocyanide, Potassii ferrocyanidum, $K_4Fe(CN)_6.3H_2O = 419.62$ (*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.

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):

$$\underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{3K_4Fe(CN)_6} + \underset{\substack{\text{Ferric}\\\text{chloride.}}}{4FeCl_3} = \underset{\substack{\text{Potassium}\\\text{chloride.}}}{12KCl} + \underset{\substack{\text{Ferric ferro-}\\\text{cyanide.}}}{Fe_4(FeC_6N_6)_3.}$$

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:

$$\underset{\substack{\text{Potassium}\\ \text{ferrocyanide.}}}{K_4Fe(CN)_6} + \underset{\text{Chlorine.}}{Cl} = \underset{\substack{\text{Potassium}\\ \text{chloride.}}}{KCl} + \underset{\substack{\text{Potassium}\\ \text{ferricyanide.}}}{K_3Fe(CN)_6}.$$

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:

$$\underset{\text{Cyanide.}}{R—C\equiv N,} \qquad\qquad \underset{\text{Isocyanide.}}{R—N\equiv C,}$$

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:

$$\underset{\text{Methyl cyanide.}}{CH_3.CN} + 2H_2O = \underset{\text{Acetic acid.}}{CH_3.CO_2H} + NH_3.$$

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:

$R—S—C\equiv N$, sulphocyanate. $R—N=C=S$, isosulphocyanate.

The organic sulphocyanides 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:

$$-CH_2-CH{=}CH_2,\ \text{allyl.} \qquad -CH_2-\overset{|}{C}H-CH_2-,\ \text{glyceryl.}$$

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. 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

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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?

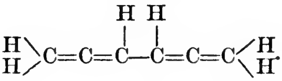
methane derivatives differ considerably in many respects, and, as a general rule, aromatic compounds cannot be converted into fatty compounds, or the latter into aromatic compounds, without suffering the most vital decomposition of the molecule, and in many cases this transformation cannot be accomplished 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.

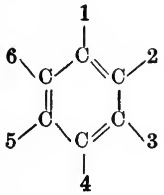
If benzene were of the nature of a fatty compound, we should expect to find its structure correspond to a formula of this kind:

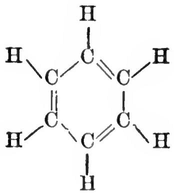


This representation would indicate that benzene ought to behave like a highly unsaturated compound. Moreover, we should expect to obtain two isomeric compounds by replacing either a centrally located hydrogen atom or one occupying a terminal position.

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.*

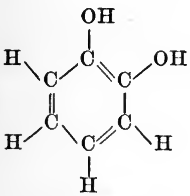
In view of these and many other facts the conclusion is that the six carbon atoms in benzene are united into a cycle or ring, and that each carbon atom is in combination with one hydrogen atom. This view was first put forth by August Kekulé in 1865. Graphically the closed carbon chain and also benzene (usually referred to as Kekulé's benzene hexagon) are represented thus:



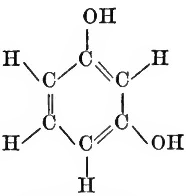


This formula for benzene accounts for the facts mentioned above. Moreover, if two hydrogen atoms are replaced by substituting atoms or radicals, three isomeric products are obtained.

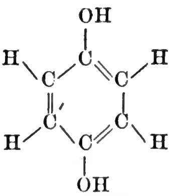
For instance, we know three different substances which have been obtained by replacement of two hydrogen atoms in benzene by two hydroxyl groups. This would indicate that it makes a difference, as far as the properties of a compound are concerned, in which relative position the introduced radicals stand 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.

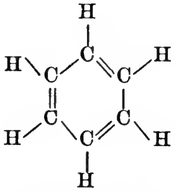
Designating the hydrogen atoms in benzene with numbers, thus: $C_6\overset{1}{H}\overset{2}{H}\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$, the above 3 compounds show that in one case the hydrogen atoms 1 and 2, in the second 1 and 3, in the third 1 and 4 have been replaced by OH. The compounds 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 dioxybenzene; 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 pyro-catechin, *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.

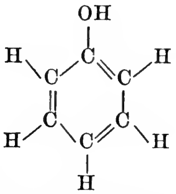
Benzene derivatives. The analogy existing between methane- and benzene-derivatives may be shown by comparing the composition of a few derivatives:

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,	$C_3H_5\left\langle\begin{matrix}OH\\OH\\OH\end{matrix}\right.$	Pyrogallol,	$C_6H_3\left\langle\begin{matrix}OH\\OH\\OH\end{matrix}\right.$
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,	$SO_2\left\langle\begin{matrix}C_2H_5\\OH\end{matrix}\right.$	Benzene-sulphonic acid,	$SO_2\left\langle\begin{matrix}C_6H_5\\OH\end{matrix}\right.$
Malonic acid,	$CH_2\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$	Phthalic acid,	$C_6H_4\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$
Tartaric acid,	$C_2H_2\left\langle\begin{matrix}2OH\\2CO_2H\end{matrix}\right.$	Salicylic acid,	$C_6H_4\left\langle\begin{matrix}OH\\CO_2H\end{matrix}\right.$
Ethyl ether,	$\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O$	Phenyl-ether,	$\left\{\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\rangle O$
Methyl-ethyl ether,	$\left\{\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\rangle O$	Methyl-phenyl ether, anisol,	$\left\{\begin{matrix}CH_3\\C_6H_5\end{matrix}\right\rangle O$

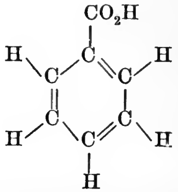
The following graphic formulas may serve to illustrate the constitution of some aromatic compounds:



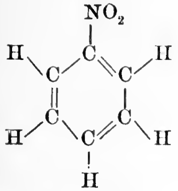
Benzene, C_6H_6.

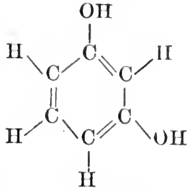


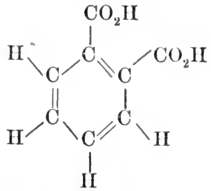
Phenol or carbolic acid, $C_6H_5.OH$.

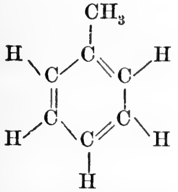


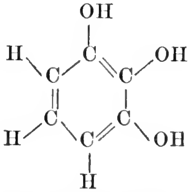
Benzoic acid, $C_6H_5.CO_2H$.

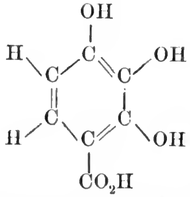

Nitro-benzene, $C_6H_5NO_2$.

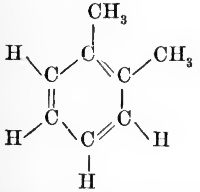

Resorcin, $C_6H_4(OH)_2$.

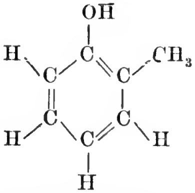

Phthalic acid, $C_6H_4(CO_2H)_2$.

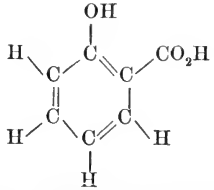

Toluene, methyl-benzene, $C_6H_5.CH_3$.

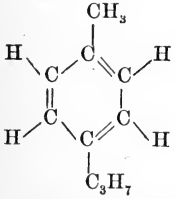

Pyrogallol, $C_6H_3(OH)_3$.

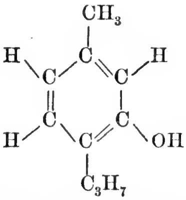

Gallic acid, $C_6H_2.CO_2H.(OH)_3$.

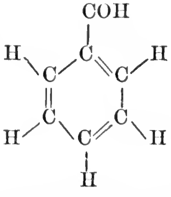

Xylene, di-methyl-benzene, $C_6H_4.(CH_3)_2$.


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 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-iso-propyl-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:

$$C_6H_5.CO_2H + Ca(OH)_2 = CaCO_3 + H_2O + C_6H_6.$$

Experiment 67. Mix 25 grammes of benzoic acid with 40 grammes 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.

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 nitrobenzene. 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 205° C. (401° 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 is also known.

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:

$$C_6H_5Br + CH_3Br + 2Na = C_6H_5CH_3 + 2NaBr.$$

Toluene, as well as the other hydrocarbon derivatives of benzene, possesses 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.

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.

Amino compounds of benzene.

Aniline, Phenyl-amine, $C_6H_5NH_2$. The constitution of amines, to which class aniline belongs, has been considered in Chapter 49. 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 combines with acids to form well-defined salts.

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:

$$\underset{\text{Aniline.}}{C_6H_7N} + \underset{\text{Toluidine.}}{2C_7H_9N} + 3O = \underset{\text{Rosaniline.}}{C_{20}H_{19}N_3} + 3H_2O.$$

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 blue color is produced. A third quantity treat with solution of cupric sulphate and potassium chlorate: a dark color is the result.

Acetanilide, Acetanilidum, $C_6H_5.NH.(CH_3CO) = 134.09$, (*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

$$NH\begin{matrix}\diagup C_6H_5 \\ \diagdown C_2H_3O.\end{matrix}$$

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 gramme 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 gramme 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.

Compound acetanilide powder, Pulvis acetanilidi compositus, is a mixture of 70 parts of acetanilide, 10 parts of caffeine, and 20 parts of sodium bicarbonate. It is one form of the numerous headache powders in the market, in which acetanilide, the cheapest of the common antipyretics, is a common constituent. Sodium bicarbonate increases the solubility of the acetanilide.

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-benzol-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.

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 hydrochloride, Methylthioninæ hydrochloridum, $C_{16}H_{18}N_3SCl = 317.36$ (*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 grammes 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 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:

$$\underset{\substack{\text{Aniline}\\\text{hydrochloride.}}}{C_6H_5.NH_2HCl} + HONO = \underset{\substack{\text{Diazo-benzene}\\\text{chloride.}}}{C_6H_5.N_2.Cl} + 2H_2O.$$

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.

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 (see page 432), 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 Bismark 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 (see page 410). 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:

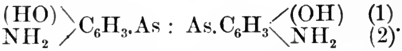
$C_6H_5.NO_2$ Nitrobenzene.	$C_6H_5.N_2.C_6H_5$ Azobenzene.	$C_6H_5.NH_2$ Phenylamine.
$C_6H_5.PO_2$ Phosphinobenzene.	$C_6H_5.P_2.C_6H_5$ Phosphobenzene.	$C_6H_5.PH_2$ Phenylphosphine.
$C_6H_5AsO_2$ Arsinobenzene.	$C_6H_5.As_2.C_6H_5$ Arsenobenzene.	

Arsenobenzene, $C_6H_5.As : As.C_6H_5$, is obtained by the reduction of phenylarsine 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:

$$\underset{\text{Aniline arsenate.}}{C_6H_5NH_2.(HO)_3AsO} = \underset{\text{Para-aminophenyl arsonic acid.}}{NH_2.C_6H_4.AsO(OH)_2} + H_2O$$

The sodium salt of this acid is atoxyl.

Dioxydiaminoarsenobenzene, 
$\begin{matrix}(HO)\\NH_2\end{matrix}\!\!>C_6H_3.As : As.C_6H_3\!<\!\!\begin{matrix}(OH) & (1)\\NH_2 & (2)\end{matrix}$. 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.

Phenols are hydroxyl derivatives of benzene. The name is a general one for all such compounds. Phenols are allied to the tertiary fatty alcohols, as they contain the characteristic grouping $= C - OH$. According to the number of hydrogen atoms replaced by hydroxyl, we find mono-, di-, and tri-hydroxy phenols, corresponding to the similarly constituted alcohols. Phenols differ from common alcohols in not yielding aldehydes or acids by oxidation.

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:

$$C_6H_6 + H_2SO_4 = \underset{\substack{\text{Benzene}\\\text{sulphonic acid.}}}{C_6H_5SO_3H} + H_2O.$$

$$C_6H_5SO_3Na + NaOH = \underset{\text{Phenol.}}{C_6H_5OH.} + Na_2SO_3.$$

The phenol is liberated from its alkali salt by an acid, and is purified by further appropriate treatment.

Phenol, $C_6H_5OH = 93.34$ (*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 tri-brom-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*), 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.

Nitro-phenols. Mono-, di-, and trinitro-phenols are known. Mononitro-phenol is formed by the action of dilute nitric acid on phenol; the di- and tri-nitro- derivatives are formed by further nitration. Mononitro-phenol is of interest also because it is used in the manufacture of acetphenetidin.

Acetphenetidin, Acetphenetidinum, $C_6H_4.O(C_2H_5).NH(C_2H_3O) = 177.79$ (*Phenacetin*). When mononitro-phenol, $C_6H_4.NO_2.OH$, is treated with reducing agents, the oxygen of NO_2 is replaced by hydrogen, and *amino-phenol*, $C_6H_4.OH.NH_2$, is formed. The methyl ether of this compound, $C_6H_4.O(CH_3).NH_2$, is known as *anisidin*, and the ethyl ether, $C_6H_4.O(C_2H_5).NH_2$, as *phenetidin*. By the action of glacial acetic acid upon para-phenetidin, 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 gramme 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-aminophenol, 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 difficultly soluble white powder. *Salophen*, *saliphen*, *phenocoll*, *salocoll*, etc., are similar derivatives.

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.

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, only the ortho acid is formed:

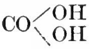
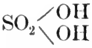
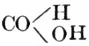
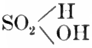
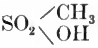
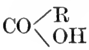
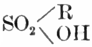
$$C_6H_5OH + H_2SO_4 = C_6H_4(OH)SO_3H + H_2O.$$

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.

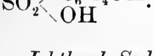
Ortho-phenolsulphonic acid (*Sozolic acid, Aseptol*) occurs on the market as a 33 per cent. solution. It is a syrupy liquid, having a reddish color and a feeble odor. It is used as an antiseptic.

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.

Sulphonic acid has been spoken of before, when it was shown that mercaptans are converted into compounds termed sulphonic acids. These acids may be looked upon as derivatives of sulphurous acid, obtained from it by replacement of hydrogen by radicals. The relation existing between carbonic and sulphonic acids may be represented by the following formulas:

Carbonic acid,	 $CO\langle\begin{matrix}OH\\OH\end{matrix}$	Sulphuric acid,	 $SO_2\langle\begin{matrix}OH\\OH\end{matrix}$
Formic acid,	 $CO\langle\begin{matrix}H\\OH\end{matrix}$	Sulphurous acid,	 $SO_2\langle\begin{matrix}H\\OH\end{matrix}$
Acetic acid,	 $CO\langle\begin{matrix}CH_3\\OH\end{matrix}$	Methyl-sulphonic acid,	 $SO_2\langle\begin{matrix}CH_3\\OH\end{matrix}$
Any compound carbonic acid,	 $CO\langle\begin{matrix}R\\OH\end{matrix}$	Any sulphonic acid,	 $SO_2\langle\begin{matrix}R\\OH\end{matrix}$

According to this view, phenolsulphonic acid is represented by the formula,


$SO_2\langle\begin{matrix}C_6H_4OH\\OH\end{matrix}$.

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.

Cresol, $C_7H_7OH = 107.25$. 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.).

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, Creosotum. 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, $C_6H_3.CH_3.OCH_3.OH$.

From carbolic acid beechwood creosote may be distinguished by requiring as much as 150 parts of water for solution; by being miscible with the official collodium 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 (*Creosotal*) 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.

Guaiacol, $C_6H_4.OH.OCH_3 = 123.13$, found in beechwood creosote to the extent of from 60 to 90 per cent., is a derivative of the diatomic phenol *catechol* (pyrocatechin), $C_6H_4(OH)_2$, obtained from it by replacing a hydroxyl hydrogen atom by methyl, CH_3. Guaiacol is consequently monomethyl catechol. 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 catechol, is a colorless, aromatic, oily liquid, having the same boiling-point as guaiacol.

A number of derivatives of guaiacol are in 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 $= 162.86$, 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, Safrolum, $C_6H_3.C_3H_5.OOCH_2$. 1 : 3 : 4 $= 160.86$ (*Shikimol, Allyl-pyrocatechol 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.

Thymol, $C_{10}H_{14}O$ or $C_6H_3.CH_3.C_3H_7.OH = 149.66$ (*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, $(C_6H_2.CH_3.C_3H_7.OI)_2 = 545.76$ (*Dithymol-diiodide, Aristol, Annidalin*). 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.

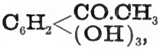
Resorcinol, $C_6H_4(OH)_2$. 1 : 3 = 109.22 (*Resorcin, Meta-dihydroxy-benzene*). It is formed by fusing different resins, such as galbanum, asafœtida, etc., with caustic alkalies, but it is now made almost altogether from benzene by heating the latter with fuming sulphuric acid to 257° C., whereby benzene-meta-disulphonic 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 hydroquinol.

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 tri-hydroxy-benzene—*i. e.*, a phenol. Pyrogallol crystallizes in colorless needles, melts at 131° C. (268° F.), is easy 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.

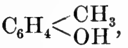
Phloroglucinol, $C_6H_3(OH)_3$. 1 : 3 : 5 (*Phloroglucin, Symmetrical trihydroxy-benzene*), results when resorcin and several resins, as gamboge, dragon's blood, etc., are fused with potassium hydroxide. It forms colorless prisms, melting at 218° C., very soluble in water and alcohol, and of a sweet 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 trihydroxy-benzene. 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.

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,*  $C_6H_4<\begin{matrix}CH_3\\OH\end{matrix}$, 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 all respects like the latter; thus they combine readily with oxygen to form acids and behave generally like unsaturated compounds.

Benzaldehyde, Benzaldehydum, $C_6H_5.COH = 105.25$. 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.

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:

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Glucose.}}{2C_6H_{12}O_6} + \underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Benzaldehyde.}}{C_7H_6O.}$$

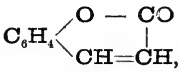
The oil is obtained by maceration of bitter almonds with water, and subsequent distillation when it distils over with hydrocyanic acid and steam, and separates as a heavy oil in the distillate.

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.

Cinnamic aldehyde, Cinnaldehydum, $C_6H_5.CH:CH.COH = 131.07$ (*Artificial oil of cinnamon, 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.

Vanillin, Vanillinum, $C_6H_3.OH.OCH_3.COH.\ 4:3:1 = 150.92$ (*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. 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,  $C_6H_4\left\langle\begin{array}{l}O - CO \\ \qquad\quad | \\ CH{=}CH,\end{array}\right.$ 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 $C_6H_5CO_2H$ = 121.13. 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.

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, sodium hydroxide, or lithium carbonate, the official salts *ammonium benzoate*, $NH_4C_7H_5O_2$, *sodium benzoate*, $NaC_7H_5O_2.H_2O$, and *lithium benzoate*, $LiC_7H_5O_2$, are obtained. The three 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.

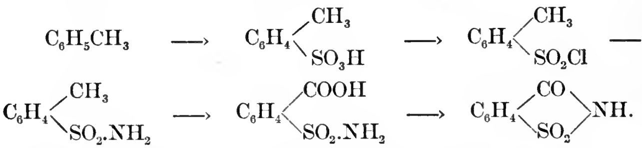
Ethyl para-amino-benzoate, $C_6H_4(NH_2)(COOC_2H_5)$ (*Anesthesin*), is a local anesthetic, introduced as a substitute for cocaine. It is a white, odorless, tasteless powder, melting at 90° to 91° C., almost insoluble in cold and difficultly soluble in hot water. It is soluble in 6 parts of alcohol. 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, $C_6H_4.CO.SO_2.$-$NH = 181.77$ (*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:



$$C_6H_5CH_3 \longrightarrow C_6H_4\begin{cases}CH_3\\SO_3H\end{cases} \longrightarrow C_6H_4\begin{cases}CH_3\\SO_2Cl\end{cases} \longrightarrow$$

$$C_6H_4\begin{cases}CH_3\\SO_2.NH_2\end{cases} \longrightarrow C_6H_4\begin{cases}COOH\\SO_2.NH_2\end{cases} \longrightarrow C_6H_4\begin{cases}CO\\SO_2\end{cases}NH.$$

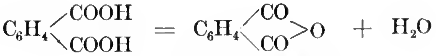
Other methods of preparing saccharin have been devised.

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.

Phthalic acid, $C_6H_4\begin{matrix}\diagup COOH & (1)\\ \diagdown COOH & (2).\end{matrix}$ 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:



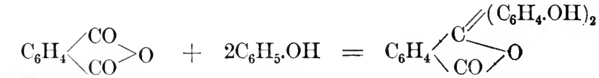
$$C_6H_4\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix} = C_6H_4\begin{matrix}\diagup CO\\ \diagdown CO\end{matrix}\!>O + H_2O$$

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. 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:

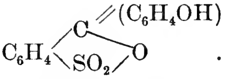
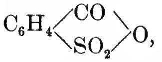


$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + 2C_6H_5.OH = C_6H_4\left<\begin{matrix}C{=}(C_6H_4.OH)_2\\CO\end{matrix}\right>O$$

Phthalic anhydride. Phenol. Phenolphthalein.

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 Gm., given as powder, in cachets, capsules, or pills. In obstinate cases 0.5 Gm. 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,  $C_6H_4\left<\begin{matrix}C{=}(C_6H_4OH)\\SO_2\end{matrix}\right>O$. This substance is analogous to phenolphthalein, and may be obtained in a similar manner by heating together phenol and the anhydride of orthosulphobenzoic acid,  $C_6H_4\left<\begin{matrix}CO\\SO_2\end{matrix}\right>O$, 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 $C_6H_4OH.CO_2H$ = 137. 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:

$$\underset{\text{Sodium phenolate.}}{C_6H_5ONa} + CO_2 = \underset{\text{Sodium phenol carbonate.}}{NaC_6H_5CO_3.}$$

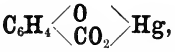
Sodium phenol carbonate is isomeric with sodium salicylate and is actually converted into the latter compound by being heated to 130° C. (266° F.), in tightly closed vessels, or in vessels through which carbon dioxide passes.

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*, $NaC_7H_5O_3$, *ammonium salicylate*, $NH_4C_7H_5O_3$, and *lithium salicylate*, $LiC_7H_5O_3$, all of 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 is official and 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, $(C_6H_4(OH)CO_2)_2Sr + 2H_2O$, which is official, 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,  $C_6H_4\left\langle\begin{matrix}O\\CO_2\end{matrix}\right\rangle Hg$, 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 $C_6H_4(OH)COOCH_3$ 1 : 2 = 150.92. 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 methyl 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 $C_6H_4(OH)COOC_6H_5$ 1 : 2 = 212.47. 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.

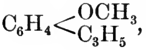
Salol heated with potassium hydroxide solution causes its decomposition into phenol, which can be recognized by its odor, and potassium salicylate, from which crystalline salicylic acid will separate upon supersaturating the liquid with hydrochloric acid. An excess of bromine-water produces a white precipitate 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 more simple 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:

$$2C_6H_4<\substack{OH\\COOH} = C_6H_4<\substack{OH\\COOC_6H_5} + H_2O + CO_2.$$

Anisic acid, $C_6H_4<\substack{OCH_3\\CO_2H}$ (*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.

Gallic acid, Acidum gallicum, $HC_7H_5O_5 + H_2O$ or $C_6H_2(OH)_3.CO_2H + H_2O = 186.65$. 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.

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, $C_{13}H_9O_7.COOH = 319.66$ (*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.

The official or 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.

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.

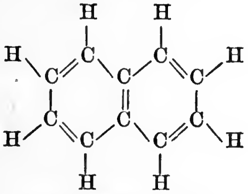
2. Add a few drops of potassium hydroxide: a brown coloration results.

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.

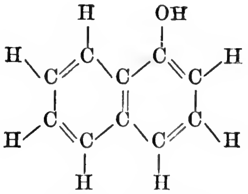
4. Tannic acid precipitates solutions of gelatin, albumin, gelatinized starch, tartar emetic, and most of the alkaloids.

The Naphthalene series.

Naphthalene, Naphthalenum, $C_{10}H_8 = 127.10$. 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, $C_{10}H_8$.

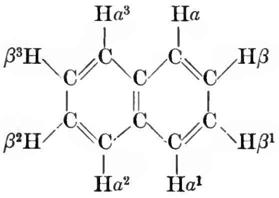


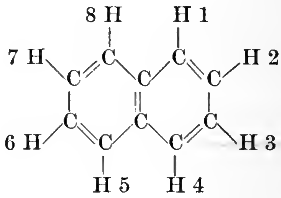
Naphthol, $C_{10}H_7.OH$.

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 α, α^1, α^2, α^3 are alike, and β, β^1, β^2, β^3 are alike, but bear a different relation from that of the α 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 α hydrogen is replaced, are known as *alpha-* or *α-derivatives,* the others as *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, $C_{10}H_7OH = 142.98$. This monatomic phenol bears to naphthalene the same relation as phenol 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, $C_{10}H_7$-SO_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.

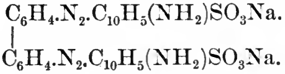
Beta-naphthol benzoate, $C_6H_5COOC_{10}H_7$ (*Benzoyl-naphthol*), is obtained by the action of benzoyl chloride on beta-naphthol at 170° C. It is a white crystalline powder, melting at 107° C., tasteless, odorless, and insoluble in water, but soluble in alcohol, chloroform, and hot ether. It splits into beta-naphthol and benzoic acid in the intestines.

Beta-naphthol-bismuth (*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:



$$\begin{array}{l} C_6H_4.N_2.C_{10}H_5(NH_2)SO_3Na. \\ | \\ C_6H_4.N_2.C_{10}H_5(NH_2)SO_3Na. \end{array}$$

Four mono-sulphonic acids are formed when beta-naphthylamine is treated with sulphuric acid.

Santonin, Santoninum, $C_{15}H_{18}O_3 = 244.29$, 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.

Pyrrol, 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 subtances, among which pyridine and pyrrol are found. Pyrrol has but weak basic properties, is insoluble in water, and has an odor like chloroform.

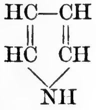
A solution of pyrrol in alcohol, treated with iodine in the presence of oxidizing agents, such as ferric chloride, deposits after some time crystals of *tetra-iodo pyrrol.* This compound is official under the name of *iodol, iodolum,* $C_4I_4NH = 566.17$. It is a pale-yellow, crystalline powder, almost insoluble in water, soluble in 9 parts of alcohol, 1 to 2 parts of ether, and 15 parts of fatty oils; it is, when pure, tasteless and odorless, and contains of iodine 88.97 per cent.

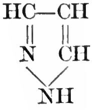
Antipyrine, Antipyrina, $C_{11}H_{12}N_2O = 186.75$ (*Phenyl-dimethyl-isopyrazolon*). When phenyl-hydrazine is heated with *diacetic ether,* $CH_3CO.CH_2.COOC_2H_5$, a substance is formed known as phenyl-methyl-isopyrazolon.

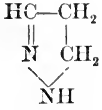
In this compound a second hydrogen atom may be replaced by methyl, when phenyl-dimethyl-isopyrazolon is formed, which is the substance to which the name antipyrine has been given.

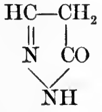
Antipyrine is a white, crystalline, odorless powder, having a slightly bitter taste; it fuses at 113° C. (235° F.), is soluble in less than its own weight of water, in 1 part of alcohol, in 1 part of chloroform, but only in 50 parts of ether.

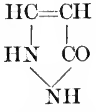
The structure of antipyrine and its relation to pyrrol and isopyrazolon may be shown by the constitutional formulas:

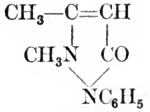

Pyrrol.


Pyrazol.


Pyrazolin.


Pyrazolon.


Isopyrazolon.


Phenyl-dimethyl-isopyrazolon.

Analytical reactions:

1. 0.2 gramme 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 gramme 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:

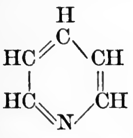
$CH_3.H$ Methane.	$C_6H_5.H$ Benzene.	$C_5H_4N.H$ Pyridine.
$CH_3.CO_2H$ Acetic acid.	$C_6H_5.CO_2H$ Benzoic acid.	$C_5H_4N.CO_2H$. Nicotinic acid.

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.

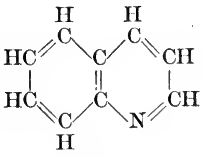
Pyridine is a colorless liquid, having a sharp, characteristic odor, strongly basic properties, and a boiling-point of 116° C. (241° F.).

Quinoline, C_9H_7N (*Chinoline*), 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.).

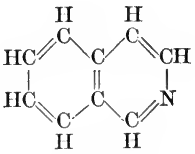
The constitution of pyridine and quinoline is supposed to correspond to benzene and naphthalene respectively, one of the groups CH having been replaced by an atom of nitrogen, thus:



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.

Kairine, $C_{10}H_{13}.NO.HCl$. The name kairine has been given to the hydrochloride of methyl-oxychinoline 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.

51. 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	$(C_{10}H_{16})_x$.

Isopene 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 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

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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.

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, Elastica (*Caoutchouc*) 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 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 acids converts camphor into *camphoric acid*, acidum camphoricum, $C_8H_{14}(CO_2H)_2$, a colorless, crystalline, fusible substance having an acid taste; it is slightly soluble in water, readily in alcohol and ether.

Cineol, Eucalyptol, $C_{10}H_{18}O$, 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.

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.

52. 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 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; not precipitated by bicarbonates are strychnine, brucine, veratrine, atropine, and a few rare alkaloids.

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 decinormal solution of mercuric-potassium iodide, $HgI_2.(KI)_2$, made by dissolving 13.546 grammes mercuric chloride and 49.8 grammes 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 grammes 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

PLATE VI.

ALKALOIDS.

1

Morphine treated with nitric acid.

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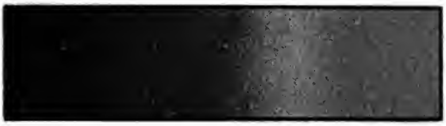
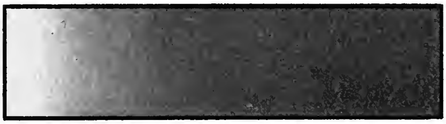

Morphine treated with solution of ferric chloride.

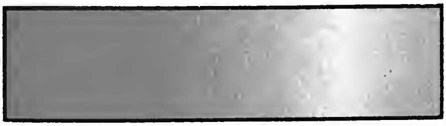
3

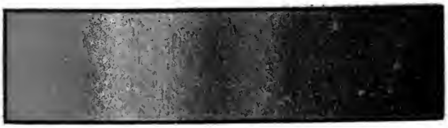
Codeine treated with bromine water and ammonia water.

4

Quinine treated with chlorine water and ammonia water.

5

Strychnine treated with sulphuric acid and potassium dichromate.

6

Brucine treated with nitric acid and with sodium thiosulphate.

7

Physostigmine treated successively with ammonia water, alcohol, acetic acid, and again with ammonia water.

8

Veratrine treated with sulphuric acid.

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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.

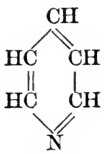
The above method for detecting alkaloids in the presence of organic matter generally answers the requirements of students.

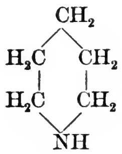
The practical toxicologist has in most cases of poisoning some data (deduced from the symptoms before death, or from the results of the post-mortem examination) pointing to a certain poison, which, of course, facilitate his work considerably.

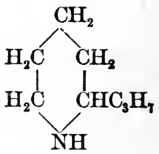
Classification of alkaloids. While the constitution of many alkaloids has as yet not been determined, others have been shown to be derivatives, or to contain the nuclei of either pyridine, quinoline, or isoquinoline. Closely related to pyridine are the liquid bases coniine, nicotine, and sparteine, as 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 their structure, which is this:


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, Piperina, $C_{17}H_{19}NO_3 = 283.04$. 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. The U. S. P. emphasizes this by giving to piperin the ending *in* and not *ine*, which is used for all true alkaloids. 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, $C_8H_{17}N$, 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 faintly 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, $C_{17}H_{23}NO_3 = 287.04$ (*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* and *sulphate* are 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.

Hyoscine, $C_{17}H_{21}NO_4$. Found together with hyoscyamine in Hyoscyamus. The alkaloid is known only in an amorphous, semi-solid state, but the salts, of which the *hydrobromide* is official, crystallize readily. Hyoscine 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.

Scopolamine hydrobromide, $C_{17}H_{21}NO_4HBr\,3H_2O$, is the hydrobromide of an alkaloid obtained from plants of the Solanaceæ, and is chemically identical with hyoscine hydrobromide.

Cocaine, Cocaina, $C_{17}H_{21}NO_4 = 300.92$. 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 centigramme 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-tetramethyldiamido 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.

Beta-eucaine hydrochloride, $C_5H_7N.(CH_3)_3(C_6H_5COO).HCl$, is a salt of trimethyl-benzoyl-hydroxypiperidine. It is a white powder, soluble in 20 parts of water and in 14 parts of alcohol. Its solutions can be boiled without change, and are precipitated by alkalies or carbonates. It is a local anesthetic like cocaine, but weaker, and does not dilate the pupil or contract the blood-vessels. 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 crystals, 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. A 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, $C_{20}H_{24}N_2O_2.3H_2O = 375.46$. This formula represents the official alkaloid, but it is also known 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, $(C_{20}H_{24}N_2O_2)_2H_2SO_4.7H_2O = 866.15$. 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, $C_{20}H_{24}N_2O_2.H_2SO_4.7H_2O = 544.33$. 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 hydrochloride,	$C_{20}H_{24}N_2O_2.HCl.2H_2O$	= 393.76.
Quinine hydrobromide,	$C_{20}H_{24}N_2O_2.HBr.2H_2O$	= 420.06.
Quinine salicylate,	$2(C_{20}H_{24}N_2O_2.C_7H_6O_3)H_2O$	= 935.54.

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 alkaline 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 in ether. The sulphate, which crystallizes with 3 molecules of water, is official.

Strychnine, Strychnina, $C_{21}H_{22}N_2O_2 = 331.73$. 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., 5).

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 ferrocyanide.

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 milligrammes 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 milligrammes 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 causes 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 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 benzene (which dissolves chiefly the narcotine, but not the morphine salts), is the *deodorized opium* of the U. S. P.

Morphine, Morphina, $C_{17}H_{19}NO_3.H_2O = 303$ (*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 acetate,	Morphinæ acetas,	$C_{17}H_{19}NO_3.C_2H_4O_2.3H_2O$.
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 three 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.

Heroin, $C_{17}H_{17}(C_2H_3O_2)_2NO$, is diacetyl-morphine, 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 *hydrochloride*, 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, $C_{17}H_{17}NO_2.HCl$ (U. S. P.), 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, $C_{18}H_{21}NO_3.H_2O = 314.83$. 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.

Dionin, $C_{19}H_{23}O_3N.HCl + H_2O$, 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.

Stypticin, $C_{12}H_{13}O_3N.HCl$ (*Cotarnine hydrochloride*), is a salt of cotarnine, an oxidation product of narcotine, similar to hydrastinine. Cotarnine is obtained by boiling narcotine for a long time with water, or by heating it with dilute nitric acid. Stypticin 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, $C_{21}H_{21}NO_6 = 380.32$. Found together with berberine in the rhizome of Hydrastis Canadensis (golden seal) in quantities varying from 0.1 to 0.2 per cent. 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.

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. 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. 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 $C_5H(CH_3)_3N_4O_2.H_2O$ = 210.64 (*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.

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 sodium salicylate, $C_7H_7N_4O_2.Na + C_7H_5O_3.Na$ (*Diuretin*), 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 50 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.

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 *sulphate* and *salicylate* are official. Both are white or yellowish-white crystalline powders, which have a bitter taste. The sulphate is readily, the salicylate sparingly soluble in water.

Analytical reactions:

1. Five milligrammes 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, $C_{34}H_{47}NO_{11}$. 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, $C_{22}H_{25}NO_6 = 396.23$. 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 hydrate 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 decomposition 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 micro-organisms 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 micro-organisms 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 toxines 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, not well be 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, $NH_2.C_2H_5$; *Diëthylamine*, $NH.(C_2H_5)_2$; *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, $C_5H_{15}NO_2$, has been found in animal tissues, in a number of plants (hops, ergot, Indian hemp, white mustard, etc.), and in putrid matters. It is much less 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. The more important leucomaines will be mentioned in the physiological part.

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.

VII.

PHYSIOLOGICAL CHEMISTRY.

53. PROTEINS.

General remarks. Physiological chemistry is that part of chemistry which has more especially for its object the various chemical changes which take place in the living organism of either plants or animals. It considers the chemical nature of the different substances used as "food," follows up the changes which this food undergoes during its absorption and assimilation in the organism, and treats, finally, of the products eliminated by it. The chemical changes taking place in the organism are either normal (in health) or abnormal (in disease). The abnormal products formed under abnormal conditions are generally termed "pathological" products.

Of the three classes of organic compounds, viz., fats, carbohydrates, and proteins, from which our food-supply is chiefly derived, the first two have been considered in the part on Organic Chemistry, while the study of proteins is taken up in this chapter.

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 *α*-amino-acids[1] and their derivatives, *e. g.*, *α*-amino-acetic acid or glycocoll; *α*-amino-propionic acid or alanine; phenyl-*α*-amino-propionic acid or phenylalanine; 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 nucleoproteins are dextrorotatory. Proteins are distinguished by the ease with which they undergo chemical change under the influence of 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 will be explained more fully later on; they 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.*

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[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 α, the next one by β, the next one by γ, etc. Thus, lactic acid is α-hydroxy-propionic acid, $CH_3.CHOH.COOH$; alanine is α-amino-propionic acid, $CH_3.CHNH_2.COOH$; glycocoll is α-amino-acetic acid, $CH_2NH_2.COOH$; hydracrylic acid is β-hydroxy-propionic acid, $CH_2OH.CH_2COOH$.

I. Simple proteins.

These are protein substances which yield only α-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 white of an 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 c.c. 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. (Plate VIII., 1.)

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 c.c. 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 grammes

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. (Plate VIII., 2.) (It may be necessary to heat the solution before a distinct color appears.)

This reaction is given by biuret, hence its name.

Boil a small quantity of protein in a test-tube with absolute alcohol; filter, wash with absolute alcohol, then with ether, and use the dry material for the following tests.

4. *Adamkiewicz's reaction.* Dissolve a small quantity of the protein by boiling with glacial acetic acid. Allow to cool, and, holding the test-tube in an inclined position, let 2 c.c. of concentrated sulphuric acid flow down the side of the tube. A violet or purple color develops where the liquids meet.

This reaction is due to tryptophane, and is produced by an impurity in the acetic acid used, *i. e.*, glyoxylic acid, CHO—COOH (Hopkins-Cole). A few drops of a dilute solution of glyoxylic acid can be added when the acetic acid used fails to give a positive test.

5. *Lieberman's reaction.* To some of the dry protein add concentrated hydrochloric acid: the protein turns deep blue to violet. On standing, the color fades. Probably due to tryptophane.

Many of the above color-reactions will be given by the cleavage-products of proteins, and by various other substances, but the proteins alone will respond to all of the five tests.

(*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** 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 fibre 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.

Reticulin, occurring in reticular tissue, and *skelatins,* forming the skeletal tissues of invertebrates, are classed with the albuminoids.

(*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. Several groups of glycoproteins are differentiated as follows:

Mucins are secreted by the larger mucous glands of the body, by certain mucous membranes, and are found also in the connective tissue and umbilical cord. The mucins are soluble in water containing a little alkali. The solution is mucilaginous, and with acetic acid gives a precipitate insoluble in an excess of the acid. This precipitate is not formed in the presence of 5 to 10 per cent. of sodium chloride. The solution is not coagulated by heat nor precipitated by potassium ferrocyanide. An acid solution containing salts is precipitated by tannic acid, and a similar neutral solution by alcohol, as also by salts of heavy metals. Mucins when pure are acid in reaction, and give the protein color-reactions.

Mucoids are certain mucin-like substances, such as colloid and ovomucoid, and differing from the mucins in solubility and certain other physical properties. The mucoids are not precipitated by acetic acid.

Chondroproteins (chondromucoid, amyloid) yield chondroitin-sulphuric acid as one of the decomposition-products. This latter has the power to reduce cupric oxide and to precipitate proteins; it is sometimes found in the urine.

Chondromucoid occurs in cartilage; it resembles the mucins in solubility and other properties.

Amyloid occurs pathologically as an infiltration in the spleen, liver, kidneys, and other organs. Amyloid is insoluble without decomposition. It gives the biuret, xanthoproteic, Millon's, and Adamkiewicz's reactions.

The reactions with the following coloring-matters are characteristic for amyloid: It is colored red by aniline-green; also red by methyl-aniline iodide, especially after the addition of acetic acid; violet or blue by iodine and sulphuric acid; and reddish-brown or violet by iodine.

(*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. (Further discussion under Blood.)

(*e*) **Lecithoproteins.** Compounds of the protein molecule with lecithins, which will be considered later. (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.

Alkali and acid metaproteins (albuminates) have certain properties in common. Both are insoluble in water or neutral salt solution, but easily soluble in the presence of a small amount of either an acid or an alkali. The solution does not coagulate on boiling, but is completely precipitated when neutralized. A solution in dilute acid is also precipitated by saturation with magnesium sulphate, ammonium sulphate, or sodium chloride, while a solution in alkali is not precipitated by similar treatment. Although agreeing in many reactions, alkali and acid metaproteins are essentially different. Thus the alkali metaproteins have decided acid properties, as can be shown by the fact that on the addition of calcium carbonate they dissolve in water with the liberation of carbon dioxide, a property not possessed by acid metaproteins.

As part of the nitrogen is eliminated during the formation of alkali metaproteins, the latter cannot be converted into acid metaproteins by treatment with acids; the reverse change, however, may be brought about.

(*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.

The temperature of coagulation is constant for any certain protein; it is, however, considerably modified by the presence or absence of acids, alkalies, and salts in the solution. Fractional coagulation by gradual heating of a solution of several proteins affords a rough means of separation.

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.

Primary proteoses (protalbumoses) are precipitated by one-half saturation with ammonium sulphate.

Secondary proteoses (deutero-albumoses) are precipitated by complete saturation with ammonium sulphate.

There are several subdivisions of primary and secondary proteoses, viz., hetero-proteoses, dysproteoses, the different properties of which are not definite.

(*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 anti-peptones, 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 effected 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 be comprised in 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), $C_5H_{10}.NH_2.CO_2H$.
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 (see Pancreatic Digestion), 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 (Fig. 81). It is very slightly soluble in water, more so in the presence of alkalies and mineral acids, insoluble in alcohol and ether. (For a method of preparing tyrosine and leucine from proteins, see Pancreatic Digestion.)

Analytical reactions of tyrosine.

1. Place a few crystals of tyrosine on a slide, and warm gently; they do not melt. (Crystals of fatty acids found in pus resemble tyrosine in general appearance, but melt when heated, and are insoluble in hydrochloric acid.)

2. To a very small quantity of tyrosine add water and a few drops of Millon's reagent. On boiling, the mixture turns rose red; and on standing a deeper red color develops. (All phenols and their derivatives show this reaction.)

3. *Peria's reaction.* Place a small quantity of tyrosine upon a watch-glass, add a few drops of concentrated sulphuric acid, and heat for half an hour over a boiling water-bath. Allow it to cool and pour into 15 c.c. of water contained in a porcelain evaporating dish. Warm, neutralize with powdered barium carbonate, filter while hot, evaporate the filtrate to a few cubic centimeters, and add a very dilute ferric chloride solution: a violet color appears.

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 (Fig. 80). When pure it forms white, glittering, flat crystals.

Analytical reactions of leucine.

1. Heat slowly in a dry test-tube a very small portion of leucine; it sublimes in the form of woolly flakes. If heated above its melting-point, 170° C. (338° F.), it decomposes into carbon dioxide and amylamine, the latter substance having a characteristic odor. The reaction is this:

$$C_6H_{13}NO_2 = CO_2 + C_5H_{11}NH_2.$$

2. Heat a little leucine in a dry test-tube, add a piece of caustic soda and a few drops of water. Heat until the caustic soda melts, when ammonia is given off. Allow to cool, dissolve in a little water, and acidulate with dilute sulphuric acid: the odor of valeric acid is noticeable. (Leucine, by this treatment, takes up oxygen and decomposes into valeric acid, ammonia, and carbon dioxide.)

3. Dissolve a little leucine in water, decolorize if necessary with animal charcoal, filter, render alkaline with caustic soda, and add 2 drops of cupric sulphate solution. The cupric hydroxide which is

precipitated at first dissolves on shaking, giving a blue solution which is not reduced on heating.

4. *Sherer's reaction* (applicable only to very pure leucine). Evaporate carefully to dryness on a platinum foil a small portion of leucine with a few drops of nitric acid. The residue is almost transparent, and turns yellow or brown on the addition of caustic alkali. If this mixture be again carefully concentrated, an oil-like drop is obtained, which runs over the foil in a spheroidal state.

Hydrolysis.

In the animal body a certain kind of decomposition, called *hydrolysis* or *hydrolytic cleavage*, is particularly prominent. By cleavage is meant the breaking up of a complex molecule into simpler ones, for example, the splitting up of dextrose into alcohol and carbon dioxide:

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2.$$

When the splitting is accompanied by the decomposition of water and the taking up of its constituents by the decomposition-products, it is known as hydrolytic cleavage or hydrolysis. The special kind of hydrolysis is sometimes indicated by adding the suffix "lysis" to a root designating the nature of the substance decomposed, as *proteolysis* for hydrolytic cleavage of proteins. A familiar example of this kind of cleavage is the inversion of cane-sugar by boiling with acidified water:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

Hydrolytic cleavage, as has been shown, can be brought about outside the body—by heat, with or without the aid of acids or alkalies, and by the action of certain substances called enzymes.

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 50, *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.

While enzymes will be fully considered later, the following two are mentioned here because they furnish official preparations.

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 or scales. It should be capable of digesting not less than 3000 times its own weight of freshly coagulated and disintegrated egg albumin.

Experiment 72. Use the U. S. P. process for the valuation of pepsin, as follows: "Mix 9 c.c. of diluted hydrochloric acid with 291 c.c. of distilled water, and dissolve the pepsin in 150 c.c. of the acid liquid. Immerse a hen's egg, which should be fresh, during fifteen minutes in boiling water; remove the pellicle and all of the yolk; rub the white, coagulated albumin through a clean No. 40 sieve. Reject the first portion that passes through the sieve, and place 10 Gm. of the succeeding portion in a wide-mouthed bottle of 100 c.c. capacity. Add 20 c.c. of the acid liquid, and with the aid of a glass rod tipped with cork or black rubber tubing, completely disintegrate the albumin; then rinse the rod with 15 c.c. more of the acid liquid and add 5 c.c. of the solution of pepsin. Cork the bottle securely, invert it three times, and place it in a water-bath that has previously been regulated to maintain a temperature of 52° C. (125.6° F.). Keep it at this temperature for two and one-half hours, agitating every ten minutes by inverting the bottle once. Then remove it from the water-bath, add 50 c.c. of cold distilled water, transfer the mixture to a 100 c.c. graduated cylinder, and allow it to stand for half an hour. The deposit of undissolved albumin should not then measure more than 1 c.c.

"The relative proteolytic power of pepsin stronger or weaker than that just described may be determined by ascertaining through repeated trials the quantity of the above pepsin solution required to digest, under the prescribed conditions, 10 grammes of boiled and disintegrated egg albumin. Divide 15,000 by this quantity expressed in c.c. to ascertain how many parts of egg albumin one part of the pepsin will digest."

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, myopsin, 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.

Experiment 73. Introduce 7.5 grammes of starch into a flask, add 120 c.c. of distilled water, and boil until a translucent mixture results. Cool the resulting paste to 40.5° C. (105° F.), and add to it 0.3 gramme of pancreatin, previously dissolved in about 10 c.c. of distilled water at 40.5° C. (105° F.). Shake the flask well, maintaining the temperature of the mixture at 40.5° C. (105° F.) during five minutes; at the end of this time all of the starch should be converted into substances soluble in water, and a thin liquid be produced. Mix 2 drops of tenth-normal iodine V. S. with 60 c.c. of distilled water, and add to it 2 drops of the warm converted starch solution; no color should result, or, at most, a wine-red color, showing the presence of dextrin and maltose. The appearance of a blue or purple color indicates the presence of *unconverted starch* and that the pancreatin is below the standard—*i. e.*, that of converting not less than 25 times its own weight of starch into substances soluble in water.

54. CHEMICAL CHANGES IN PLANTS AND ANIMALS.

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.

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 the five 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. Define hydrolytic cleavage. Mention two enzymes that are official; state their sources and their function in the process of digestion.

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, $MxC_5H_2N_4O_3$.
$\left.\begin{array}{l}\text{Phosphates}\\ \text{Sulphates}\\ \text{Chlorides}\end{array}\right\}\text{ of }\left\{\begin{array}{l}\text{Calcium.}\\ \text{Magnesium.}\\ \text{Sodium.}\\ \text{Potassium.}\end{array}\right.$	$\left.\begin{array}{l}\text{Phosphates}\\ \text{Sulphates}\\ \text{Chlorides}\end{array}\right\}\text{ of }\left\{\begin{array}{l}\text{Calcium.}\\ \text{Magnesium.}\\ \text{Sodium.}\\ \text{Potassium.}\end{array}\right.$

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 or 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:

$$\begin{aligned}
CO_2 + H_2O &= H_2CO_3 \\
&H_2CO_3 - O = H_2CO_2 = \text{Formic acid.} \\
2CO_2 + H_2O &= H_2C_2O_5 \\
&H_2C_2O_5 - O = H_2C_2O_4 = \text{Oxalic acid.} \\
6CO_2 + 6H_2O &= C_6H_{12}O_{18} \\
&C_6H_{12}O_{18} - 12O = C_6H_{12}O_6 = \text{Glucose.} \\
10CO_2 + 8H_2O &= C_{10}H_{16}O_{28} \\
&C_{10}H_{16}O_{28} - 28O = C_{10}H_{16} = \text{Oil of turpentine.} \\
10CO_2 + 4H_2O + 2NH_3 &= C_{10}H_{14}O_{24}N_2 \\
&C_{10}H_{14}O_{24}N_2 - 24O = C_{10}H_{14}N_2 = \text{Nicotine.}
\end{aligned}$$

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.

Animal food. Those substances which when taken into the body yield energy, build tissue, or prevent the consumption of tissue, without injury to the organism, are called animal foods. The food taken by animals is (beside water and a few of its mineral constituents) all derived from vegetables, but it is taken from them either directly or indirectly; in the latter case it has been taken previously into and assimilated by other animals, as in case of food taken in the form of meat, milk, eggs, etc. While some animals (herbivora) feed upon vegetable, and some (carnivora) upon animal food exclusively, others are capable of taking and assimilating either.

The fact that animal food is derived from vegetable matter renders it superfluous to state that the elements taking an active part in the formation of either vegetable or animal matter are identical. Of the total number of the elements, only 15 are found as necessary constituents of the animal body. These elements are carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, chlorine, iodine, fluorine, silicon, calcium, magnesium, sodium, potassium, and iron. A few other elements, such as aluminum, manganese, copper, etc., are sometimes found in the animal system, but they cannot be looked upon as normal or necessary constituents.

The various kinds of animal food are derived chiefly from three groups of organic substances, viz., carbohydrates (sugars, starch, etc.), fats, and proteins or nitrogenous substances. The inorganic substances, such as phosphates, chlorides, etc., required by the animal in the construction of bones, for the liberation of hydrochloric acid in the gastric juice, etc., are generally found as constituents of various kinds of food or are derived from drinking-water. Milk contains all the necessary organic or inorganic constituents; bread is rich in phosphates, which latter are also found in smaller or larger quantities in nearly all kinds of vegetable and animal food.

Through the food are supplied those compounds which supply the constituents that replace the exhausted material of the living cells, and by chemical changes their inherent potential energy is converted into the heat of the body and into the kinetic energy used in working the living mechanism. While the nitrogenous substances have primarily the task of continuously replacing the wear and tear of the nitrogenous tissues, they also serve, together with non-nitrogenous food, to yield the animal heat, as also muscular and other power for the work which the body performs. To a certain extent the different nutrients can do the work of one another. Thus, the body can burn protein in place of fats or carbohydrates, but neither of the latter can replace the protein in building or repairing tissue. On the other hand, the fats and carbohydrates, while being consumed, protect the proteins.

To some extent, the animal body may be regarded as a complicated machine, in which the potential energy, supplied by the food, is converted into actual energy of heat and mechanical labor. The main difference is that in our machines the fuel serves as the source of energy only, while in the body the food is mainly changed first into tissue (thus building up and renewing the body constantly), serving as fuel afterward. While in the best steam-engine only one-tenth of the fuel is utilized as mechanical work, one-fifth of the energy of the food is realized in the human body.

Heat and muscular power are forms of energy developed by the consumption of food in the body. The amount of energy developed is the measure of the food value of any nutrient, and the unit of value is the calorie.

While each individual substance generates a definite number of calories during combustion, for practical purposes it is sufficiently accurate to estimate the average amount of heat and energy in 1 pound of either proteins or carbohydrates as 1860 calories, while that in a pound of fat is equal to 4220 calories.

It is important to notice that carbohydrates and fats are oxidized to carbon dioxide and water, thus producing the theoretical yield of energy in the body, while only part of the protein molecule is reduced to carbon dioxide and water, the remainder appearing as urea and other nitrogenous bodies possessing latent energy, which must be subtracted from the theoretical heat value of the protein.

Composition and fuel values of several important food materials are given in the following table:

	Water.	Proteins.	Fats.	Carbohydrates.	Mineral matter.	Value of 1 pound in calories.
Bread	32.0	9.0	2.0	56.0	1.0	1300
Wheat flour	12.5	11.0	1.1	74.9	0.5	1645
Oatmeal	7.6	15.1	7.1	68.2	2.0	1850
Rice	12.4	7.4	0.4	79.4	0.4	1630
White beans	12.6	23.1	2.0	59.2	3.1	1615
Dried peas	12.3	26.7	1.7	56.4	2.9	1565
Potatoes	78.9	2.1	0.1	17.9	1.0	375
Sweet potatoes	71.1	1.5	0.4	26.0	1.0	530
Turnips	89.4	1.2	0.2	8.2	1.0	185
Milk	87.0	3.6	4.0	4.7	0.7	325
Butter	10.5	1.0	85.0	0.5	3.0	3615
Cheese, full cream	30.2	28.3	35.5	1.8	4.2	2070
Cheese, skimmed milk	41.3	38.4	6 8	8.9	4.6	1165
Egg	73.8	14.9	10.5	. . .	0.8	721
Beef, sirloin	60.0	18.5	20.5	. . .	1.0	1210
Mutton, shoulder	58.6	18.1	22.4	. . .	0.9	1280
Veal, shoulder	68.8	20.2	9.8	. . .	1.2	790
Pork, fresh	50.3	16.0	32.8	. . .	0.9	1680

The relative proportions in which the two kinds of food are taken by animals depend upon the nature of the animal and upon its particular condition of existence.

Below are given in column A the daily quantity of food required to maintain a grown person in good health, with neither loss nor gain in weight, while the figures in column B refer to the quantities of food for a working man of average height and weight.

	A.	B.
Proteins	125 grammes.	130 grammes.
Fats	79 "	85 "
Carbohydrates	485 "	400 "
Inorganic salts	25 "	30 "
Water	2600 "	2600 "
Equivalent to	3050 calories.	3800 calories.

The above nutrients will be furnished by a diet consisting of 1.5

to 2 pounds of bread, 10 to 14 ounces of lean beef, 2 to 3 ounces of butter, with 2 quarts of water.

Digestibility. In providing a diet, it must be borne in mind that the *digestibility* of a food is more a measure of its nutritive value than its elementary composition. Different foods show great differences in the rapidity and completeness with which they are absorbed. Thus eggs, fresh meat, white bread, and butter are absorbed and assimilated more readily than pork, rye bread, potatoes, green vegetables, and bacon.

By digestibility of food many different conditions are, or may be, implied. Some of these, as the ease with which a certain food is digested, the time required for the process, the influence of different substances and conditions on digestion, and the effects on health and comfort, are so dependent upon individual peculiarities, that no definite rule for the measurement of food-digestibility can be established. Fortunately, the most important factor, viz., the amount digested, can be determined accurately by experiment. The method consists in analyzing and weighing both the food consumed and the feces excreted, the difference being taken as the amount digested.

In general it can be said that animal protein is easily and completely digested, while protein of vegetable food is less so. Thus, of the protein contained in potatoes, whole wheat, and rye flour, one-fourth, or more, may escape digestion, and thus be rendered useless as nourishment. About 5 per cent. of fats escape digestion, while carbohydrates are, in general, completely digested, cellulose being the only exception.

In adjusting a diet, it is important to provide sufficient protein for the building and repair of tissue, and enough of other materials to furnish the body with heat and energy for the work to be performed. A proper diet for a grown person doing moderate work should provide about 3500 calories of energy with a nutritive ratio of from 1 : 4 to 1 : 6.

The nutritive ratio is the ratio of the protein to the sum of all the other nutritive ingredients. The fuel value of fats is two and a quarter times that of proteins and carbohydrates, that of the two latter being considered to be alike. In calculating the nutritive ratio, the quantity of fats is multiplied by 2.25, and the product added to the weight of carbohydrates. The sum divided by the weight of protein gives the nutritive ratio.

If less protein be administered than is needed for repair, although a sufficient number of calories be provided, more nitrogen will be excreted in the urine than is contained in the food. When the protein is given in sufficient quantity to replace the worn tissues, sufficient calories being also provided for, a *nitrogenous equilibrium* is established—*i. e.*, the nitrogen excreted equals the nitrogen administered. Should more protein than is necessary be administered, with sufficient calories, then more nitrogen is excreted and thereby the equilibrium, as far as nitrogen is concerned, is rapidly re-established.

During the periods of growth and convalescence from acute disease the proteins can be increased in the body by increase of protein food. The nitrogenous equilibrium is then less rapidly re-established, as nitrogenous matter is utilized in the construction of new tissue. When the quantity of food absorbed is greater than is required for repair and energy, the carbohydrates are converted into fat, and this, with the excess of fat from the food, is stored up in the fatty tissue of the body, to be drawn upon whenever needed. In starvation no tissue decreases as much as the fatty. The fatty tissue of the animal body is a depot where, during proper alimentation, nutritive material of great value is stored, to be given off as it may be needed.

Nutrition. In the process of nutrition five phases may be distinguished, viz.: *Digestion, absorption, anabolism, catabolism,* and *excretion* of waste products. These processes are commonly spoken of collectively as *metabolism.*

Digestion is the process of converting food material into dialyzable compounds, or into other forms of matter capable of absorption. Absorption is the mechanical process of transferring the digested materials from the alimentary canal into the circulation. Anabolism includes the synthetic changes taking place after they are absorbed until they have become a part of living cells. Catabolism includes those destructive changes which take place chiefly in consequence of oxidation, the oxygen being supplied during the process of respiration. Excretion of waste products is the discharge of that material which is no longer needed in the system.

Digestion. It has been stated before that foods are divided into two classes, inorganic and organic, and that the latter are subdivided into proteins, carbohydrates, and fats. As a rule, the inorganic foods are taken into the body without chemical change. Before the organic foods can be absorbed they have to undergo digestion. This is the process by which organic compounds capable of acting as foods are so altered that they may be absorbed. The process of digestion will be fully considered in a later chapter.

Absorption, anabolism, catabolism, excretion. While these subjects, particularly absorption and excretion, are considered later under the various organs concerned (see Index), a brief statement of the changes in the various food-stuffs, subsequent to their absorption, is made here.

Carbohydrates. The carbohydrates, mainly as dextrose, are carried from the intestine by the portal system to the liver, where the bulk of them is dehydrated and converted into glycogen. Some of the dextrose is changed into glycogen by the muscle, and in this organ and the liver a reserve-supply of glycogen is stored up. This glycogen forms the most readily available source of energy for the body. When used it is first split into dextrose, and then oxidized to carbon dioxide and water, passing probably through a lactic acid stage. The sugar metabolism is so carefully controlled and is influenced by so many factors that the details are not clear. The question has been largely studied by observation of cases of spontaneous and experimental diabetes. This term implies much more than a mere glycosuria; hyperglucæmia (excessive amount of sugar in the blood) must be present, and there is a profound change in the handling of carbohydrates by the body, as well as some derangement of the protein and fat metabolism. The pancreas plays an important rôle and furnishes an internal secretion from the islands of Langerhans, which probably enables the muscle to split and oxidize the glycogen as it needs it. The muscle is thus involved, as well as the liver, in sugar control. The adrenal is thought perhaps to control the transportation of sugar in the body, for example, its removal from the liver to the muscle; while the thyroid seems to have an inhibitory action upon both the pancreas and the adrenal. Phloridzin produces an increased permeability of the kidney to sugar, but not a true diabetes.

Fats. Shortly after the emulsified fats reach the blood through the thoracic duct from the intestine, there occurs a peculiar change in them whereby they become dialyzable, soluble in water, and insoluble in ether. The nature of this change is entirely obscure. The fats are deposited in the body as fats and form a reserve store of potential energy. A small proportion is synthesized into the lecithins. While the fat of any animal tends to remain true to the composition characteristic of that animal, there is so little change in fat during digestion that it is possible to recognize, in the tissue of the animal, foreign fats which have been introduced with the food. The fat of the body is derived primarily from the fat of the food, but is also formed in considerable amount from carbohydrates. The location of this transformation of carbohydrate to fat is unknown. There is a possibility that protein also may form fat, as it can undoubtedly form sugar, which might be further changed to fat. Experiments in feeding foreign fats have shown that the so-called fatty degenerations of the liver, etc., are not transformations of protein into fat, but that the fat is brought by the blood and deposited in the diseased organ. When fat is burned it is first saponified. The final products are carbon dioxide and water. The acetone bodies of the urine are believed to represent steps in the incompleted oxidation of the fats.

Proteins. After the proteins enter the portal blood as native proteins they pass through the liver, probably with little change, and are distributed to the tissues. Here a part enters into the repair or the growth of the protein tissues (" tissue protein "), while a part is immediately broken down without actually being incorporated by the tissues ("circulating protein"). This is evidenced by the marked increase in the nitrogenous excretion which appears shortly after protein ingestion. It is important to notice that carbohydrate and fat can replace one another in the diet, but that neither can replace protein to more than a slight extent. Indeed, it has very recently been shown that not all proteins have the same nutritive value (Osborne and Mendel). Thus, an animal can thrive upon a single protein, such as casein, egg-albumen, or glutenin (wheat). It will live, but will not grow to maturity upon gliadin (wheat) or hordein (barley) alone. It will not even live upon zein (maize). This difference in typical proteins is undoubtedly due to differences in the amino-body content of the protein. Zein contains no lysine or tryptophane. It has long been known that the albuminoid substance, gelatin, containing no tryptophane and no tyrosine, cannot replace protein.

It is believed that these deficiencies in amino-acids make it impossible for the organism to build up its native protein from such material.

The specific waste products of protein (meat) metabolism, the nitrogenous excreta, appear mainly in the urine, and will for the most part be considered in that connection, while the formation of urea and certain other substances will be discussed with the liver.

Respiration. The most important changes in respired air are the changes in the quantities of oxygen and carbon dioxide. Pure air, after being dried, contains, by volume, of oxygen 20.8 per cent., of nitrogen 79.2 per cent., and a quantity of carbon dioxide (0.04 per cent.) so small that it need not be considered. When 100 volumes of air have been breathed once, it gains a little more than four parts of carbon dioxide and loses a little more than five parts of oxygen; so that the composition of 100 volumes of inspired air, when expired, is, after being dried, oxygen 15.4 parts, nitrogen 79.2 parts, and carbon dioxide 4.3 parts by volume.

Much the greater portion of the oxygen lost from respired air enters into combination with the hæmoglobin; a small portion is absorbed by the blood-serum. The immediate source of the carbon dioxide is the blood, in which it exists partly in simple solution and partly in a loose combination with hæmoglobin.

The blood is the common carrier of the body: from the alimentary canal it receives ultimately all the food material; from the lungs it receives oxygen; these it carries to the tissues for their sustenance;

from the tissues it receives the products of catabolism, and carries them to their proper organs of elimination.

The bright red color of the arterial blood is due to oxyhæmoglobin. A large portion of this oxygen absorbed by the hæmoglobin is given up to the tissues as the blood passes through the capillaries, and we have then the reduced hæmoglobin, to which is due the dark color of the venous blood.

In almost the reverse manner, the hæmoglobin takes up carbon from the tissues and conveys it to the lung. It is important to note that carbon dioxide, in distinction from carbon monoxide, is not attached to hæmoglobin in the same manner in which the oxygen is attached. It has been shown that the dark color of the venous blood is not due to the presence of carbon dioxide, but to a decrease of the oxygen.

The details of the manner in which oxidation in the animal body is induced and how it proceeds are not known. In some way the atmospheric oxygen, which under ordinary conditions has no action on the proteins, fats, and carbohydrates, is so changed as to become active. It is commonly believed that the process is carried on by enzymes, some of which (peroxidases) have been actually demonstrated, while others (oxygenases) are merely hypothetical (see page 637).

Waste products of animal life. The changes which the food suffers after having been absorbed by the animal system are extremely complicated, and far from being thoroughly understood. Numerous products and organs are formed and nourished from and by the blood; among them muscular, nerve, and brain substance, excretions and secretions,[1] such as milk, saliva, bile, gastric and pancreatic juice, etc., together with bones, teeth, hair, and many others.

Most of these substances (some secretions, such as milk and others, excepted) suffer a constant oxidation in the system, and are finally eliminated as waste products; in regard to the intermediate compounds formed in the tissues we know little, but it is highly probable that the reduction of the complicated food material to the simple forms of the waste products is very gradual. There are three channels through which the waste products are given off; they are the lungs, the skin, and the kidneys. By the lungs are eliminated chiefly carbon dioxide and some water, by the kidneys urine (which is a weak aqueous solution of urea, uric acid, urates, phosphates, chlorides, and sulphates of calcium, magnesium, sodium, potassium, etc.), and by the skin are constantly eliminated carbon dioxide and water, and during the process of sweating also more or less of the constituents of urine.

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[1] An *excretion* consists of material detrimental to the organisms, and removed from it by certain glands. A *secretion* contains peculiar compounds especially elaborated by the glands for the purpose of serving certain requirements of the organism or its offspring. Thus, urea and sweat are excretions, while pepsin and milk are secretions.

There is also excretion through the intestinal tract.

Chemical changes after death. After the death of either a plant or an animal, a chemical decomposition commences which finally results in the formation of those inorganic compounds from which the plant originally derived its food, viz., carbon dioxide, water, ammonia, sulphates, phosphates, etc. This decomposition of a dead body is generally a simultaneous fermentation or putrefaction, aided by decay or slow combustion.

There are numerous intermediate products formed, which differ according to the nature of the decomposing substance, or according to the conditions (degree of temperature, amount of moisture and air present, etc.) under which the decomposition takes place.

During the decomposition of dead vegetable matter (especially of moist wood) the intermediate products are frequently called *humus,* which substance (or better, mixture of substances) forms the chief part of the organic matter in the soil.

During the decomposition of dead animals, the sulphur is first eliminated as hydrogen sulphide, and a number of other intermediate products have been shown to be formed; among them certain organic bases called *ptomaines* or *cadaveric alkaloids,* substances which have been spoken of in Chapter 52. The decomposition of organic matter may be prevented under conditions which have been mentioned heretofore in connection with putrefaction.

55. ANIMAL FLUIDS AND TISSUES.

Constituents of the animal body. The animal body consists mainly of three kinds of matter, viz., water, organic, and inorganic matter. It contains of water about 70 per cent., of organic matter 25 per cent., and of inorganic matter about 5 per cent. The water may be determined by drying a weighed quantity in an air-bath at a temperature of 100° to 105° C. (212°–221° F.); the organic matter is estimated by burning the dried substance, and the inorganic matter

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QUESTIONS.—What is the difference between vegetable and animal life from a chemical point of view? Mention the chief substances serving as plant food. Explain the formation of organic substances in the plant. What elements enter into the animal system as necessary constituents? The members of which three groups of organic substances are chiefly used as food by animals? Give a full explanation of respiration. Explain the term calorie, and state the use made of it in valuation of food. Which points should be considered in the selection of a diet? What are the waste products of animal life, and through which channels are they eliminated? What is the final result of the decomposition of dead plants or animals?

(ash) by weighing the residue. Some of the elements which are left in the inorganic residue have, however, been actually constituents of organic compounds; iron, for instance, which is left in the ash, has been chiefly a constituent of hæmoglobin; sulphur, left as a sulphate, may have been a constituent of albumin, etc.

The complex nature of the various organic matters has been referred to in the preceding chapter, and will be more fully considered below; but it may be mentioned here, that some of these organic substances (or groups of substances) may be separated by a successive treatment of the animal matter with various solvents. Thus, by treating with ether or carbon disulphide, all fats may be extracted; by then treating with alcohol and water successively other substances (generally termed *extractive matter* or *extractives*) are dissolved, which may be obtained by evaporating the solution.

The relative quantities of the three constituents in some of the animal fluids and tissues is shown in the following table:

	Water.	Organic and volatile matter.	Inorganic residue (ash).
Saliva	99.50	0.32	0.18
Gastric juice	99 43	0.33	0.24
Pancreatic juice	90.97	8.18	0.85
Bile	85.92	13.30	0.78[1]
Chyle	91.80	7.40	0.80
Lymph	91 80	7.40	0.80
Pus	87.00	12.20	0.80
Cows' milk	87.00	12.25	0.75
Human milk	86.80	12.85	0.35
Blood	79.50	19.70	0.80
Blood-corpuscles	54.60	44.68	0.72
Blood-serum	90.50	8.68	0.82
Urine	95.70	3.00	1.30
Bone (varies widely)	22.00	26.00	52.00
Dentine	10.00	25 00	65.00
Enamel	0.40	3.60	96.00

Among the extractives are found creatine and creatinine, urea, uric acid, organic salts, etc. After the fatty matter and the extractives have been removed there remains an elastic and somewhat horny mass, which consists chiefly of proteins (albumin, fibrin, globulin, etc.).

The complete separation of all substances is extremely difficult on account of the great similarity in properties of many of these substances, and the rapid changes which they suffer when acted upon by solvents or chemical agents.

As the nature or composition of many of the inorganic salts present in the animal tissues is changed during the burning off of the organic

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[1] The metals in combination with the biliary acids are not included.

matter, it is necessary to determine them either in the aqueous solution (extract) or by subjecting the animal matter to dialysis, by which process they may be more or less completely separated from the organic matter, which is left in the dialyzer, while the salts pass through the membrane.

Blood. Two kinds of blood are distinguished, the arterial or oxidized and the venous or deoxidized blood. Arterial blood as it is present in the system, or immediately after it has been drawn from the body, is a red liquid of an alkaline reaction and a specific gravity of about 1.055. Upon examination under the microscope blood is seen to consist of a colorless fluid, called *plasma*, in which float small globules or *corpuscles*, which make up about 40 per cent. of the whole volume of blood. These corpuscles are of three varieties, viz., red and white corpuscles, and blood-plates. The *red corpuscles* of blood, or *erythrocytes*, which give to the blood its color, are biconcave, circular, non-nucleated disks, about $\frac{1}{3200}$ of an inch in diameter. When viewed through the microscope they are of a faint greenish-yellow color, while *en masse* they show the color of arterial blood. The *white corpuscles* of blood, or *leucocytes*, are round or irregularly shaped nucleated cells; they are devoid of coloring-matter, and are far less numerous than the red corpuscles. The *blood-plates* are colorless, oval, round, or lenticular disks, measuring generally less than one-half of the diameter of red corpuscles.

Specific gravity. This varies in healthy adults between 1.046 and 1.067, but under pathological conditions may vary between 1.025 and 1.068.

The specific gravity can be determined by permitting a drop of blood to fall into a mixture of chloroform and benzol presenting a specific gravity of about 1.055. If the drop sinks to the bottom, more chloroform must be added; if it floats on the surface, benzol has to be added until it floats midway in the liquid. The specific gravity of the mixture, which is now identical with that of the blood, is determined by a delicate hydrometer.

Reaction. The alkaline reaction of blood is due to the presence of sodium bicarbonate, $NaHCO_3$, and disodium phosphate, Na_2HPO_4, both of which have a weak alkaline reaction. While blood reacts alkaline to litmus, it is neutral to phenolphthalein, and according to the newer concept of alkalinity (an excess of dissociated hydroxyl ions over the dissociated hydrogen ions present) it is nearly neutral. For clinical purposes it is still regarded as alkaline, and the extent of this alkalinity to litmus or lacmoid has some importance. There are no very satisfactory methods of titration. That one most used (Dare) depends upon the disappearance of the spectrum of hæmoglobin as a solution of blood is gradually neutralized. Tartaric acid, $\frac{N}{200}$, is the acid used, and the addition of acid is made by means of a specially devised pipette until the two absorption bands become no longer visible through the spectroscope.

The alkalinity of the blood may be estimated by mixing 5 c.c. of freshly drawn blood with about 45 c.c. of a 0.25 per cent. solution of ammonium oxalate (which prevents coagulation) and titrating this mixture with a $\frac{N}{25}$ solution of tartaric acid, using as an indicator lacmoid paper soaked in a concentrated solution of magnesium sulphate.

For clinical purposes, where often but small quantities of blood are available, the following method may be used. The blood is drawn into a capillary pipette up to the mark etched on the stem; the pipette is next tilted to admit a bubble of air into the bore, and then $\frac{N}{25}$ sulphuric acid is drawn in to the mark. The exactly equal volumes of blood and acid thus obtained are transferred to a watch-glass, well mixed, and a drop of the mixture then tested with lacmoid paper. If an acid or alkaline reaction be shown, the operation is repeated with weaker or stronger acid until the resulting mixture is neutral.

Odor. The peculiar odor of blood, differing widely in different animals, is due chiefly to the presence of certain volatile fatty acids. Addition of sulphuric acid renders the odor more distinct.

The composition of blood. The following table, taken from Howell, lists the more important constituents of blood-plasma:

- Proteins.
  - Fibrinogen.
  - Paraglobulin.
    - Euglobulin.
    - Pseudoglobulin.
  - Serum-albumin.
  - Nucleo-protein.
- Extractives.
  - Fats.
  - Sugar.
  - Urea.
  - Jecorin.
  - Glucuronic acid.
  - Lecithin.
  - Cholesterin.
  - Lactic acid.
- Salts.
  - Chlorides
  - Carbonates
  - Sulphates
  - Phosphates
  - of
    - Sodium.
    - Potassium.
    - Calcium.
    - Magnesium.
    - Iron.
- Enzymes and unknowns.
  - Internal secretions.
  - Enzymes.
    - Lipase.
    - Glycolase, etc.
  - Immune bodies (amboceptors).
  - Complements.
  - Opsonins.

The proteins of blood-plasma. There are three important proteins in blood-plasma: serum-albumin, serum-globulin (paraglobulin), and fibrinogen. Of the other proteins described, the nucleo-protein seems to be the best founded. As fibrinogen is directly concerned in the clotting of blood, it will be described in that connection. The albumin and the globulin of the blood are typical members of their respective classes, and possess all the qualifications of these classes and of proteins in general. They are found together also in the lymph and in various other fluids of the body. There is some evidence that the albumin is in reality made up of two or three different albumins, while the globulin can be divided into two portions by fractional precipitation. Thus, on adding saturated ammonium sulphate solution to plasma, all the globulin will be precipitated before the sulphate solution amounts to 50 per cent. of the resulting mixture. The so-called euglobulin will precipitate between 28 and 36 per cent. of saturation with ammonium sulphate, and the pseudoglobulin between 36 and 44 per cent. Under these conditions no albumin will be cast down. If, however, solid ammonium sulphate be now added to the point of saturation, all of the albumin will be precipitated.

Coagulation. When blood leaves the body and is allowed to stand a while, it will be seen that the entire mass has coagulated—*i. e.*, has been converted into a semi-solid, gelatinous material known as the *blood-clot*, or the *placenta sanguinis*. Later it will be observed that a small quantity of straw-colored liquid, known as the *blood-serum*, appears on top of the clot. While the latter shrinks in volume the quantity of serum increases, the clot finally floating in the liquid, which itself ultimately gelatinizes in consequence of the coagulation of the serum-albumin. Clot consists of fibrin holding in its meshes blood-corpuscles, which may be removed by washing the clot in a stream of water.

The coagulation of blood can be prevented in various ways. After the injection of albumose into a vein of a dog the blood does not coagulate on leaving the body. If the blood be drawn directly into a saturated solution of magnesium sulphate, in the proportion of 3 to 1, or into a solution of potassium oxalate, so that the mixture contains at least 1 per cent. of oxalate, no coagulation takes place. The plasma obtained from such blood is known as peptone, salt, and oxalate plasma, respectively.

Coagulation of blood may be retarded by rapidly cooling it. If the blood of a horse, whose blood always coagulates slowly, be received into a cold, narrow glass cylinder, and allowed to stand at 0° C., the blood may be kept fluid for several days. The corpuscles will deposit in a red layer from the plasma.

It may readily be shown that the clotting of blood is due to a change of some kind which converts the soluble protein fibrinogen into an insoluble form called fibrin. Fibrinogen is one of the globulins, it coagulates at a temperature of from 50° to 60° C., and is precipitated by half-saturation with sodium chloride. It is present also in lymph.

It is well known that the clotting of fibrinogen is produced by an organic substance formerly called fibrin-ferment, but preferably called thrombin, as it is probably not an enzyme. It is also known that this thrombin is active only in the presence of calcium salts; that is, that inactive thrombin (prothrombin or thrombogen) is changed by calcium into the active form. It is, however, possible to remove the calcium from activated thrombin without impairing its activity; therefore the calcium does not enter directly into the conversion of fibrinogen into fibrin.

As calcium is present in all blood, it is evident that in circulating blood either prothrombin must not be present as such, or, if present, its activation by the calcium must be prevented by some antagonistic substance (antithrombin), for otherwise clotting would occur within the blood-vessels, which does not happen under normal conditions. Accordingly, there are two theories to explain these facts.

Morawitz believes that in order to convert prothrombin into thrombin, not only calcium but also a secondary organic substance (thrombokinase) must be present, and that this thrombokinase is furnished to blood which has escaped from the blood-vessels by the injured leucocytes and platelets. The other view, to which Howell inclines, is that prothrombin is transformed into thrombin by calcium salts alone, and that this change is prevented by the antithrombin of the circulating blood, and that when the blood is shed the injured cells set free a zymoplastic substance which counteracts the antithormbin and leaves the calcium free to convert the prothrombin into thrombin.

The different methods of preventing the clotting of blood are to be explained thus: The cooling of blood probably prevents the formation of the thrombokinase, or the thromboplastic substances, by preserving the cells intact. The addition of oxalate solution removes the calcium salts by precipitation. The injection causes the production of antithrombin in the injected animal.

Blood-serum differs from plasma only in containing no fibrinogen and much active thrombin.

Experiment 74. (*Separation of the proteins of blood-plasma and of blood-serum.*)

a. Fibrinogen. To 5 c.c. of salt or oxalate plasma add an equal volume of saturated solution of sodium chloride. Fibrinogen is precipitated, carrying with it the prothrombin. Filter and preserve the filtrate for the separation of albumin and globulin, as detailed below.

Dissolve the fibrinogen and prothrombin in a little dilute salt solution, add an excess of calcium chloride, and keep the mixture at 40° C. for a few minutes. Shreds of fibrin are formed and precipitated.

b. To 25 c.c. of blood-serum, contained in a mortar, add 20 grammes of ammonium sulphate and rub with a pestle until the fluid is saturated with the salt. Filter through dry filter-paper, acidulate the filtrate with acetic acid, and boil. No change occurs, as both proteins have been precipitated completely.

c. To 25 c.c. of blood-serum add 25 c.c. of a saturated solution of ammonium sulphate; filter; and wash with a saturated solution of the salt. Under this treatment only serum-globulin is precipitated, while serum-albumin is kept in solution. Heat the filtrate to boiling: serum-albumin is coagulated. Place some of the residue left on the filter (globulin) in a test-tube and pour water on it; the protein dissolves by virtue of the small quantity of salt adhering to it. Heat the solution to boiling: coagulation takes place.

d. Saturate 25 c.c. of serum with magnesium sulphate: serum-globulin is precipitated, serum-albumin remains in solution.

Serum-albumin and serum-globulin give the ordinary protein reactions.

A quick method to obtain fibrin is to stir or whip blood with twigs immediately after it has been shed. Under these conditions the fibrin does not entangle the blood-corpuscles, but separates as a stringy mass, which adheres to the twigs used for stirring. The remaining part, being made up of the corpuscles suspended in the serum, is designated as defibrinated blood.

Red blood-corpuscles when wet contain of water, 54.63 per cent.; hæmoglobin, 41.1 per cent.; other proteins, 3.9 per cent.; fats (chiefly cholesterin and lecithin), 0.37 per cent. The quantity of water in corpuscles varies widely, and most likely ranges in healthy blood from 76 to 80 per cent. Dried corpuscles contain about 90 per cent. of hæmoglobin.

While red blood-corpuscles can be broken up (laked) by the addition of various substances to the blood, the simplest way is by the addition of water, which reduces the osmotic pressure of the plasma, and consequently causes the salts of the corpuscles to attract an excess of water, whereby the corpuscle is ruptured and its constituents go into solution. In order to avoid this action on the blood-cells and a similar action on the tissue cells, it is customary in surgical procedures, and especially in intravenous injections, to use a solution of equal osmotic pressure with the blood. Such a solution is the "*normal salt solution*," made up usually of 0.9 per cent. sodium chloride in distilled water, which is the simplest solution that has been found to have no very deleterious effect.

Blood-pigments. The hæmoglobins or blood-pigments are the chief constituents of red blood-corpuscles; they contain from 0.4 to 0.6 per cent. of iron, and show a slight difference in composition; when in powder form they all have a blood-red or brick-red color; they all crystallize, but not with equal facility. Hæmoglobin is the substance which carries oxygen to the various tissues, as described in the previous chapter. It belongs to the class of conjugated proteins.

Experiment 75. Pour some freshly drawn venous blood into four volumes of a saturated solution of sodium sulphate contained in a vessel which stands in ice; mix and set aside for several hours; no coagulation occurs and the corpuscles settle to the bottom of the vessel. Pour off the supernatant liquid, collect the sediment on a filter, and wash it first with cold solution of sodium sulphate and then with water.

Prepare hæmoglobin from these corpuscles as follows: agitate the collected mass violently with small quantities of ether until the corpuscles are nearly dissolved; allow the liquid to settle, filter, render the filtrate slightly acid with acetic acid, and add alcohol as long as the precipitate first formed continues to dissolve; cool the red solution to 0° C. (32° F.) for several hours, when crystals of hæmoglobin will form; collect these on a filter and wash with an ice-cold mixture of alcohol and water.

Hæmoglobin, also called *reduced hæmoglobin,* occurs only in small quantity in arterial blood, in larger quantity in venous blood, and is almost the only coloring-matter in the blood after asphyxiation. A solution of hæmoglobin has a most remarkable attraction for oxygen, with which it enters into a molecular combination, forming *oxyhæmoglobin.* The power of hæmoglobin to take up oxygen depends on the iron it contains. The solution of oxyhæmoglobin will give up oxygen to reducing agents or when subjected to a sufficiently low oxygen pressure. It is due to this property of the oxyhæmoglobin that arterial blood gives up oxygen to the tissue.

Methæmoglobin is a transformation-product of oxyhæmoglobin found in sanguinous transudates and cystic fluids; it also occurs in the urine during hæmaturia and hæmoglobinuria; and in the blood and urine after poisoning with potassium chlorate, amyl nitrite, alkali nitrates, and several other bodies.

Hæmochromogen. When hæmoglobin is acted upon by acids, alkalies, etc., it is split into globin (a histone) and hæmochromogen. The latter forms only about $\frac{1}{25}$ of the hæmoglobin molecule, contains all of the iron present, and consequently the group to which the oxygen is attached when oxyhæmoglobin is formed. In the presence of oxygen hæmochromogen is rapidly converted into hæmatin.

Hæmatin. Just as hæmochromogen is split from hæmoglobin, hæmatin is derived from oxyhæmoglobin. It is a comparatively simple substance, having the formula $C_{34}H_{34}N_4FeO_5$. It is found in the feces after hemorrhage in the intestine, and also after a diet consisting largely of red meats. Hæmatin has been found in urine after poisoning with arsenetted hydrogen. Hæmatoporphyrin ($C_{34}H_{38}N_4O_6$) is obtained when hæmatin is hydrolyzed.

Hæmatoporphyrin occurs in traces in normal urine; it is found in greater quantity in urine after the use of sulphonal. Hæmatoporphyrin is isomeric with the bile-pigment bilirubin, and a pigment closely resembling urobilin has been obtained by the action of reducing agents on hæmatoporphyrin. It is noteworthy that this substance does not contain iron.

Carbon monoxide hæmoglobin is a molecular combination of one molecule of hæmoglobin and one molecule of carbon monoxide. The combination is stronger than that between oxygen and hæmoglobin and this explains the poisonous action of carbon monoxide, which causes death by replacing the oxygen of the blood. A similar and even more stable chemical combination is formed with hæmoglobin by nitric oxide.

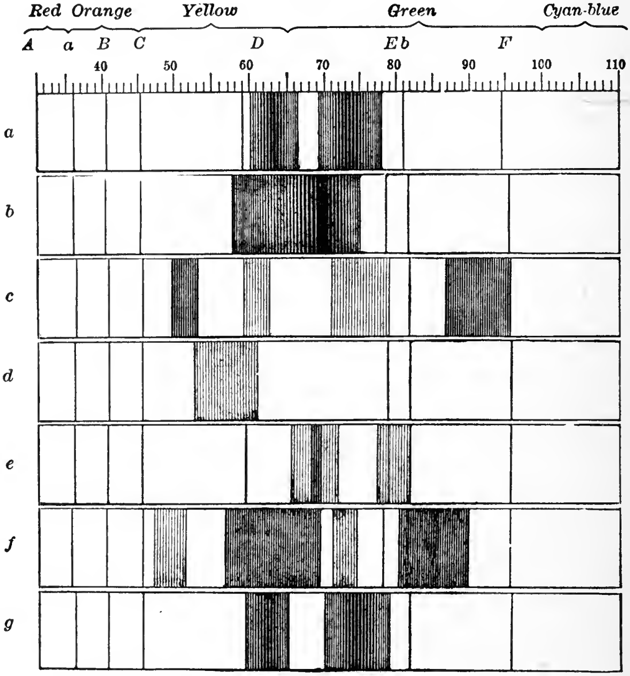
Carbon dioxide hæmoglobin (*carbo-hæmoglobin*). Hæmoglobin has the property of forming an unstable compound with carbon dioxide, the CO_2 is, however, not attached to the same portion of the molecule as that to which the oxygen (in oxyhæmoglobin) is attached. Thus, the presence of carbon dioxide does not prevent the absorption of oxygen by hæmoglobin, which is in great contrast to the action of carbon monoxide, and is important in the process of respiration.

Spectroscopic examination. The different hæmoglobins are distinguished chiefly by their absorption-spectra. In the following description the violet end of the spectrum is assumed to be on the observer's right.

a. Oxyhæmoglobin. Dilute 10 c.c. of blood with 90 c.c. of water, and filter. Place part of the solution in a glass vessel with parallel sides and examine with a spectroscope. When the solution is so concentrated the spectrum will probably be entirely shut off as far as the yellow or orange, but on gradually diluting with water a spectrum is finally seen which shows two absorption-bands to the right of the *D* line. The right-hand band is broader, fainter, and less sharply defined than the other, and the color of the light which emerges from the left limb of the left hand is yellow. When the solution is further diluted the bands disappear simultaneously. (Fig. 72, *a*.)

b. Reduced hæmoglobin. When a solution of oxyhæmoglobin is treated with a reducing agent the coloring-matter loses oxygen and is changed to hæmoglobin. Stokes' fluid is the most suitable reagent for reducing, and is prepared as follows: Dissolve 3 grammes of selected crystals of ferrous sulphate in cold water and add a cold aqueous solution of 2 grammes of tartaric or citric acid. Make up with water to a volume of 100 c.c., and immediately before using add ammonia-water until the precipitate which forms at first is redissolved.

FIG. 72.



Absorption-spectra of blood constituents. *a*, oxyhæmoglobin. *b*, reduced hæmoglobin. *c*, methæmoglobin. *d*, hæmatine. *e*, reduced hæmatine. *f*, hæmatoporphyrin. *g*, carbon monoxide hæmoglobin.

Prepare a solution of oxyhæmoglobin which will show the characteristic absorption-bands. Allow a few drops of Stokes' fluid to flow into the solution, when its color changes to a purple or violet, and the spectrum shows a single broad diffused and poorly defined band, as though two oxyhæmoglobin bands had gone together and had been displaced to the left (Fig. 72, *b*). When the solution is agitated with air its color changes to bright red and the spectrum again shows oxyhæmoglobin.

c. Methæmoglobin. To a dilute solution of blood add a drop or two of a freshly prepared 10 per cent. solution of potassium ferricyanide. The color of the solution becomes brown. Add just enough sulphuric acid to give a slightly acid reaction and examine spectroscopically, when the spectrum is seen represented in Fig. 72, *c*. On rendering the solution slightly alkaline and adding a few drops of Stokes' fluid the methæmoglobin changes to hæmoglobin, and on agitating with air into oxyhæmoglobin. These changes can easily be followed with the spectroscope.

d. Acid hæmatin. To a few drops of undiluted blood add a drop or two of acetic acid. The hæmoglobin is broken up into a histon called globin, and a non-protein substance called hæmin. The solution which results is almost black, but on diluting with water is seen to be red. The spectrum has a band in the red, almost coincident with the band shown by methæmoglobin in neutral or acid solution.

e. Alkaline hæmatin. To a portion of acid hæmatin solution add sodium hydroxide until the precipitate which forms has redissolved. The solution will be alkaline and, if properly diluted, will show a poorly defined band to the left of the *D* line. It is usually observed, however, that the entire spectrum is absorbed except the red. (Fig. 72, *d.*)

f. Reduced hæmatin (Hæmochromogen). Reduce a portion of alkaline hæmatin solution with Stokes' fluid, and after properly diluting examine spectroscopically. Two sharply defined dark bands are seen between *D* and *E*, which seem to be coincident with the bands produced by oxyhæmoglobin. It will be noted, however, that the light which emerges on the left of the left band is plainly green. By diluting the solution with water the band on the right may be made to disappear, while the other band is still very dark. (Fig. 72, *e.*)

g. Hæmatoporphyrin. Add a drop of blood to a few c.c. of concentrated sulphuric acid, mix well, dilute with water, and render alkaline with sodium carbonate. The spectroscope shows four bands. (Fig. 72, *f.*)

h. Carbon monoxide hæmoglobin. Pass a slow current of carbon monoxide (illuminating-gas, containing carbon monoxide, may be used) through 50 c.c. of blood until its color is bright red. Examined spectroscopically, the bands seen occupy nearly the same position as those of oxyhæmoglobin, but they do not disappear on treatment of the solution with Stokes' fluid. (Fig. 72. *g.*)

On adding to 10 c.c. of carbon monoxide hæmoglobin solution 15 c.c. of a 20 per cent. solution of potassium ferrocyanide the mixture shows a bright-red color. On treating oxyhæmoglobin solution in the same way, it assumes a grayish-brown or green color.

Examination of blood-stains. Blood-stains may be recognized, after having been washed off with as little water as possible, by the following methods:

1. Examine the reddish fluid under the microscope for blood corpuscles.

2. Evaporate a drop of the fluid on a microscope slide with a minute fragment of sodium chloride, cover with a cover-glass, allow a drop of glacial acetic acid to enter from the side and warm gently; abundant crops of hæmin crystals are seen under the microscope after cooling.

3. Add a drop of the fluid to some freshly prepared tincture of guaiacum in a test-tube and float on the surface of an ethereal solution of hydrogen dioxide; a blue ring forms at the junction of the ethereal solution and the guaiacum. (Blood is, however, not the only substance showing this reaction.

4. The spectroscope shows bands characteristic of hæmoglobin.

5. The biologic blood-test. This test depends upon the fact that animals (rabbits) injected with human blood-serum will develop a specific antibody. This antibody is present in the blood-serum of the injected animal and is termed a "precipitin," because it produces a visible precipitate when the serum of the animal is mixed with a solution of human blood-serum. As the technique is very intricate, and the results are worthless unless carefully controlled, no details can be given here. Positive results can be obtained with blood or blood-stains many years old. Human protein of other origin (milk, semen, etc.) and protein from the higher anthropoid apes will also give positive results.

The immune bodies of the blood-serum. When foreign protein is introduced into an animal by injection or, as in disease, by infection with bacteria, it is found that there is a response on the part of the animal which causes the presence of certain substances (immune bodies, antibodies) in the circulating blood. These have a specific action upon the foreign protein. To this class belong agglutinins, lysins, etc. Agglutinins are capable of causing an agglutination or clumping of the corresponding bacteria. They have proved of great clinical value in the diagnosis of typhoid fever by means of the Widal reaction. This test consists in observing microscopically or macroscopically a mixture of active typhoid bacilli and the blood-serum of the patient. If agglutinins are present, and the bacteria are clumped within a certain time by a certain dilution of serum, it is shown that the patient has, or in some cases has had, typhoid fever. Bacteriolysins are antibodies capable of dissolving the corresponding bacteria. Opsonins are capable of producing some change in bacteria, whereby it becomes possible for the leucocytes of the blood to ingest them (phagocytosis). They are normally present in varying amounts. It is manifest that these bodies form a part of the defensive mechanism of the body. They have so far not been of great assistance therapeutically, but promise to be of great value in the prophylaxis of certain diseases, as in the typhoid vaccination by injections of killed cultures of B. typhosus.

In this connection it is important to note that bacteria form several classes of toxins or poisons. Ptomaines are produced by the effect of bacteria upon the medium in which they are growing. Bacterial toxins are substances which, in distinction to ptomaines, are elaborated by the bacteria within the bacterial cells. These are substances of doubtful chemical structure and are divided into two classes: (1) Endotoxins, toxins existing mainly in connection with the bacterial cell, going into solution with difficulty and possessing in such solution only a moderately poisonous action. (2) Soluble toxins, readily removed from the bacterial cell by solution and giving a solution of strong toxic action.

It has been found that an animal which has been treated with bacteria-producing soluble toxins has present in its blood a specific antibody which is capable of neutralizing the toxin of the corresponding bacteria. This substance is called an antitoxin and protects, from the poisonous effects of the toxin, not only the original animal (active immunity), but also other animals into which the antitoxin-containing serum may be injected (passive immunity). This production of passive immunity has been widely used in the treatment of diphtheria and the prophylaxis of tetanus. In other bacterial diseases, such as typhoid and streptococcus infections, where the toxins present are mainly endotoxins, the production of an antitoxin conferring passive immunity has not been successful.

In the case of some of these antibody reactions it is found that a third substance is necessary. This substance is commonly called the complement; and in this connection the antibody is termed the amboceptor, and the foreign protein the antigen. The amboceptor and the complement are both present in the blood-serum. Complement is an unstable substance present in all fresh blood, and is not specific, that is, it will enable any amboceptor to act upon the corresponding antigen. Amboceptor is fairly stable, is usually present only in response to the introduction of some antigen, and is specific, that is, it will act only upon its corresponding antigen.

As amboceptor will act upon antigen only in the presence of complement, the presence or absence of complement in a solution may readily be shown by mixing the solution with a suitable amboceptor and antigen, when the presence of complement is shown by the occurrence of the interaction of the amboceptor and antigen, while its absence is shown by the failure of the reaction. The reagents commonly used are red blood-corpuscles and the corresponding hæmolysin (amboceptor), since the interaction is shown by a visible change, hæmolysis, and if no reaction occurs the mixture remains unchanged.

This procedure is used in the Wassermann reaction for syphilis. If a mixture be made of the blood-serum of a syphilitic patient, an emulsion of animal lipoids, and complement, it is found that the complement becomes absorbed or fixed, so that if the mixture be tested for complement by the addition of red blood-corpuscles and the corresponding hæmolysin, no hæmolysis will occur. If, on the other hand, the patient has not syphilis, no fixation of complement will occur, the complement will be left free to act, and will produce hæmolysis when the corpuscles and hæmolysin are added.

Ehrlich, in explaining his theory of immunity, begins by describing the cell as consisting of a certain group of atoms forming an essential nucleus which is combined with several different groups of atoms, called side-chains, varying in composition and structure.

Each of these side-chains has atoms arranged in such a way that they present affinities for combining with groups of atoms of nutrient or other material circulating in the animal fluids. These groups he calls *receptors*, and the arrangement of atoms, by virtue of which combination occurs, a *haptophore group*.

Thus, specific lysis is due to the action of a complement on a specific cell through a specific amboceptor, the chemical reaction being due to the presence, in the chemical structure of the cell, of a receptor having a group of atoms haptophorous with a group of atoms of the amboceptor, which, in turn, has a group haptophorous with one of the complement.

Lymph is a clear, colorless, or slightly yellow liquid of a faint alkaline reaction; in composition it closely resembles blood-serum. It contains less protein, particularly less fibrinogen, the salts and extractives are present in about the same amount. Lymph coagulates more slowly and less firmly than blood. The term "chyle" is applied to the lymph of the lacteals and thoracic duct when it is clouded by the fat absorbed from the food in the intestine.

Bone is chemically distinguished from other tissues by the large quantity of inorganic salts which it contains. Dried bones contain about 31 per cent. of organic matter combined with 69 per cent. of mineral matter. 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.		Child five years.		Man twenty-five years.	
Organic matter,	43.42	per cent.	32.29	per cent.	31.17	per cent.
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.

Experiment 76. Pour upon 3 grammes of bone 10 c.c. of water, and then 10 c.c. of hydrochloric acid. (Notice that carbon dioxide is liberated.) The dilute acid dissolves the mineral constituents of the bone, leaving the organic matter (ossein) as a swollen mass, which retains the shape of the bone.

Decant the acid solution, and to part of it add an excess of ammonia, then acidify with acetic acid. The greater part of the precipitate formed by ammonia will dissolve. The insoluble part contains traces of silica, but is chiefly ferric phosphate, most of which is derived from the blood in the bone. Filter and test portions of filtrate for phosphoric acid with ammonium molybdate and for calcium with ammonium oxalate. Dissolve the washed precipitate on the filter with a little hydrochloric acid, and test for phosphoric acid as above, and for iron with potassium ferrocyanide. (The detection of the mineral constituents of bone may be carried out with the ash left from incinerating bone.)

Wash the ossein, obtained above, first with water, then with dilute solution of sodium carbonate, and finally with water again. Put the washed ossein in a beaker with a little water and boil until most of the ossein has been dissolved. Neutralize, if necessary, with sodium carbonate, and filter while hot into a test-tube. On standing, the solution gelatinizes more or less completely. Ossein is converted into gelatin by this treatment.

Gelatin. The purest commercial form of gelatin is known as *isinglass,* prepared from the sounds or air-bladders of certain fishes; it is much used as an article of food in creams and jellies. An impure gelatin, prepared from animal refuse (hoofs, bones, hides, etc.), forms common *glue,* and its solution in acetic acid is sold as *liquid glue.* In a pure state gelatin is a colorless or slightly yellowish, transparent, tasteless mass. The presence of gelatin often prevents the formation of precipitates by holding them in suspension in a finely divided state, so that they may pass through filter-paper.

The nutritive value of gelatin is discussed under Metabolism (page 646).

As gelatin contains no tyrosine and no tryptophane, it will be found that the results obtained with the xanthoproteic and Millon tests below are only faintly positive, being due to impurities.

Tests for gelatin. Pour upon a gramme of gelatin 25 c.c. of water and allow to stand twenty-four hours. The gelatin now is swollen, but not dissolved. Decant the water, add 8 c.c. of distilled water, heat over a water-bath until the gelatin dissolves, then cool. To the gelatinous mass, thus obtained, add about 50 c.c. of water and heat again until dissolved. Use this solution for the following tests:

1. Add tannin, or hydrochloric acid and phosphotungstic acid: voluminous precipitates are formed.
2. Boil a portion with one-third its volume of nitric acid: a faint-yellow color is produced, showing the presence of an aromatic radical.
3. Add caustic potash and a little cupric sulphate: a blue to violet color appears without a trace of red. (Difference from albumoses and peptones.)
4. Boil with Millon's reagent: a faint pink or red color. (Difference from proteins in general.)
5. Add bromine-water: a heavy yellow precipitate is formed, possessing tough, adhesive properties.
6. Add a few drops of acetic acid and boil; add acetic acid and potassium ferricyanide; add mercuric chloride. Precipitation takes place in neither case. (Difference from simple proteins.)

Note that gelatin solidifies on cooling and becomes liquid again on the application of heat (difference from proteins in general).

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.

Hair, nails, horns, hoofs, feathers, epithelium, are nearly identical in composition. They all contain cholesterin and nitrogenous substances termed *keratins,* which are probably not distinct chemical compounds, but mixtures of several substances similar in composition and properties.

Cholesterin fats are very resistant to the action of putrefactive bacteria, and the occurrence of these fats in combination with the keratins serves as a protection to the skin surface from the attacks of the ever-present bacteria.

Muscle. The chemical composition of the various morphological elements of striated muscle is not definitely known. Fresh, inactive muscle has an amphoteric reaction—*i. e.,* it colors red litmus-paper faintly blue, and blue litmus-paper slightly red. After activity or death the reaction becomes acid. If the blood is removed from muscle immediately after death, and the muscle is then quickly cut and frozen, an alkaline fluid can be pressed out, the *muscle-plasma,* which contains the proteins of muscle. Muscle-plasma coagulates spontaneously, separating a protein body, myosin, and yielding a serum, *muscle-serum.* A similar change takes place in the muscle shortly after death, causing the hardening of the muscle observed in *rigor mortis.*

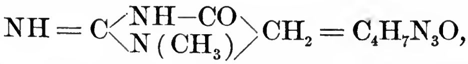
The more important constituents of muscle are considered here without attempting a morphological distinction.

Proteins of muscle. There is at present no generally accepted view as to the nature of the essential proteins of muscle tissue. This is due largely to the many different names given them, which are in almost hopeless confusion. It seems certain that there are at least two proteins in living muscle which have the power of coagulating after death. V. Fürth calls the less abundant of these myosin and its coagulated form myosin fibrin; the second he calls myogen, and says that it is converted first into an intermediate stage, and finally into myogen fibrin. Myosin belongs to the globulins and myogen resembles the albumins. The coagulation of these proteins appears to take place spontaneously, as no enzyme has been satisfactorily demonstrated. The process is probably not analogous to the clotting of fibrinogen.

Carbohydrates of muscle. There are present in muscle varying amounts of dextrose and glycogen, which form probably the most important source of energy for the work of the muscle. The dextrose is brought by the blood-stream, and any excess over the amount needed for immediate use is converted into glycogen by the muscle, and is held in reserve in this form. When a muscle does work, *i. e.*, when it contracts, the glycogen is split again into dextrose, which is then oxidized with a resulting liberation of energy. It is possible to show that the carbon dioxide of the muscle is increased in amount, and that there is also a formation of lactic acid. It is believed that this lactic acid represents an incomplete oxidation of the sugar. In the burning of dextrose by the muscle tissue, an internal secretion or hormone produced by the pancreas is believed to play an important part.

Muscle extractives. The extractive bodies of the muscle are important, and are both nitrogenous and non-nitrogenous. Among the first, creatine, the xanthine bases, urea, and uric acid deserve mention. Non-nitrogenous extractives always present are inosite, glycogen, sugar, and lactic acid.

Creatine (*Methyl-guanidine-acetic acid*),  $NH = C\left\langle\begin{array}{l}NH_2\\ N(CH_3).C_2H_3O_2\end{array}\right.$ $=C_4H_9N_3O_2$, occurs in muscles of vertebrates, in the brain, blood, transudates, and the amniotic fluid. When pure, it forms colorless, transparent, rhombic prisms. The crystals are soluble in 75 parts of cold, much more soluble in hot water, slightly soluble in alcohol, insoluble in ether. The solution is neutral to litmus, though creatine is a weak base, combining with some of the acids to form crystalline salts. Creatine may be obtained by the action of cyanamide on sarcosine (methyl-glycocoll).

Creatinine,  $NH = C\left\langle\begin{array}{l}NH-CO\\ N(CH_3)\end{array}\right\rangle CH_2 = C_4H_7N_3O$, is the anhydride of creatine, and may be obtained by boiling creatine with acids, when a molecule of water is split off. *Vice versâ*, creatinine may be converted into creatine. Creatinine is readily soluble in water and alcohol, but nearly insoluble in ether; it crystallizes in colorless prisms; the solution is slightly alkaline to litmus. Creatinine is a strong base, forming well-defined salts; it also forms an insoluble double compound with zinc chloride, for which reason the latter is often used to precipitate creatinine. The occurrence of creatinine in urine will be considered later.

Experiment 77. *a. Preparation of creatine.* Digest 400 grammes of finely divided lean beef with 500 c.c. of water at a temperature of 50° C. (122° F.); filter the mass through cloth, press out well, and repeat the operation twice with 1000 c.c. of water, bringing the mixture to the boiling-point each time; then evaporate the mixed filtrates to about one liter. (In place of the liquid extract, thus obtained, a solution of commercial extract of beef may be used.) Acidify the solution with acetic acid, heat to boiling, and filter off the coagulated proteins; to the cold filtrate add basic lead acetate as long as a precipitate is formed, filter and precipitate excess of lead by passing hydrogen sulphide through the solution. Finally filter, evaporate filtrate over a water-bath to a syrup, and set aside. After a day or two crystals of creatine will be found, which, if too highly colored, may be redissolved in water, decolorized with bone-black, and recrystallized.

b. Conversion of creatine into creatinine. Heat 0.5 gramme of creatine with 10 c.c. of dilute sulphuric acid for half an hour over a water-bath; then dilute with 25 c.c. of water and add a sufficient quantity of powdered barium carbonate to neutralize the acid. Next filter, evaporate the filtrate to about 5 c.c., and use this solution of creatinine for the following tests:

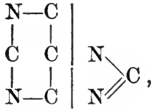
1. To a few drops of the solution add an equal volume of an alcoholic solution of zinc chloride. Creatinine zinc chloride, $(C_4H_7N_3O)_2.ZnCl_2$, crystallizes in warty lumps, composed of fine needles or prisms.

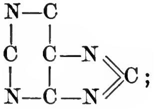
2. *Weyl's reaction.* Add, drop by drop, a freshly prepared, dilute solution of sodium nitroprusside, $Na_2Fe(CN)_5NO$, until the solution is colored yellow; then add drop by drop a dilute solution of sodium hydroxide: a fine transient ruby-red color is obtained which soon passes into yellow. Acidulate solution with acetic acid and warm: solution turns green, then blue, the color being due to the formation of Prussian blue.

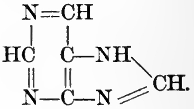
3. To a very dilute solution of creatine add a trace of an aqueous solution of picric acid and render faintly alkaline: the solution turns intensely red.

Xanthine bases are a group of nitrogenous substances produced in the organism as the result of the cleavage of nucleins. They are closely related to one another, as also to uric acid, from which they may be obtained by synthetic processes. Indeed, an increased secretion of uric acid follows their ingestion as food. While eleven xanthine bases have been isolated from the cell, only four (xanthine, hypoxanthine, guanine, and adenine) are found in the muscle. Conjointly the xanthine bases are also termed *alloxur bases* or *purine bases.* The first named refers to the fact that the nucleus of xanthine bases is assumed to be made up of the carbon-nitrogen nuclei of *allox*an, $C_4H_2N_2O_4$ (an oxidation-product of uric acid), and *ur*ea,

CN_2H_4O. When the two nuclei occur joined together into one nucleus the latter is known as the *purine-nucleus.* Purine itself is a hypothetical compound containing this nucleus.


Alloxan nucleus. Urea nucleus.


Purine nucleus.


Purine.

By oxidation, or by replacement of hydrogen atoms in purine with the radicals OH, NH_2, NH, or by introducing the methyl group, CH_3, the different purine bases or allied compounds have been formed. These bodies are also closely related to the vegetable bases caffeine and theobromine, and also to uric acid, as shown in the following table:

Purine	$C_5H_4N_4$
Hypoxanthine (oxypurine)	$C_5H_4N_4O$
Xanthine (di-oxypurine)	$C_5H_4N_4O_2$
Uric acid (tri-oxypurine)	$C_5H_4N_4O_3$
Heteroxanthine (methyl-xanthine)	$C_5H_3(CH_3)N_4O_2$
Paraxanthine (dimethyl-xanthine) Isomeric with theobromine	$C_5H_2(CH_3)_2N_4O_2$
Caffeine (trimethyl-xanthine)	$C_5H(CH_3)_3N_4O_2$
Adenine (amino-purine)	$C_5H_3(NH_2)N_4$
Guanine (amino-oxypurine)	$C_5H_3(NH_2)N_4O$
Carnine (dimethyl-uric acid)	$C_5H_2(CH_3)_2N_4O_3$

Uric acid and the xanthine bases take up water and yield qualitatively the same decomposition-products when treated with fuming hydrochloric acid under pressure, viz., ammonia, carbon dioxide, glycocoll, and formic acid.

Xanthine and hypoxanthine (*sarcine*) occur generally together, though in small quantities, in urine and in almost all tissues. In larger quantity they are found in the meat-extracts. When pure these bodies are colorless powders, almost insoluble in water, alcohol, and ether. With acids they form crystallizable salts, and with silver nitrate double compounds, which are employed in the separation of the bases from fluids.

Phosphocarnic acid is a glyco-nucleoprotein, occurring in muscle; it yields on hydrolysis succinic acid, carbon dioxide, phosphoric acid, a carbohydrate, and carnic acid, a protein almost identical with peptone. It forms soluble compounds with the alkaline earths, and also an iron compound (carniferrin) soluble in alkalies; these properties serve as a means to carry these metallic compounds through the body. (Lacto-phosphocarnic acid is an analogous compound found in milk.)

Muscle pigment. Muscle, even when completely freed from blood, has a red color, due to a pigment which is some slight modification of blood hæmoglobin.

Of *non-nitrogenous bodies* found in muscle, inosite and sarcolactic acid, which have been previously considered, deserve mention.

Experiment 78 (*Preparation of sarcolactic acid*). Dissolve 20 grammes of commercial meat-extract in 200 c.c. of water, add basic lead acetate as long as a precipitate is formed; filter and evaporate filtrate to a syrupy consistence. Then add 200 c.c. of 96 per cent. alcohol; filter and evaporate the filtrate to dryness over a water-bath. Dissolve the residue in 40 c.c. of water and 20 c.c. of sulphuric acid. Extract this solution twice with an equal volume of ether in a separatory funnel. Filter the ethereal solutions and evaporate the ether with proper precautions. The residue, consisting of a colorless liquid, is sarcolactic acid, to which apply:

Uffelmann's test for lactic acid. To an aqueous solution add a few drops of Uffelmann's reagent (10 c.c. of a 2 per cent. solution of carbolic acid in water, to which a few drops of ferric chloride solution have been added). A yellow color is produced.

Inorganic constituents of muscle are chiefly mono- and dipotassium phosphate, with smaller portions of sodium bicarbonate, salts of magnesium and calcium, some iron salts, and traces of sulphates and chlorides.

Meat-extracts are of two kinds, those from which the proteins and peptones have been removed, and those containing besides proteins large quantities of the basic extractives. Articles of the first class are destitute of nutritive value, and the second derive no nutritive value from the extractive constituents. The physiological effect of the flesh bases seems to be in the direction of nerve stimulants, and for this reason they are to be classed with tea and coffee as adjuncts to food, not as true foods.

The **thyroid gland** contains iodine in some form of protein combination, known as *thyro-iodine;* this compound contains 9.3 per cent. of iodine.

Desiccated thyroid glands, Glandulæ thyroideæ siccæ. 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 the adrenals, have some influence on sugar metabolism, which is not yet understood.

The **suprarenal glands** contain a substance which has the power of constricting the blood-vessels of the body, and thus causing a great but transient rise in blood-pressure. This substance has been found to be methylamino-ethanol-dioxy-benzol, $C_6H_3(OH)_2.CH(OH).CH_2.NH.CH_3$. It is used particularly to produce local anæmia, and is called by various names: suprarenalin, suprarenin, adrenalin, epinephrin.

Desiccated suprarenal glands, Glandulæ suprarenales siccæ. 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.

Brain consists of so many individual parts that the analysis of it as a whole is of little value, and to separate these parts successfully is a task not yet accomplished. Brain, as a whole, contains lecithin, cholesterin, protagon, and many other substances, some of which are distinguished by the large quantity of phosphorus they contain.

The gray matter contains albumin, globulin, nucleoprotein, and nuclein. Neurokeratin forms the neuroglia. In the white matter is found *protagon*, a very complex substance containing nitrogen and phosphorus. It yields on hydrolysis a lecithin, fatty acid, and cerebroside. The *cerebrosides* are nitrogenous substances free from phosphorus, yielding on hydrolysis galactose, sometimes called brain-sugar. Fused with caustic potash, or boiled with nitric acid, they form palmitic or stearic acids. Three cerebrosides are known: cerebrin, kerasin, and encephalin.

The term "lipoids" is applied to an indefinite group of organic substances, which are, like the fats, soluble in ether and alcohol. These substances are present in many kinds of tissue, and are particularly abundant in the brain and in nerve fibres. The more important membranes are cholesterin and the phosphorized fats (phosphatides, lecithins). The cerebrosides are also classed here. The function of these substances is entirely unknown. Their abundance in brain tissue is the basis of the well-known theory that the anæsthesia produced by ether and chloroform is due to the solvent action of these substances upon the lipoids.

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 glycerin-phosphoric acid by substitution of hydrogen atoms with two fatty acid radicals and a base, choline.

Glycerin-phosphoric acid,  $C_3H_5{<}\begin{matrix}(OH)_2\\ OPO(OH)_2\end{matrix}$, is obtained by the action of glycerin on phosphoric acid, when combination takes place with elimination of water, thus:

$$C_3H_5(OH)_3 + H_3PO_4 = C_3H_5(OH)_2.H_2PO_4 + H_2O.$$

Glycerin-phosphoric acid is a syrupy liquid yielding easily soluble salts, some of which are used medicinally. The hydroxyl hydrogen is replaceable by acid radicals and the hydrogen of phosphoric acid by bases. Thus, by introducing the radicals of stearic acid and of choline distearyl-lecithin is obtained of the composition, $C_3H_5(C_{18}H_{35}O_2)_2.HPO_4.C_2H_4N(CH_3)_3OH$.

Choline (*Trimethyl-oxyethyl-ammonium hydroxide*), $N(CH_3)_3.C_2H_5O.OH$, has been mentioned as one of the ptomaines. 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 substance neurine, mentioned on page 620. On the other hand, choline by oxidation is converted into *muscarine*, a ptomaine even more poisonous than neurine.

Cholesterin, $C_{27}H_{45}OH$. This substance has been classed by physiologists among the fats, because it is greasy and soluble in ether, but its chemical constitution is that of an alcohol. It is found chiefly in bile, but also in blood, nerve-tissue, brain, contents of the intestines, feces, etc.; its presence in certain vegetables, as pease, beans, etc., has also been demonstrated. Cholesterin combines with fatty acids to form fats.

Cholesterin crystallizes in colorless, rhombic plates, which are insoluble in water, alkalies, and dilute acids, but soluble in ether. It sometimes forms in the organism solid masses, known as *biliary calculi* or *gall-stones*, some of which are almost pure cholesterin.

Cholesterin is an unsaturated, secondary alcohol, and a derivative of the terpenes.

Reactions of cholesterin:

1. Place a small quantity of cholesterin on a slide, moisten with a drop of 80 per cent. sulphuric acid, and cover with a cover-glass. Allow a little iodine solution to run in under the cover-glass and examine it with the microscope. The cholesterin crystals pass through many shades of colors, gradually becoming brown or violet or clear blue.

2. Evaporate, in a shallow porcelain dish, a small quantity of cholesterin with hydrochloric acid containing a trace of ferric chloride. A blue residue is formed.

QUESTIONS.—What three kinds of matter are found as constituents of the animal body, and how can they be determined quantitatively? Mention the chief constituents of blood, and state those which predominate in serum and in the corpuscles respectively. What substances cause the clotting of blood, and what explanation can be given? How may blood-stains be recognized? What are the characteristics of the different hæmoglobins? Describe methods for determining the specific gravity and the alkalinity of blood. How can the proteins of blood-serum be separated? Mention the principal constituents of muscles, bone, teeth, and hair. State the properties and reactions of creatine and gelatin. What is the composition of glycerin-phosphoric acid, and in what form of combination does it exist in the body?

56. DIGESTION.

General remarks. It has been stated that foods are divided into two classes, inorganic and organic, and that the latter are subdivided into proteins, carbohydrates, and fats; and also that the term digestion refers to the process by which organic foods are altered in such a manner that they may be absorbed.

The process of digestion is both mechanical and chemical. By the mechanical part of the process the food-material is disintegrated, propelled along the alimentary canal, and mixed with the different digestive secretions. These latter cause a chemical change, usually hydrolysis, of the food, converting it into soluble and easily absorbable substances. For convenience of study the process is divided into salivary, gastric, and intestinal digestion; and the secretions and chief alterations of the nutrients in these portions of the tract are considered separately. It should be remembered, however, that these three processes are closely interdependent, and any disturbance of function, mechanical or chemical, in one part of the digestion will disturb and derange all.

Salivary digestion. The first part of the process of digestion is accomplished in the mouth, and consists in the breaking up of the food by the teeth and mixing it with saliva, the process being known as *mastication*. In addition, the saliva, to a limited extent, converts starch into maltose. This action of the saliva is due to its ferment *ptyalin*. Other functions of the saliva are to keep the mucous membrane of the mouth moist and to lubricate the food bolus.

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 substance. 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 micro-organisms. 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 uræmia. 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 also 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 split into maltodextrin and erythrodextrin; the latter gives a red color with iodine. These dextrins are next split and yield maltose, maltodextrin, and achroödextrin, which are not colored by iodine. From achroödextrin more maltodextrin and maltose 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 79. Mix intimately 1 gramme 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 626).

4. Acidify with acetic acid and add ferric chloride: a red color, due to the formation of ferric sulphocyanide, is produced.

Gastric digestion. The food, after mastication, passes through the œsophagus into the stomach. Here the mass is kneaded by the contractions of the muscular wall of the stomach and is acted on by the gastric juice. By this treatment with the aid of the fluids ingested the food is converted into a turbid liquid, known as *chyme.* A small portion of the digested mass is absorbed through the stomach wall, but most of the food, after being completely acted upon, passes through the pylorus into the duodenum.

Gastric juice is a liquid secreted by the follicles of the stomach. It can be obtained, in a fairly normal condition, either from animals (dogs) or from man, by the aid either of gastric fistulæ or of the stomach-pump. It is a thin, nearly colorless liquid, having a somewhat sour taste, an acid reaction, and a specific gravity varying from 1.002 to 1.003. The total solids are about 0.5 per cent., nearly one-half being inorganic salts, chiefly the chlorides and phosphates of alkali and alkaline earth metals. The organic matter present, and amounting to about 0.3 per cent., is chiefly pepsin and a little mucin.

The secretion of gastric juice is not continuous, and is brought about by chemical irritation of the gastric mucuous membrane or by psychic influence. A strong desire for food will cause a flow of the juice; chemical irritation, as by the alkaline mass of food and saliva, causes a slower but more continuous flow. The quantity of juice secreted during digestion varies with the quantity and quality of the food.

The average composition of pure gastric juice may be approximately stated thus:

Water	99.26	per cent.
Pepsin and other organic matter	0.30	"
Rennin	?	"
Free hydrochloric acid	0.22	"
Alkali chlorides	0.20	"
Phosphates of calcium, magnesium, and iron	0.02	"

The acidity of gastric juice is due chiefly to hydrochloric acid, present in quantities varying from 0.1 to 0.3, or even 0.4 per cent.; to a slight extent also to organic acids and acid salts. The presence of free acid in gastric juice cannot be demonstrated until about twenty minutes after the swallowing of food; this is due to the power of proteins to form compounds with hydrochloric acid. During this time the ptyalin of saliva is active in the hydrolysis of starch. The gastric juice is the only secretion of the body containing free acid. The mode of production of the hydrochloric acid is not understood. While it is known that it is derived from the chlorides of the blood, the details of the process are not yet worked out. The function of the acid is to activate the enzymes of the stomach which are secreted in the zymogen state, and to aid in peptic digestion. It also has a marked antiseptic action upon the contents of the stomach and upper intestine. Organic acids, chiefly lactic, are frequently found in the stomach, but these are not secreted in the gastric juice itself, but are produced by some fermentative action from the food after it has entered the stomach. Lactic acid is never found in a normal stomach unless it was present in the food before ingestion. It is often present in cases of gastric stagnation with a decreased hydrochloric output. These cases may be either benign or, more often, malignant in origin. Thus, the persistent occurrence of lactic acid with a diminution or absence of hydrochloric acid is an indication of serious disturbances, possibly of cancer of the stomach.

The origin of the lactic acid is the carbohydrate food; other food material may of course produce other organic acids (*e.g.*, butyric acid from butter).

The enzymes of gastric juice. The two important enzymes of the stomach are pepsin and rennin, which are secreted in an inactive or zymogen form, and are activated by the hydrochloric acid of the gastric juice. In addition to these there is probably a lipolytic enzyme (gastric lipase) present. In the cardiac end of the stomach the reaction does not become acid for some time after digestion commences, and the ptyalin of the saliva continues its action on the starches during this time.

Digestive action of gastric juice. The conversion of proteins into peptone is a progressive reaction due to the action of pepsin in hydrochloric acid solution. Simple proteins are first changed into syntonin, an acid albuminate; this is split into compounds known as primary proteoses (proto-proteoses, protalbumoses). By further action these primary proteoses form secondary proteoses (deutero-proteoses, deutero-albumoses), which are finally split, forming peptones.

Peptone is the end-product of gastric digestion, is diffusible, and is not further changed by pepsin. The intermediate products exist at the same time in gastric digestion, their relative quantities depending on the length of time the action has progressed.

While it is believed that gastric digestion normally carries the decomposition of proteins no further than this, it is possible to split proteins into the amino-bodies by pepsin-hydrochloric acid digestion outside of the body.

Compound proteins are split by gastric juice, the simple proteins formed being digested as above stated. The nucleoproteins yield a peptone free from phosphorus, the nuclein split off being unchanged. Collagen is first converted into gelatin, which then forms successively an acid albumin, proto-proteose, deutero-proteose, and gelatin-peptone. Elastin is changed slowly, while keratins are not changed at all.

Rennin is a milk-curdling enzyme present in all normal human gastric juice. It is absent in chronic catarrh of the stomach and other diseases. Its presence in gastric juice is shown by its action on milk, and will be considered in the article on clinical examination of gastric juice.

Absorption in the stomach. It has been shown that the stomach is able to absorb sugars, peptones, salts, and some drugs. However, the absorption is not extensive unless concentrated solutions are present, and probably plays no great part in normal metabolism.

Experiment 80. (*Artificial gastric digestion.*) Dissolve 2 grammes of scale pepsin in 1000 c.c. of 0.4 per cent. hydrochloric acid. To this solution add about 250 grammes of protein. The protein material may be fresh or dried blood-fibrin, the meat-residue from the preparation of creatine (Experiment 77), or the whites of 18 eggs, previously boiled and finely divided. The fresh fibrin or the egg-albumin may be added directly to the digestive fluid. The meat-residue or dried fibrin should first be boiled with a liter of water, containing 1 c.c. of hydrochloric acid, until the material gelatinizes; it must be cooled before mixing it with the digestive fluid. Keep mixture in a thermostat at a temperature of 40° C. (104° F.) for ten days. Filter the solution, heat the filtrate to 50° C. (122° F.), and neutralize with sodium carbonate, when *syntonin* is precipitated.

Evaporate filtrate from syntonin to about 200 c.c., adding sodium carbonate if necessary to keep solution neutral during evaporation, filter, and saturate solution with ammonium sulphate, when *proteose* is precipitated, while *peptone* remains in solution.

To purify the proteose, dissolve the precipitate in water, heat to boiling, and add barium carbonate until all ammonium sulphate is decomposed. Filter, evaporate filtrate to a small volume, and pour solution into double the volume of 95 per cent. alcohol, when proteose is precipitated as a sticky mass. To obtain it as a powder, allow the mass to remain in contact with the alcohol for two hours, transfer to absolute alcohol for one hour, and then to ether for an hour; then collect on a filter and dry between filter-paper. The proteose thus obtained is a mixture of primary and secondary proteoses.

Use an aqueous solution of this proteose for the following tests: Acidulate a portion with acetic acid and add an equal volume of saturated solution of sodium chloride. The solution becomes cloudy, clearing again when heat is applied, and becoming cloudy again when cool. (Characteristic of proteoses.) Other portions of the solution use for the xanthoproteic, Millon's, and biuret reactions.

Proteoses will give positive precipitation tests with acetic acid and ferrocyanide, and with trichloracetic acid. Peptones will give negative results with the same tests.

To obtain peptone, the filtrate from the proteose is heated and 20 grammes of ammonium sulphate are added to remove traces of proteose. The filtrate, after being concentrated by evaporation, is treated with barium carbonate, alcohol and ether, exactly as directed above for proteose. Use some of the peptones for the xanthoproteic, Millon's, and biuret reactions.

Clinical examination of gastric juice. The chemical examination of gastric juice, or of contents of stomach, is now considered of great importance in the diagnosis of diseases of the stomach. The juice for examination is obtained as follows: On an empty stomach, the patient partakes of a test-meal, consisting usually of bread and water, and an hour after or later (depending upon the form of meal administered) the contents of the meal are withdrawn by means of a stomach-tube. The liquid is filtered and used for further examinations. These examinations consist of the following determinations: *a.* reaction; *b.* presence of free acids; *c.* presence of free hydrochloric acid; *d.* presence of lactic and other organic acids; *e.* total acidity; *f.* estimation of free acids; *g.* estimation of free hydrochloric acid; *h.* estimation of combined hydrochloric acid; *i.* estimation of total organic acids; *j.* presence of pepsin and pepsinogen; *k.* presence of rennin and rennin zymogen; *l,* detection of proteins; *m,* detection of carbohydrates.

In case a sufficient supply of gastric juice cannot be obtained for the reactions below, the student should prepare the following solutions: *A.* A 0.25 per cent. hydrochloric acid; *B.* A mixture of 10 parts of *A* and 40 parts of water; *C.* A solution of 0.8 gramme of lactic acid in 100 c.c. of water; *D.* A 2 per cent. solution of albumose in water. Make reactions *b* and *c* with solution *A*, repeat with *B*, and with a mixture of 1 part of *B* and 2 parts of *D*.

a. Reaction. This should be, and in all normal juices is, distinctly acid to litmus-paper.

b. Free acids. The presence of free acids is detected by congo-red paper. This paper is prepared by soaking unsized paper in a 1 per cent. aqueous solution of congo-red, and drying. If a drop of juice is placed upon the paper, the presence of free acids is indicated by the change of color from red to blue; if the blue color is intense, free hydrochloric acid is present. (Neither combined hydrochloric acid nor acid salts, such as acid phosphates, act on congo-red.)

c. Free hydrochloric acid. There are a number of reagents for the detection of free hydrochloric acid. The more important of these are: tropæolin 00, phloroglucin-vanillin, resorcin, and dimethyl-amino-azobenzol.

Tropæolin 00. Dissolved in water, the 1 per cent. brownish-yellow solution of tropæolin 00 (diphenylamine-orange) is changed to a brown-red or deep-red color upon the addition of juice containing free hydrochloric acid. Upon gentle evaporation and heating a lilac color is produced. The same reaction may be made with filter-paper, soaked for some time in an alcoholic solution of the reagent, allowed to dry, and used as test-paper. Hydrochloric acid turns this paper brown, and upon heating the brown color changes to blue. (The paper does not keep unchanged over a month.)

Phloroglucin-vanillin. This reagent is made by dissolving 2 parts of phloroglucin and 1 part of vanillin in 30 parts of alcohol. It is a very sensitive and reliable agent for the detection of free hydrochloric acid. Five drops of the solution mixed with an equal quantity of gastric filtrate are gently heated over a Bunsen flame. On complete evaporation a distinct red color or tinge appears in the presence of not less than 0.01 per cent. of hydrochloric acid. The formation of cherry-red crystals indicates the presence of large quantities of the acid. Organic acids have no action on this reagent.

Resorcin. This reagent is equally as sensitive as, and more stable than, phloroglucin-vanillin. The solution is obtained by dissolving 5 parts of resublimed resorcin and 3 parts of cane-sugar in 100 parts of dilute alcohol. The manner of testing with this reagent is the same as described above for phloroglucin-vanillin; a bright-red tinge or color appears, even when very small quantities of free hydrochloric acid are present.

Dimethyl-amido-azobenzol. A 0.5 per cent. solution of this substance in alcohol is mixed with a few drops of the stomach contents, and in the presence of as little as 0.002 per cent. of free hydrochloric acid a cherry-red color develops.

d. Lactic acid. (Use solution *C.*) Uffelmann's reagent answers best for detecting this acid. It is made by adding 1 or 2 drops of ferric chloride solution to 10 c.c. of a 1 per cent. carbolic acid solution, and diluting this solution with water until it assumes an amethyst-blue color. To 2 c.c. of this solution an equal volume of gastric juice is added. In the presence of at least 0.01 per cent. of lactic acid the liquid assumes a pure yellow color. As the presence of too much hydrochloric acid (or even of some other substances) prevents the change, it is well to shake (in doubtful cases) 10 c.c. of juice with 50 c.c. of ether, evaporating the ethereal solution to dryness, dissolving the residue in a few drops of water, and adding to this solution, which contains the lactic acid, the above reagent.

Butyric acid changes Uffelmann's reagent to brownish yellow. Butyric and acetic acids may be recognized by their odor.

It has been mentioned that the total acidity of gastric juice is due to acid salts, organic acids, free and combined hydrochloric acid. Clinically it is sometimes necessary to estimate the acidity due to each. This is done by the following method.

e. Total acidity. This is best determined by titration with an alkali; the estimation is conducted as follows: To 10 c.c. of the filtered liquid a few drops of phenolphthalein solution are added, and to the mixture deci-normal potassium hydroxide solution is slowly added from a burette until the liquid assumes a slight reddish tint, which does not disappear on stirring.

It is customary to express the acidity in percentages, according to the quantity of deci-normal potassium hydroxide used. Thus, 52 per cent. acidity would indicate that every 100 c.c. of gastric filtrate are exactly neutralized by 52 c.c. of deci-normal potassium hydroxide.

Though the total acidity is due to a mixture of free and combined hydrochloric acid, organic acids, and acid salts, it is frequently expressed as hydrochloric acid. As 1 c.c. of deci-normal alkali solution corresponds to 0.003618 gramme of HCl, the number of c.c. of alkali used multiplied by the factor stated, gives the grammes of HCl in the 10 c.c. of juice used. Suppose 5.2 c.c. of alkali were required; this would correspond to 5.2×0.003618, equal to 0.0188 gramme of HCl in 10 c.c., or to 0.188 per cent.

f. Estimation of free acids. Both free hydrochloric and organic acids change the bright-red color of congo-red to blue, while alkalies restore it to red. Acid salts, such as acid phosphates, have no effect on this indicator. If, therefore, a titration of 10 c.c. of filtered gastric juice, to which enough of congo-red solution has been added to impart a distinct blue color, is made (as above described for total acidity), then the number of c.c. of deci-normal potassium hydroxide solution used to restore the red color indicates the quantity of free acid present. The calculation is made as above mentioned.

g. Estimation of free hydrochloric acid. The use of dimethyl-amino-azobenzol as an indicator for free hydrochloric acid has been mentioned above. For quantitative work 10 c.c. of gastric filtrate are mixed with 5 drops of the dimethyl-amino-azobenzol solution, and this mixture is titrated with $\frac{N}{10}$ sodium hydroxide solution. The disappearance of the reddish color indicates when the reaction is completed. The difference between the estimation of total free acids (*f*) and that of free hydrochloric acid (*g*) indicates the quantity of organic acids present.

h. Estimation of combined hydrochloric acid. To 10 c.c. of gastric juice add 3 drops of a 1 per cent. alizarin solution and titrate with $\frac{N}{10}$ alkali until the solution assumes a clear violet color. The acidity thus determined is due to free hydrochloric acid, acid salts, and organic acids. The difference between the results of titration with alizarin (*h*) and with phenol-phthalein (*e*) shows acidity due to combined hydrochloric acid, while the difference between the titration with alizarin (*h*) and that with dimethyl-amino-azobenzol shows acidity due to organic acids and acid salts.

i. The total organic acids, free and combined, may be determined by neutralizing 10 c.c. of gastric juice, using phenolphthalein as an indicator, evaporating the neutral solution to dryness and incinerating the residue. By this operation the organic acids are converted into carbonates, which are titrated with $\frac{N}{10}$ acid, and from the result the quantity of organic acid is calculated, usually as lactic acid.

j. Pepsin and pepsinogen. In case free acid is present, 10 c.c. of gastric juice are placed in a beaker, and a small bit of dried fibrin or a lamella of blood albumin (Merck), is added, and the beaker placed in a thermostat at a constant temperature of 38° to 40° C. (100° to 104° F.). Pepsin is indicated by the rapid solution of the flake of albumin. If free hydrochloric acid is absent, the juice is rendered acid with a drop of this acid and then tested in the manner described.

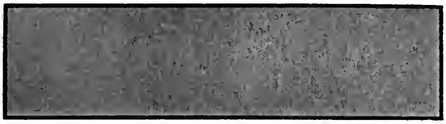
k. Rennin enzyme and rennin zymogen. Rennin is tested for as follows: 10 c.c. of gastric juice are exactly neutralized with decinormal alkali and mixed with an equal volume of neutral unboiled milk. The mixture is placed in a thermostat at 38° C. (100° F.). If a casein coagulum is formed in ten to fifteen minutes, the coagulation is due to the rennin enzyme.

Rennin zymogen is detected thus: 10 c.c. of gastric juice are

PLATE VII.

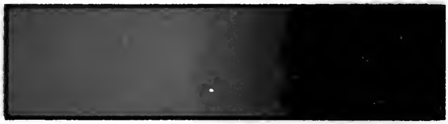
INDICATORS FOR ALKALIES AND ACIDS.

1



Litmus.

2

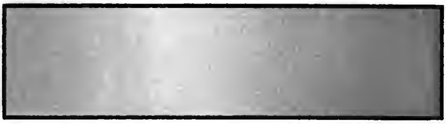


Congo red.

3

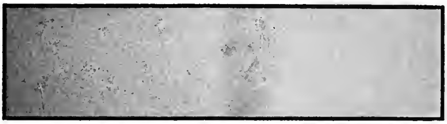
Phenolphthalein.

4



Methyl-orange; Dimethyl-amido-azobenzol; Tropæolin D.

5



Alizarin for acids.
Uffelmann's test for lactic acid.

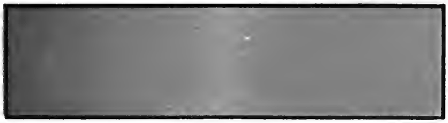
6

Günzburg's phloroglucin-vanillin test or Boas' resorcin test for free hydrochloric acid.

7

Methyl-violet.

8



Hæmatoxylin.

A. Hoen & Co. Lith. Baltimore, Md.

The colors on the left indicate alkaline, those on the right acid reaction.
For explanation see page in Index.

rendered feebly alkaline and mixed with 2 c.c. of a 1 per cent. solution of calcium chloride and 10 c.c. of milk. If the rennin zymogen be present, a heavy cake of casein is precipitated in a few minutes.

l. Detection of proteins. Of these, syntonin, albumoses, and peptones are to be looked for. *Syntonin:* The gastric filtrate is exactly neutralized, whereupon a cloudiness or precipitate is formed, which is soluble both in alkalies and in acids. *Albumoses:* These are precipitated by a saturated solution of ammonium sulphate, while peptones remain in solution. *Peptones:* These are recognized by the biuret-test. The juice is rendered strongly alkaline with potassium hydroxide and a few drops of a cupric sulphate solution (1 in 1000) are added. A red color indicates the presence of peptones.

m. Detection of carbohydrates. Starch is recognized by the blue color produced by iodine solution (1 iodine, 2 potassium iodide, 100 water). The reaction is less marked in proportion to the amount of starch converted into dextrin and sugar.

Erythrodextrin gives a mahogany-brown color, and *achroödextrin* remains unchanged by the iodine solution. Inasmuch as sugar is present in the test-meal itself, it is useless to test for this substance.

Intestinal digestion. The changes in food taking place in the small intestine are much more complex and far-reaching than those occurring in the stomach. Little or no absorption takes place from the stomach, and the alterations in the food brought about by the gastric juice can be considered as being largely preparatory for the action of the digestive fluids of the intestine. The close dependence of one part of the process of digestion on the other is shown by the normal effect of the entrance of chyme into the duodenum. The acid chyme causes a reflex secretion of the pancreatic juice, the bile, and the intestinal juice, the digestive fluids of the intestine. These fluids are all alkaline, and are secreted in sufficient quantity to neutralize the chyme and to provide the degree of alkalinity most suitable for the action of the ferments which complete the process of digestion. A slight increase of the acidity of the gastric contents is followed by an increase in the secretion of the digestive fluids of the intestine. Intestinal digestion depends upon three secretions: (1) the pancreatic juice; (2) the bile; (3) the succus entericus, the secretion of the intestine.

Pancreatic secretions. The secretions of the pancreas are of two kinds, an external, the pancreatic juice, which flows into the intestine, and an internal secretion, which passes directly into the blood, and has a governing power over the metabolism of sugar and the conversion of glycogen into sugar by the liver.

Pancreatic juice. There is no thoroughly reliable analysis of this highly complex liquid on record. It is an alkaline liquid containing from 3 to 6 per cent. of solids, two-thirds of which are of organic, one-third of inorganic nature. Among the organic constituents are a number (certainly three, probably four) of enzymes: 1. *Amylopsin* converts starch into sugar (this action is more energetic than that of ptyalin); 2. *Trypsin* converts proteins into peptones (this action takes place in alkaline, but not in acid solution, as in case of pepsin); 3. *Steapsin* decomposes fats into glycerin and fatty acids; 4. A milk-curdling enzyme. The inorganic solids are chiefly alkali chlorides and carbonates, with some calcium, magnesium, and iron phosphates.

The quality of the food has an unmistakable influence on the composition of the juice and on the quantity of the different enzymes. Thus, the juice is always richest in diastatic enzyme after a bread diet, and richest in steapsin after a meal consisting of much fat.

The secretion of pancreatic juice is thought to be caused by stimuli reaching the pancreas by two routes: (1) nervous stimuli by the sympathetic nerves; (2) chemical stimuli by the blood-stream. The chemical substance concerned is termed *secretin,* and is formed in the intestine as soon as hydrochloric acid is admitted from the stomach during the course of digestion. The HCl acts upon a substance normally present (prosecretin), transforming it to secretin, which is absorbed and carried by the blood to the pancreas. Secretin belongs to the class of bodies called *hormones.*

The trypsin of the pancreatic juice is for the most part secreted in an inactive or zymogen state (trypsinogen), and becomes active when it meets the kinase of the intestine (enterokinase). The other enzymes (amylopsin, steapsin) are secreted mainly in the active condition.

Amylopsin (*diastase*) is closely related to ptyalin, and converts raw or boiled starch into erythrodextrin, achroödextrin, and finally into maltose and dextrose. The dextrose is probably formed by the invertin of the intestinal juice.

Experiment 81. (*Diastatic action of pancreatin.*) Dissolve 1 gramme of pancreatin in 500 c.c. of water, and after standing at 40° C. (104° F.) for two hours filter the solution. Mix in a test-tube equal volumes of the solution and starch paste, prepared as directed in Experiment 79, and heat at 40° C. (104° F.). Notice that the material gradually becomes transparent, reduces Fehling's solution, and is not colored blue by iodine solution. Repeat the experiment with a boiled solution of pancreatin, and notice that it has no effect on starch, the enzyme having been destroyed by heat. (The pancreatin solution itself should be tested with Fehling's solution, as the commercial article is frequently adulterated with sugar.)

Steapsin (*lipase*) splits the neutral fats into fatty acids and glycerin. The liberated fatty acids combine with alkali of the pancreatic juice, forming soap. The action of lipase is materially aided by the presence of bile, although it is not understood how this occurs.

Experiment 82. (*Fat-splitting action of steapsin.*) (Fresh pancreas must be used for the experiment.) Shake about 2 grammes of butter with a few c.c. of lukewarm water, to which a drop of caustic soda solution has been added. After cooling shake with an equal volume of ether, pour the ethereal solution on a watch-glass and allow the ether to evaporate. To the neutral butter fat thus obtained add a piece of fresh pancreas the size of a pea, mix the materials intimately by rubbing, and place in a thermostat at 40° C. (104° F.). After a few minutes the odor of butyric acid will be recognized.

Shake a gramme of butter fat, obtained as above, with about 5 c.c. of lukewarm water, render slightly alkaline with sodium carbonate, using rosolic acid as an indicator, add some fresh pancreas converted into a thin paste by grinding with water, and keep the mixture at 40° C. (104° F.) for twelve hours. Notice that the mixture turns yellow, due to the acid liberated from the butter fat. The experiment when made with boiled pancreas does not show liberation of acid.

Trypsin breaks down proteins by a series of changes almost identical with those produced by pepsin. It is, however, most active in an alkaline medium, and has a more rapid and complete action than that of pepsin. The digestions by pepsin and trypsin are to a certain extent supplementary to each other, for it is found that proteins subjected to both are more thoroughly decomposed than by either one alone. Under normal conditions it is probable that tryptic digestion produces a considerable amount of amino-bodies, and that the remainder of the peptones and proteoses are split up by the intestinal enzyme, erepsin.

Experiment 83. (*Artificial tryptic digestion.*) To 250 grammes of protein add a solution of 5 grammes of sodium carbonate, 3 grammes of pancreatin, and 5 c.c. of chloroform. Keep in a thermostat at 40° C. (104° F.) for ten days. Then filter off a few c.c. of the liquid and add bromine-water. A violet color is produced, due to tryptophane. Acidify the digested mixture with acetic acid, boil, filter, evaporate filtrate to 150 c.c., and allow to stand in a cool place. In a few hours crystals of tyrosine will be deposited. Decant the mother-liquor and purify the tyrosine by recrystallizing from a solution containing a little ammonia. Use the crystals to test for tyrosine (see Index).

Evaporate the mother-liquor from the tyrosine to a thin syrup, add 200 c.c. of hot alcohol, allow the mixture to cool, and filter. Evaporate the filtrate to dryness, dissolve the residue in water, and boil with freshly prepared lead hydroxide. Allow to cool, filter, free the filtrate from lead by means of hydrogen sulphide, and evaporate to a small volume. The leucine which is precipitated on standing is best separated from the mother-liquor by placing the mass on a plate of porous clay. Use the crystals to make reactions for leucine (see Index).

Bile, secreted by the liver, is a thin, transparent liquid of a golden-yellow color, and a specific gravity of 1.020; it has a very bitter taste and an alkaline reaction; it varies widely in composition, the total solids ranging from 9 to 17 per cent., being always highest after a meal; its composition, moreover, is highly complex; the following is an average of five analyses of bile from subjects with healthy livers:

Water	91.68	per cent.
Mucus and pigment	1.29	"
Taurocholate of sodium	0.87	"
Glycocholate of sodium	3.03	"
Fat	0.73	"
Soaps	1.39	"
Cholesterin	0.35	"
Lecithin	0.53	"

Bile obtained after death is of a brownish-yellow color; freed from mucus it will remain undecomposed for an almost indefinite period. The mucus may be separated by the addition of diluted alcohol and subsequent filtration.

The quantity of bile discharged daily by a grown person may be put at from 1000 to 1700 c.c., or from 23 to 47 ounces, but a considerable quantity of this discharged bile is reabsorbed in a changed form by the intestines; only a small amount of bile matters (in a decomposed state, however) is contained in the feces.

Bile is to be regarded both as a secretion and an excretion, as will be seen below in the statements concerning its constituents. It has long been believed that bile is an intestinal antiseptic. Its action is, however, weak and probably unimportant, as it has been found that certain bacteria (B. typhosus, B. coli) grow well in media containing bile.

Biliary pigments. Several pigments have been found in bile, but it is probable that only two, bilirubin and biliverdin, occur in normal bile.

The bile-pigments are formed in the liver from hæmoglobin by a process in which the iron is split off and retained in the organism. While the pigments of the bile are regarded as waste products of metabolism, a certain portion of them is absorbed in the intestine, is excreted again by the liver, and also by the kidneys (as urochrome and urobilin). That portion which passes out with the feces is reduced to stercobilin (isomeric with urobilin).

Bilirubin, $C_{16}H_{18}N_2O_3$, is a reddish-yellow pigment derived from hæmatin, which it resembles. It is sparingly soluble in water, alcohol, and ether, readily soluble in hot chloroform and carbon disulphide.

Biliverdin, $C_{32}H_{36}N_4O_8$, is a green powder existing in green biles; it is formed from bilirubin by mild oxidation.

Tests for biliary coloring-matters. A reaction known as *Gmelin's test* may be applied in different ways:

1. Place into a test-tube a few c.c. of a chloroform solution of bilirubin, and pour down the side of the inclined tube an equal volume of yellow nitric acid in such a manner that the liquids do not mix. At the line of junction colored rings appear, being green nearest the solution of the coloring-matter, and progressively blue, violet, red, and yellow. (Plate VIII., 7.)

2. Place on a white porcelain slab a few drops of the solution and alongside of it a drop of yellow fuming nitric acid. On causing the two liquids to come in contact a play of colors as above is seen at the junction.

3. Expose an alkaline solution of bilirubin to the air in an open vessel; it turns green, owing to the formation of biliverdin. The latter answers also to Gmelin's test.

Biliary acids. *Glycocholic acid*, $C_{26}H_{43}NO_6$, and *taurocholic acid*, $C_{26}H_{45}NO_7S$, exist as sodium salts in the bile of man and most animals. Both salts may be obtained as colorless crystals, which dissolve in water, forming solutions with an acid reaction and an intensely bitter taste. Both acids are easily decomposed by heating with alkalies or with dilute acids, also by the action of putrefying material or by chemical changes taking place in the intestines. In all these cases are formed *cholic acid*, $C_{24}H_{40}O_2$, and a second product, which in the case of glycocholic acid is *glycocoll*, amino-acetic acid, $CH_2.NH_2.CO_2H$, and in the case of taurocholic acid, *taurine*, amino-ethyl-sulphonic acid, $NH_2.C_2H_4.SO_3H$.

These acids are formed in the liver, and very likely from some protein material; the mode of formation is, however, not known. As in the case of the bile-pigments, the bile acids in part represent waste material, while a part is reabsorbed by the intestine. The physiological activity of bile acids is concerned mainly with the fats; they aid the saponification by lipase, and promote the absorption of fat (probably by their solvent action). They are believed to hold the cholesterin of the bile in solution.

Test for biliary acids. The biliary acids and their salts show a characteristic reaction known as *Pettenkofer's test.* This reaction is shown by adding very little cane-sugar to the liquid substance under examination, and adding concentrated sulphuric acid in such a manner that the temperature does not rise above 70° C. (158° F.). In the presence of biliary acids a beautiful cherry-red color is developed, which gradually changes to dark reddish-purple. The red liquid when examined spectroscopically shows two absorption-bands, one at F, the other near E, between D and E. Bile acids are not the only substances which show the colors of Pettenkofer's test, but the spectroscopic examination will clear up doubtful cases.

Experiment 84. Evaporate ox-bile to a thick syrup, digest it with 5 parts of pure, cold alcohol for two hours, and filter. Mix the filtrate, which contains sodium glycocholate and taurocholate, with freshly prepared animal charcoal, boil and filter; evaporate to dryness in a water-bath, redissolve in the smallest possible amount of pure alcohol, and add ether until the solution becomes markedly turbid. A white, crystalline mass is deposited in a few hours or days; this is known as *Plattner's crystallized bile,* and is a mixture of the two sodium salts mentioned.

Dissolve the mass in a small volume of water, adding a little ether and then dilute sulphuric acid; glycocholic acid crystallizes out in shining needles. Taurocholic acid is easiest prepared by using dog's bile, which contains no glycocholic acid.

Apply the Pettenkofer test to the glycocholic acid obtained.

Cholesterin and *lecithin* in the bile are present in considerable amount. They are regarded here as waste products.

Biliary calculi consist chiefly of cholesterin, and in addition they contain bile-pigment, the bile acids combined with calcium, calcium soaps, and calcium carbonate.

Experiment 85. (*Examination of biliary calculi.*) Boil the freshly powdered stones with water to remove bile, filter, and extract the dry residue with a mixture of alcohol and ether. Filter, and evaporate the filtrate to a small volume, when crystals of cholesterin will be deposited. Purify the crystals by dissolving them in boiling alcohol to which a fragment of sodium hydroxide has been added, and treating the mixture in a separatory funnel with ether. By evaporation of the ethereal solution cholesterin is obtained in a pure condition. Apply the tests for the same (see Index).

The residue of the calculi, insoluble in ether and alcohol, consists of the inorganic salts and bile-pigments. Dissolve the salts by pouring dilute hydrochloric acid over the contents in the filter, and show in filtrate the presence of calcium by neutralizing with ammonia, acidifying with acetic acid, and adding ammonium oxalate, when calcium oxalate is precipitated. To a portion of the hydrochloric acid solution add potassium ferrocyanide; sometimes a red precipitate is formed, due to the presence of traces of copper in the calculus.

The residue left on the filter consists of bilirubin. Purify it by washing with water, drying, and heating the mass with chloroform. On filtering and evaporating the solution in a watch-glass rhombic plates or prisms of bilirubin are left, which examine microscopically, and to which apply the tests mentioned above.

Succus entericus. The small intestine secretes several important enzymes: erepsin, which acts mainly upon the proteoses and peptones, splitting them into peptides and amino-bodies; inverting enzymes acting upon the disaccharides (invertase, maltase, lactase); and enterokinase, which is necessary for tryptic digestion. In addition the small intestine forms the prosecretin, from which the stimulating hormone secretin is derived and carried to the pancreas. The succus intestinalis is alkaline, and aids in neutralizing the acid from the stomach.

Fermentative and putrefactive changes. In addition to the alterations brought about by the digestive enzymes, the food also undergoes fermentative and putrefactive changes, due to the action of bacteria, always present in the intestine. Some of these bacteria convert carbohydrates into acetic, butyric, lactic, and succinic acids, while carbon dioxide, methane, and hydrogen are also liberated. Certain fats probably form neurine and similar toxic substances. By putrefaction of proteins are formed: phenol, several aromatic derivatives, notably indole and skatole, volatile fatty acids, carbon dioxide, methyl-mercaptan, and hydrogen sulphide.

As intermediate products, the bacteria convert to some extent the food material into the same substances which are formed by the action of pancreatic juice; these products, however, are not useful to the organism, but are only intermediate stages of far-reaching decompositions. The end-products of bacterial action pass out of the intestine in the feces and as flatus, or are absorbed and carried to the liver, where most of the aromatic compounds are conjugated with potassium acid sulphate, and in this form are secreted in the urine. Thus the quantity of aromatic sulphates in the urine is a measure of putrefaction in the intestine.

Absorption in the small intestine. It seems advisable under this heading to follow in outline the foodstuffs from their ingestion to their delivery into the circulation.

The carbohydrates are first acted upon by the saliva, ptyalin splitting the starches into maltose, and maltase splitting the maltose into dextrose. While this action continues for some time in the cardiac end of the stomach, it is, in all, not very extensive. There is no gastric enzyme acting upon carbohydrates, but a small amount of the simple sugars may be absorbed here. In the intestine the starches are energetically attacked by the amylopsin (diastase) of the pancreas, and the disaccharides are converted into the monosaccharides by the inverting enzymes of the succus entericus. In this manner almost all of the starch and sugar of the food is normally reduced to the hexose form, the greater part being dextrose, with some lævulose, galactose, and pentose (from cane-sugar, milk-sugar, and various vegetables respectively). These simple sugars are absorbed by the small intestine, transferred as such to the blood-stream, carried directly to the liver by the portal vein, and here stored up as glycogen. If an excessive amount of sugar, particularly a simple sugar, be eaten, it is absorbed more rapidly than the organism is able to care for it, and it will appear unchanged in the urine (*alimentary glycosuria, lævulosuria,* etc.). The exact mechanism of this fact is not known. It is commonly believed that the liver is unable to convert more than a certain amount of sugar into glycogen, hence there results an excessive quantity of sugar in the blood, which excess is excreted by the kidneys. The amount of sugar which can be eaten at one time without a resulting excretion is termed the *assimilation limit* of that sugar. The assimilation limit differs for the different sugars and in different individuals.

Fats undergo less digestive change than either carbohydrates or proteins. Their digestion occurs mainly in the intestine, and consists primarily of a saponification into glycerin and fatty acid by the lipase of the pancreas. The biliary fatty acids combine with the alkali of the intestinal contents to form soaps, which produce an emulsification of the neutral fat still present. This emulsification is believed to be of importance in offering a greater surface of fat for the action of the lipase. The bile has two important actions in fat digestion, the bile salts aid the action of the lipase and also act as solvents for both the fatty acids and the soaps. It is believed now that little or no fat is absorbed in the form of an emulsion, and that the greater part is taken up as glycerin and fatty acid (soap). The glycerin is, of course, readily soluble, while the fatty acid is very likely in solution with the bile salts. Apparently the glycerin and fatty acid are at once resynthesized in the mucous membrane of the intestine to neutral fat and passed into the lacteals as an emulsion, which, in turn, is carried to the general circulation by the thoracic duct.

Proteins are digested by three enzymes, pepsin (stomach), trypsin (pancreas), and erepsin. The three carry out what is fundamentally the same process. The pepsin action is exerted mainly to effect the earlier actions, *i. e.*, the change from protein through primary and secondary proteose to peptone; the erepsin is concerned mainly with the later transformation from peptone to polypeptide and amino-bodies (amino-acids), while the action of trypsin is important throughout the entire decomposition. The general course and ultimate results of protein digestion are now fairly clear, and it is universally accepted that proteins are absorbed in the form of the amino-bodies or, perhaps, in part as fairly simple polypeptides, the protein nuclei of Abderhalden. The digestion of protein is believed to have a deeper significance than (as in the case of the carbohydrates and fats) the mere production of soluble and dialyzable substances. As the protein material absorbed by the intestine is converted again to protein, and as the ingested (foreign) protein must give rise to a different (native) protein, it is easy to see that this change must be much more readily carried out if the foreign protein is first split into its component parts, the amino-bodies. Abderhalden believes that not all the protein is necessarily split entirely to amino-acids, but part may remain in the polypeptide form and serve as a nucleus to which the other amino-bodies may be added which are needed for the production of the native protein. The native protein thus formed is conveyed by the portal system to the liver.

Absorption in large intestine. As the large intestine secretes no enzymes, the only digestive action here is due to the enzymes which have been brought down from above. This is probably not of any great moment, as experimental work has shown that, with the exception of water, there is little absorption by the large intestine. It is, however, true that clinical work with rectal feeding shows that persons may be sustained to a certain extent by rectal injections of predigested food mixtures.

Feces consist of the unabsorbed material from the food, the waste material excreted from the blood, detached epithelium, and the secretions of the intestine. The odor depends largely on the indole and skatole, to a less degree on valeric and butyric acids, and on hydrogen sulphide present. The quantity and composition of feces passed depend on the nature of the food and the energy of the digestive powers. A grown person in normal condition discharges from 100 to 250 grammes (4 to 9 ounces) daily. A diet rich in animal proteins causes the quantity of feces to be small, while a diet rich in vegetable and starchy foods increases the quantity. An approximate analysis of the feces of a healthy adult shows:

Water	77.3 per cent.
Mucin	2.3 "
Proteins	5.4 "
Extractives	1.8 "
Fats	1.5 "
Salts	1.8 "
Resinous, biliary, and coloring-matters	5.2 "
Insoluble residue of food	4.7 "

The proteins, other than mucin, are chiefly keratins and nucleins. The principal salts are ammonium-magnesium phosphate, calcium carbonate, calcium and magnesium phosphate. The bile-pigment normally is stercobilin, derived from bilirubin by reduction.

A large proportion of the feces consists of bacteria. The microscopic examination of feces for intestinal parasites and bacteriological examinations are of great value in clinical work. The significance of the chemical findings are not yet well understood except in a few instances (*e. g.*, presence of blood and bile).

Experiment 86. (*Chemical examination of feces.*)

a. Reaction. Normally the reaction of feces is slightly alkaline to litmus.

b. Fat. Extract the feces with ether and evaporate the ethereal solution. Mix a portion of the residue with potassium acid sulphate and ignite; in the presence of neutral fat the characteristic odor of acrolein is noticed. Dissolve another portion of the residue in a mixture of alcohol and ether which has been colored blue-violet by *alkanet* (a dye derived from a plant of the same name, and used as an indicator for certain acids); a red color indicates the presence of fatty acids. (The occurrence of large amounts of fats or fatty acids in the feces may be the result of the ingestion of an excessive quantity of fat, or of imperfect digestion and absorption due to pathological conditions.)

c. Mucin. Mix the feces with lime-water, allow to stand for several hours, filter, and acidify filtrate with acetic acid. A precipitate indicates mucin. To verify the nature of the precipitate, boil it with dilute hydrochloric acid for an hour, then neutralize, and heat with Fehling's solution. A red precipitate proves the substance to have been mucin. (Mucin occurs in the feces in considerable quantity whenever there is catarrh of the large intestine, and in cases of membranous enteritis.)

d. Albumin. Mix the feces with water, acidify with acetic acid, and filter. Test the clear filtrate by adding potassium ferrocyanide. Albumin, when present, coagulates. (Albumin is found in the feces of typhoid fever patients.)

e. Proteose and peptone. Make a thin paste of feces with water, boil, and filter while hot. To the filtrate add lead acetate, filter, and apply the biuret reaction. (Proteose and peptone are found in the feces whenever much pus is produced in the intestine.)

f. Carbohydrates. Boil the residue, left from the extraction with ether (*b*), with water, filter, and evaporate filtrate to a small volume. Test the liquid for sugar with Fehling's solution, and for dextrin and starch with iodine.

g. Blood. When the blood in the feces is derived from the lower portion of the intestine the red color is so characteristic that further examination is unnecessary. When the blood comes from the upper intestine and the pigment has been altered, it becomes necessary to make a spectroscopic examination or the hæmin test, for which see page 658. For the spectroscopic examination, the feces are extracted with water containing a little acetic acid, and the liquid is extracted with ether. If blood is present, the ethereal solution is brownish red. Evaporate the solution to dryness and dissolve the residue in water containing a little sodium hydroxide. The solution is hæmatin in alkaline solution, and will show the characteristic bands, Fig. 72, e. Hæmatin may occur in feces physiologically as a result of a meat diet; pathologically, it is found after hemorrhage into the intestine from any source.

Occult blood is the name given to traces of blood occurring in the feces after small hemorrhages from ulcer of the stomach or duodenum. Its presence is shown as follows: Extract 10 grammes of feces with 25 c.c. of ether to remove fat. To the residue add 5 c.c. of glacial acetic acid and then extract again with 20 c.c. of ether. To this ethereal extract add a little powdered guaiac and then 1 or 2 c.c. ozonized turpentine. A blue color develops on shaking and standing, rendered more intense by the addition of chloroform.

Klunge's aloin test may be used in place of the guaiac reaction. Mix the acetic acid and ether extract of feces, obtained as above, with 1 or 2 c.c. of turpentine, and add immediately about 1 c.c. of a 2 per cent. solution of aloin in 70 per cent. alcohol. In the presence of blood the fluid rapidly becomes bright red in color.

h. Bile-pigments. Shake the feces with a saturated solution of mercuric chloride, filter, and add chloroform. A rose color develops at the junction of the fluids in the presence of urobilin, which is the normal bile-pigment of feces. (The absence of bile-pigment in the feces indicates disease of the liver or obstruction to the flow of bile.)

Extract feces with chloroform, and to the chloroform solution apply Gmelin's test for bile-pigments. (The presence of bilirubin or biliverdin in the stools of adults indicates catarrh of the intestine.)

i. Bile acids. Extract feces with alcohol and evaporate the filtrate to dryness. Dissolve the residue in water containing a little sodium hydroxide, and to the solution apply Pettenkofer's test. (Normally, bile acids are completely absorbed, therefore their presence in feces is pathological.)

j. Ferments. Extract the feces with glycerin, precipitate the solution with alcohol, and dissolve the precipitate in water. To part of the solution add a little starch paste, keep the mixture at 40° C. (104° F.) for several hours, and test for glucose. A positive test indicates the presence of diastatic enzyme. Digest another portion of the solution at the stated temperature with coagulated protein and a little sodium carbonate. Filter and apply the biuret reaction, which, if positive, indicates the presence of proteolytic ferment. (The various digestive enzymes are found in the feces when there is diarrhœa resulting from inflammation of the upper intestine.)

k. Inorganic constituents are determined in the usual manner after drying and incinerating the feces. Present are chiefly earthy phosphates, silica, sodium chloride and sulphate, iron compounds, etc.

Fecal calculi. Feces sometimes contain hard masses, known as coproliths and enteroliths. *Coproliths* are inspissated feces. *Enteroliths* usually consist of concentric layers of earthy phosphates and insoluble soaps around a nucleus of a piece of bone, a fruit-stone, etc. *Pancreatic stones* consist of calcium phosphate and carbonate without cholesterin or bile-pigment. *Intestinal sand* is the name given to certain small calculi occurring in the feces. They are composed of magnesium and calcium soaps, cholesterin, bile-pigment, salts of magnesium, and some of the hydroxy acids, such as succinic acid. The clinical significance of these concretions is not definitely known.

The liver. The anatomical relations of the liver indicate the importance of this organ in assimilation, digestion, and excretion. The digestive function of the liver, which is comparatively slight, and the excretory function are carried out largely by means of the bile. The digestive properties of bile have been considered.

While it is probable that the liver has some action on the protein material brought to it by the portal system directly after its digestion and absorption in the intestine, this has not been proved. It is, however, known that the main nitrogenous excretion of the body, the urea of the urine, is formed here, and is merely excreted by the kidneys. The mechanism of this urea production is not clear. It is likely that the waste nitrogen is brought to the liver in the form of ammonium salts (carbonate or carbamate), and by it is transformed into urea. Liver tissue has the power of producing such a change under experimental conditions, but it has not been proved that the process occurs normally in this manner. In birds the main nitrogenous excretion, uric acid, has also been shown to be formed in the liver.

Glycogen is one of the most important constituents of the liver, and undoubtedly represents a storage supply of carbohydrate material. It is derived for the most part directly from the carbohydrates of the food which have been split in the intestine, absorbed as dextrose and lævulose, and carried directly to the liver by the portal vein. Here these simple sugars are converted into the more complex glycogen by a process of dehydration. It is probable that some of the simple as well as the conjugate proteins can also form sugar and, hence, glycogen. Some of the sugar excreted in diabetes is certainly derived from the proteins. It is not clear, however, that such a change takes place under normal conditions. The question with regard to the fats is in somewhat the same condition. It has been shown that glycogen can be derived from glycerin; hence it can be derived from the fats which contain glycerin, but whether it is normally derived from the fats is not known. When the tissues are in need of sugar to supply them with a source of energy, the glycogen of the liver is split and is distributed by the blood-stream in the form of dextrose. This is seen especially clearly in the case of the muscles, which require a large amount of sugar, and have also the power of storing up a local supply very much as the liver stores up a general supply for the whole body. It is found that in starvation, and particularly in starvation with extensive muscular work, that the store of glycogen in both the liver and the muscles is rapidly exhausted.

Indole and skatole, formed by putrefaction in the intestine, are brought to the liver by the portal vein. *Indole,*  $C_6H_4\left\langle\begin{matrix}NH\\CH\end{matrix}\right\rangle CH$, is oxidized, forming indoxyl, C_8H_7NO, which combines with potassium acid sulphate, with elimination of water, forming indoxyl potassium sulphate, $C_8H_6NKSO_4$, which is excreted in the urine. *Skatole,* methyl-indole, $C_6H_4(CCH_3CH)NH$, is similarly converted into the oxidation product skatoxyl, C_9H_9NO, and skatoxyl potassium sulphate, $C_9H_8NKSO_4$. These substances appear in the urine as the conjugate or ethereal sulphates.

The formation of glycogen from sugar has been mentioned, and its physical properties were considered in Chapter 48.

Experiment 87. (*Preparation of glycogen.*) Digest 50 grammes of fresh liver with 500 c.c. of boiling water containing about 5 c.c. of acetic acid. Strain the liquid through muslin. The solution contains besides glycogen some protein, which remove by concentrating the liquid to a small volume and adding alternately a few drops of hydrochloric acid and of potassium mercuric iodide as long as a precipitate is formed. Filter and mix filtrate with 2 volumes of alcohol, when glycogen is precipitated; purify it by pouring off the supernatant liquid and washing it with 65 per cent. alcohol by decantation. Then cover with absolute alcohol, let stand for an hour, collect the glycogen on a filter, and dry between filter-paper.

Tests for glycogen.

1. Dissolve some glycogen in warm water: an opalescent solution resembling soluble starch solution is formed.

2. To a portion of solution add iodine solution: a reddish-brown color resembling the one produced by erythrodextrin is produced.

3. Heat some of the solution with Fehling's solution: no change occurs.

4. Acidify solution with hydrochloric acid, boil a few minutes,

cool, and neutralize. Divide solution, and heat one portion with Fehling's solution, when the formation of a red precipitate indicates the conversion of glycogen into dextrose. To the second portion add iodine: no change.

5. To some glycogen solution add about half its volume of saliva, keep the mixture at 40° C. (104° F.) for about ten minutes, and test part of solution with iodine, the other portion with Fehling's solution. The results show that glycogen has been changed as in previous test.

The liver has also a neutralizing function, by virtue of which it retains and renders innocuous various toxins and putrefactive products which are absorbed by the intestine.

57. MILK.

General properties. Milk is the secretion of the mammary glands, the presence of which is characteristic of mammalia. The milk of different animals differs somewhat in composition, but it always contains all the constituents necessary for a normal development of the various tissues, liquids, organs, etc., of the young mammal, which generally feeds exclusively upon milk for a shorter or longer period of its early life.

Milk is an opaque, aqueous solution of casein, albumin, lactose, and inorganic salts, holding in suspension small globules of fat, invested, most likely, with coatings of casein or with some other albuminous envelope. The reaction of woman's milk and that of the herbivora is normally alkaline, but that of carnivora is acid. Its specific gravity ranges from 1.029 to 1.033, but may in extreme cases vary between 1.018 and 1.045.

Experiment 88. *a.* Examine milk microscopically; notice the variously sized globules of fat, and compare the appearance of milk, cream, and skimmed milk.

b. Test with sensitive litmus-paper the reaction of fresh cows' milk and of milk that has been exposed to the air for a day or two. The former will be alkaline or amphoteric, due to the presence of mono- and di-calcium phos-

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QUESTIONS.—What is the active principle of saliva, and how does it act on starch? Explain the process of the absorption of protein. State the composition of gastric juice, explain its physiological action, and describe methods for determining its chief constituents. What substances are formed during the conversion of a simple protein into peptone? What are the functions of pancreatic juice? State the composition of the different kinds of calculi found in feces. How are fats digested and absorbed? State the general properties of bile and mention its chief constituents; describe Gmelin's and Pettenkofer's tests. What are the principal constituents of feces? State properties and reactions of glycogen.

phate; the latter will be acid, because lactic acid has been formed by the fermentation of milk-sugar.

c. Boil some fresh milk; no coagulum, but a scum is formed. After removal of the scum it is reformed on boiling. Repeat the experiment with milk that has stood some time; a coagulum is formed.

Composition. The average composition of various kinds of milk is given below, but it must be remembered that milk not only differs in certain species, but also in the same animal at different times; for instance, the quality and quantity of food taken, as also various physiological changes, have decided influence upon the milk secreted.

	Human milk.		Cows' milk.	
	Variations.	Average.	Variations.	Average.
Water . . .	90.8 to 85.3	88.30	90.2 to 83.7	86.70
Casein and albumin	1.4 to 2.5	2.00	3.3 to 5.5	4.40
Fat (butter) . .	3.0 to 3.8	3.40	2.8 to 4.5	3.65
Lactose . .	4.0 to 8.0	6.00	3.0 to 6.0	4.50
Inorganic salts .	0.2 to 0.4	0.30	0.7 to 0.8	0.75

	Goat.	Sheep.	Ass.	Mare.	Cream.
Water . . .	86.0	83.3	90.6	90.6	56 to 71
Casein and albumin	3.8	5.4	2.7	2.2	4 to 3
Fat (butter) . .	5.2	5.3	1.0	1.1	35 to 22
Lactose . .	4.3	5.2	5.3	5.8	4 to 3
Inorganic salts .	0.7	0.8	0.4	0.3	0.7 to 0.7

	Skimmed milk.	Condensed milk.	Butter.	Buttermilk.	Curd.	Whey.
Water . . .	90.6	25	15.0	90.2	59.4	93.5
Casein and albumin	3.1	14	2.2	4.1	27.7	0.8
Fat (butter) . .	0.8	10	82.0	1.0	6.4	0.3
Lactose . .	4.8	49[1]	0.3	3.7	5.0	4.5
Inorganic salts . .	0.7	2	0.5	0.7	1.5	0.6
Lactic acid . .	. .	. .	. .	0.3	. .	0.3

The inorganic salts consist chiefly of calcium or sodium phosphate and sodium and potassium chloride, but contain also some magnesium and iron. The proteins consist mainly of casein with some albumin, the proportion being in cows' milk about as 6 to 1, in woman's milk as 3 to 4.

Besides the constituents mentioned in the above analyses, milk also contains a very small quantity of extractives, among which are found urea, creatine, lecithin, citric acid, phospho-carnic acid, etc. The principles which give to milk its peculiar odor have not yet been conclusively pointed out. The gaseous constituents of milk are mainly carbon dioxide, oxygen, and nitrogen: 100 volumes of milk

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[1] Including cane-sugar added by the manufacturer.

contain of carbon dioxide 7.06, of oxygen 0.1, of nitrogen 0.7 volumes.

Milk contains several enzymes, whose natures vary with their sources. One of these, an *oxidizing ferment* (oxidase, catalase), is a constant constituent, and is of importance because its absence shows that the milk has been heated for preservation.

The presence of an oxidizing ferment in milk can thus be shown: Shake 10 c.c. of milk with 1 c.c. of tincture of guaiac, 5 c.c. oil of turpentine, and 5 c.c. of solution of hydrogen dioxide. A blue color is developed when the ferment is present.

Milk-proteins. The proteins of milk are *caseinogen, lactoglobulin,* and *lactalbumin.* Lactoglobulin and lactalbumin closely resemble the globulin and albumin of the blood-serum, and are believed to be derived from them with little constitutional change. Caseinogen is, on the other hand, a specialized protein containing phosphorus and belonging to the group of phospho-proteins. It is present in milk either in solution or perhaps in combination with phosphates in a partially insoluble form, and this combination may be responsible for some of the opacity of the milk. When milk is acted upon by rennin there is a coagulation of the caseinogen and the formation of a clot. It may readily be shown that this process takes place in two steps. First, the caseinogen is changed by the rennin to a form called paracasein. This substance remains in solution, and the nature of the change is not understood. In the second stage the paracasein forms a combination with the calcium salts of the milk and is precipitated as casein (calcium-casein). The calcium enters only in the second step and has no part in the formation of paracasein. The significance of this coagulation of milk in the stomach is not known. It is frequently stated that a peptone is split off from the caseinogen in the production of paracasein. The process may be hydrolytic in nature, and a preliminary step in the digestion of caseinogen. As implied above, no coagulation will take place if the calcium salts be removed from the milk.

Caseinogen occurs only in milk; it is a phospho-protein, yielding on hydrolysis a pseudonuclein. When dry it is a fine, white powder, insoluble in water, but soluble in dilute salt solution and in water containing a little alkali.

Caseinogen resembles the alkali albuminates in dissolving in water in the presence of calcium carbonate with evolution of carbon dioxide. The solution is precipitated by hydrochloric and acetic acids, the precipitate being soluble in slight excess, and reprecipitated by a large excess of the acid. The solution in lime-water is not precipitated by phosphoric acid, but an opaque fluid is obtained containing casein and calcium phosphate in suspension. The solution is precipitated by alum, zinc sulphate, cupric sulphate, etc. Caseinogen solutions are not coagulated by heat, but, like milk, are covered with a scum.

Experiment 89. (*Preparation of casein.*) To a mixture of 400 c.c. of milk and 1 liter of water add gradually enough (but not more) of acetic acid to precipitate the casein, which also carries down the fat. Decant the liquid, then filter, first through muslin, then through paper, reserving liquid for Experiment 93. Wash the coagulum well with water, press it as dry as possible, then grind it with 100 c.c. of alcohol, and allow to stand for an hour. Filter, dry the coagulum between filter-paper, place it with 200 c.c. of ether into a stoppered bottle and let stand for a day. Collect the precipitate on a filter and add filtrate to the alcoholic filtrate from above; the mixture will be used for Experiment 92. Rub the casein in a mortar until the ether is evaporated. To purify it from fat, mix with water and add drop by drop a 1 per cent. solution of sodium hydroxide until the greater part of the casein is dissolved. The mixture, which should not be alkaline after thoroughly stirring it, is then filtered, when some fat and suspended matter is left behind, while a fairly clear filtrate is obtained. Acidify faintly with acetic acid, wash the precipitated casein with water, alcohol, and ether, and dry between paper.

Tests for casein.

1. Apply the xanthoproteic, Millon's, and biuret reactions.

2. Dissolve casein in a 1 per cent. solution of sodium carbonate; neutralize with acetic acid, when casein is precipitated.

3. Mix some casein in a mortar with freshly precipitated calcium carbonate and water. Casein dissolves, while carbon dioxide is liberated.

4. Dissolve casein in lime-water and add dilute phosphoric acid until the solution is neutral. No precipitate is formed, but the liquid becomes turbid.

5. Heat a mixture of casein with sodium carbonate and potassium nitrate in a crucible (or dry test-tube) until all organic matter has been destroyed. Dissolve mass in water, acidify with nitric acid, filter, and add ammonium molybdate. A yellow precipitate is formed, showing the presence of phosphorus in the casein.

Experiment 90. (*Separation of the proteins.*) Saturate 20 c.c. of fresh milk with powdered sodium chloride: a precipitate consisting of caseinogen and fat is formed. Filter, wash the precipitate with saturated solution of sodium chloride, rub the moist precipitate with 20 c.c. of water, allow to stand for twenty-four hours, and filter. The solution contains caseinogen in the same condition in which it is found in milk. To a portion of the solution add acetic acid: casein is precipitated. To another portion add a solution of rennin and some calcium chloride, heat to 40° C. (104° F.) for a short time, when a precipitate of paracasein is formed.

Saturate the filtrate from caseinogen and fat with magnesium sulphate:

lactoglobulin is precipitated. The filtrate contains lactalbumin, which can be precipitated by saturating the solution with ammonium sulphate.

Experiment 91. (*Action of rennin on milk.*) To 20 c.c. of milk add 4 c.c. of a 0.1 per cent. solution of rennin, mix well, and digest at 40° C. (104° F.). A coagulum consisting of casein and fat soon forms, while an aqueous fluid (whey), containing proteins, milk-sugar, salts, and extractives, is pressed out. After adding a drop or two of acetic acid heat a portion of the whey to boiling: a voluminous coagulum of simple proteins is formed.

Repeat the above experiment with milk from which, by the addition of 2 c.c. of a 1 per cent. solution of ammonium oxalate, the calcium salts have been removed. No coagulum occurs until calcium chloride is added in a quantity sufficient to precipitate any ammonium oxalate left in solution, and to furnish the calcium salt required for precipitation.

Repeat again, boiling the mixture in order to destroy the rennin before the addition of the calcium solution; clotting will occur, showing that calcium is necessary only for the precipitation, not for the interaction between the caseinogen and the rennin.

Milk-fat. It has been mentioned above that the fat of milk is held in suspension as small globules, which are surrounded by a protein envelope. The latter prevents the solution of fat when ether is added directly to milk. If, however, a few drops of caustic alkali be added with the ether, then the envelope will be destroyed and the fat dissolves. Whenever a precipitate occurs in milk the fat is carried down with the insoluble substance and the envelope is generally destroyed. The fat of milk is a mixture of the glycerides of several fatty acids, chiefly of palmitic and oleic, with small quantities of butyric, caproic, caprylic, and stearic acids. Butter fat may be recognized by liberating the butyric acid, which has a characteristic odor.

Experiment 92. (*Liberation of butyric acid.*) Use the mixed ethereal and alcoholic filtrate from Experiment 89. Allow the ether to evaporate spontaneously, and add to the alcoholic solution of butter fat about 5 grammes of potassium hydroxide. Heat the mixture on a water-bath until a drop of it is found to be completely soluble in water, indicating complete saponification. Evaporate until odor of alcohol has disappeared; add 30 c.c. of dilute sulphuric acid, when the fatty acids are set free and butyric acid can be recognized by its odor.

Butter. Even in the thickest varieties of cream there is no cohesion between the fat globules, while in butter the fat has actually cohered. This change is accomplished by violently agitating (churning) the cream, when the fat particles gradually combine with each other, while the liquid (buttermilk) separates.

Chemically, butter is a milk-fat, containing a certain proportion, 15 or 16 per cent., of water, besides traces of casein, salts, coloring-matter, etc. For curing butter, common salt is often used; the quantity added should not exceed 5 per cent.

The composition of buttermilk has been given above; when freshly obtained from sweet cream it is a pleasant drink and a wholesome food.

Milk-sugar. Lactose. The general properties of milk-sugar have been mentioned on page 534. By hydrolysis it yields two simple sugars, dextrose and galactose; when boiled with nitric acid, saccharic and mucic acids are formed, the latter being a characteristic product of the oxidation of galactose. Solutions of milk-sugar are dextrorotatory. Lactose occurs occasionally in the urine of pregnant women, and also in the urine after ingestion of large quantities of milk-sugar.

Experiment 93. (*Preparation of milk-sugar.*) Use the aqueous filtrate obtained in Experiment 89. Free the solution from the remaining proteins by boiling and filtering; evaporate to about 75 c.c., when calcium phosphate will be deposited. Filter, evaporate to a syrup, and set aside, when crystals of lactose will be formed. The crystals may be purified by treating their solution with bone-black aud recrystallizing.

Tests for milk-sugar.

1. To solution of milk-sugar apply Fehling's, Trommer's, Moore's, Boetger's, and Nylander's tests, for which see Index.

2. Add ammonio-silver nitrate and a drop of sodium hydroxide. A mirror of metallic silver forms on heating the mixture.

3. *Indigo-test.* To a dilute solution add enough indigo-carmine to produce a blue color, and render alkaline with sodium carbonate. On heating, the blue solution becomes successively red, yellow, and colorless, or nearly so, in consequence of the deoxidizing power of the lactose. Pour the cooled solution repeatedly from one test-tube into another; the colors are reproduced in reverse order in consequence of the absorption of oxygen.

4. As grape-sugar responds to the above tests, the fermentation-test may be used for distinguishing between the two sugars. Fill two fermentation tubes with glucose and lactose solution, respectively; add yeast, let stand in a warm place, and notice that a gas rises from the glucose, but not from the lactose solution.

Physical and chemical changes in milk on standing.

After leaving the body milk undergoes physical and chemical changes. The principal *physical change* is the separation of milk into two layers: the upper, *cream*, contains practically all the fat, and its proportionate quantity of other constituents; the lower, *skimmed milk*, is almost fat-free. By removing varying quantities of skimmed milk by siphon or otherwise, the proportion of fat in the remainder of the milk is increased.

Of *chemical change*, occurs, particularly on standing in a warm place, conversion of lactose into lactic acid through lactic acid fermentation. The reaction of milk then becomes acid, the casein coagulates and separates as a solid white *curd* carrying with it fat. The remaining thin, transparent liquid, *whey*, contains all the inorganic salts, that portion of lactose which has not been decomposed, as also the lactic acid formed.

There has recently been an extensive use of milk which has been fermented by the Bacillus Bulgaricus, a powerful lactic acid producer. This use has been based upon the belief of Metchnikoff that acid-producing bacteria are antagonistic to the putrefactive bacteria which are normally present in the intestine, hence the milk is advised in cases of intestinal disorder.

Milk also undergoes another peculiar fermentation, by which it is converted into a thick, ropy, gelatinous mixture.

The decomposition of the milk-sugar and with it the "curdling" may be prevented—1, by chemical treatment with alkaline salts or antiseptics; 2, by physical treatment, such as cooling or icing, boiling and aëration; 3, by condensation or evaporation, with or without the addition of a preservative agent. All these systems of preservation, however, are subject to serious disadvantages because they either interfere with the natural constitution and properties of the milk, or because they serve their purpose for too limited a time.

The addition of alkalies such as lime-water, sodium carbonate or bicarbonate, does not prevent the lactic fermentation, but prevents the action of the liberated acid on the casein by forming a lactate of calcium or sodium.

Milk preservatives. The chemical changes in milk are best prevented by cleanliness and preservation at a low temperature. Various antiseptics, such as salicylic acid, boric acid, formaldehyde, benzoic acid, etc., are added to milk with the view of preventing decomposition. While the small quantities used appear to be harmless, yet there can be no doubt that the continued use of milk containing these preservatives is detrimental to health, especially in the case of human nurslings. For this reason many countries, States, and cities prohibit legally the use of preservatives.

Tests for preservatives in milk.

Formaldehyde. Float a mixture of 10 c.c. of milk and 10 c.c. of water in a test-tube, on concentrated sulphuric acid made pale yellow by addition of ferric sulphate. A blue to violet color at the line of junction shows the presence of formaldehyde. Pure milk gives a greenish color.

Salicylic acid. Acidify 25 c.c. of milk with acetic acid, boil, and filter. Extract the filtrate with an equal volume of ether. Shake the ether extract with a dilute (straw-colored) solution of ferric chloride. On separating, the aqueous solution shows a reddish-violet color when salicylic acid is present.

Benzoic acid. Proceed as in the foregoing test, but shake the filtrate with an equal volume of solution of hydrogen dioxide before extracting with ether. By this treatment benzoic acid is converted into salicylic acid, which is then tested for by ferric chloride.

Boric acid and borax. A few drops of the filtrate obtained as in the preceding test are mixed with a drop of strong hydrochloric acid and a drop of saturated alcoholic solution of turmeric. The mixture is evaporated to dryness on a water-bath, and a drop of ammonia added to the residue when cold. A dull-green stain shows the presence of boric acid or borax.

In addition to the test for chemical preservatives, commercial milk is now examined by bacteriological methods, the number and, if possible, the character of the organisms being determined. By extreme care in the production of milk it is possible to keep the count lower than 30,000 per cubic centimeter ("certified milk"). A cheaper method of producing good milk is by heating the milk for a certain time to a temperature below the boiling-point, which will kill all the pathogenic and many of the non-pathogenic bacteria. This method is commonly called "pasteurization." It has the disadvantage that the digestibility of the milk is lessened, an important point in infant feeding.

Experiment 94. (*Analysis of milk.*) As the proportion of fat varies at different periods of the milking, it is necessary to secure a sample from the well-mixed yield of milk. *a.* Determine the specific gravity of milk, cream, and skimmed milk by means of the lactometer (a urinometer answers the purpose).

b. Fat. Determine the total butter fat by using Babcock's method, which is as follows: Place 10 c.c. of milk into a small, specially constructed bottle provided with a long, slender, graduated neck; add 2 c.c. of a mixture of amyl alcohol 37, methyl alcohol 13, and hydrochloric acid 50 parts; then fill the bottle gradually with sulphuric acid. Place the bottle in a centrifugal machine and rapidly revolve for three minutes, when the fat is forced to the top of the mixture. Add enough warm water to float the separated fat into the neck, when the exact percentage can be read on the scale. A special form of bottle, arranged for small quantities, is manufactured for the examination of human milk.

c. Total protein. Separate the skimmed milk from the cream of the sample under observation. Dilute the skimmed milk with 4 parts of water and with this solution fill Esbach's albuminometer (see Index) to the mark *U*, add Esbach's reagent to *R*, and allow to stand 24 hours. Multiply the reading by 5; the result gives the number of grammes per liter. Skimmed milk is used in order to avoid the fat which would be carried down with the protein if whole milk were used.

d. Albumin and globulin. Dilute 25 c.c. of milk with 15 c.c. of water in a 50 c.c. flask, heat on a water-bath to 38° to 40° C. (100° to 104° F.), and add very gradually a saturated solution of potassium alum until a rapidly subsiding coagulum of casein forms. Add water to make 50 c.c., filter, and estimate the simple proteins (albumin and globulin) in the filtrate by means of the albuminometer, as above, multiplying the reading on the instrument by 2. Another method for the estimation of total protein or of the simple protein depends on the accurate determination of nitrogen in milk or in milk after the removal of casein. The percentage of nitrogen multiplied by 6.25 gives the percentage of protein.)

e. Determination of milk-sugar. Lactose can be estimated by titration with Fehling's solution; for details of the operation see chapter on Urine-analysis. A second method depends on the rotatory power of lactose: milk is freed from protein and then examined by the polarimeter.

f. Determine total solids, as well as all other constituents, by following the directions given above.

Human milk. The quantitative differences between human milk and cows' milk have been shown in the table on page 695; they consist chiefly in this, that human milk contains only about one-half the quantity of protein and of inorganic salts, but one-third more of lactose, as compared with cows' milk. In addition, it may be said that human milk is richer in lecithin; moreover, the proteins of human milk differ from those of cows' milk. When human milk is treated with acids or rennin, casein or paracasein is formed less readily than by treating cows' milk in the same way. The precipitates show marked physical differences from one another. Casein from human milk is easily and completely soluble in gastric juice, and human paracasein is precipitated in a loose and flocculent form, which is much more readily digested than the tough and more compact masses from cows' milk. The casein of human milk shows a lower percentage of carbon, nitrogen, and phosphorus, but a higher percentage of hydrogen, sulphur, and oxygen, than casein of cows' milk. Finally, *opalisin*, a protein rich in sulphur, is found in human milk exclusively.

Modified milk, used for infant feeding, is cows' milk, the composition of which has been changed so as to resemble that of human milk. The quantity of fat is increased by adding cream, or by removing part of the lower layer from milk which has separated into two layers (top milk). This mixture is diluted with water to lower the percentage of protein; milk-sugar and lime-water are then added in different proportions, according to the quantity desired.

Although the difference in the composition of human and cows' milk is considerable, the fuel value of both is nearly the same, about 315 calories to the pound of milk.

58. URINE AND ITS CONSTITUENTS.

Excretion of urine. It has been explained in a former chapter how blood absorbs the digested food as chyle, how this is acted upon by the atmospheric oxygen in the lungs, and how this arterial blood, while passing through the system, deposits proteins and other substances, receiving in exchange the products formed by the oxidation of the various tissues. These products are either gases (chiefly carbon dioxide), liquids (chiefly water), or solids held in solution by the water. These waste materials must necessarily be eliminated from the system, and this result is accomplished principally by the kidneys.

The urine is the most important animal excretion; in it are eliminated the nitrogenous waste materials as well as most of the water and soluble mineral substances. A study of the composition of the urine will give important information regarding metabolism, the nature of the chemical processes taking place within the body, as also of the condition of the urinary organs.

General properties. Normal human urine, when in a fresh state, is a clear, transparent aqueous liquid, of a lighter or deeper amber color, having a peculiar, faintly aromatic odor, a bitter, saline taste, a distinct acid reaction on blue litmus-paper, and a specific gravity heavier than water (averaging about 1.020).

In urine, shortly after cooling, especially if it be concentrated, a light, cloudy film of mucus is formed, which slowly sinks to the bottom; the acid reaction gradually increases, small yellowish-red

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QUESTIONS.—Mention the five principal constituents of milk. To what group of compounds does casein belong, how is it obtained, and what are its reactions? Give tests for milk-sugar, and state how it may be distinguished from grape-sugar. What physical and chemical changes does milk suffer on standing? Describe the processes used for preserving milk; what are their advantages and disadvantages? Give approximately the quantities of the chief components of cream, skimmed milk, butter, buttermilk, curd, whey, and cheese; also state how the materials are obtained from milk. Describe the advantages of the combined use of the lactometer and creamometer in testing milk. What are the differences between human and cows' milk? What is paracasein? Give a process for the complete quantitative analysis of milk.

crystals of acid urates, or uric acid, are deposited. In this condition the urine may often continue unchanged for several weeks, provided the temperature be low. If, however, the temperature be above the mean, decomposition speedily takes place. The urine is then found to be covered with a thin, shining, and frequently iridescent membrane, fragments of which sink gradually to the bottom. The urine then becomes turbid, acquires a pale color, its reaction becomes alkaline, and it begins to develop a nauseous ammoniacal odor, due to the products formed by the decomposing action of certain microörganisms (chiefly bacterium ureæ and micrococcus ureæ) upon urea, which is converted into ammonium carbonate and ammonium carbamate. The change from an acid to an alkaline urine causes the precipitation of earthy phosphates, ammonium-magnesium phosphate, ammonium urate, etc.

Points to be considered in the analysis of urine. They are:

1. Color, odor, general appearance—whether clear, smoky, cloudy, turbid, etc.
2. Reaction—whether acid, neutral, or alkaline to test-paper.
3. Specific gravity, and amount for twenty-four hours.
4. Examination of sediments, microscopically and chemically.
5. Chemical examination for the various normal and abnormal constituents.

Samples of urine should always be drawn from the well-mixed and exactly measured quantity of the total urine discharged in twenty-four hours.

If the specimen cannot be examined promptly it should be preserved in a stoppered bottle by the addition of a very small amount of chloroform (3 to 5 c.c. to one liter of urine).

Color. Normal urine is generally pale yellow or reddish yellow, but it may be as colorless as water, or as dark brownish-black as porter; a reddish and smoky tint generally indicates the presence of blood, and a brownish-green suggests the presence of the coloring-matter of bile.

The nature of the normal coloring-matters of urine is as yet doubtful; the existence of three separate pigments has been demonstrated; they have been named *urobilin*, *urochrome*, and *uroerythrin*, and, most likely, are products of the decomposition of biliary matters. Numerous other substances, such as indican, occur occasionally in the urine, and produce various colors, especially when the urine is exposed to air and light, or when acted on by reagents.

Urochrome is the yellowish pigment of urine; the quantity excreted, as far as known, has no clinical significance. It is probably a derivative of bilirubin.

Uroerythrin is a red pigment, and causes the pink color often seen in urinary sediments. It occurs in very minute quantity in normal urine, and is increased by muscular activity, profuse sweating, excessive eating, alcohol excess, digestive disturbance, circulatory disturbance of the liver, malaria, pneumonia, and many other pathological conditions. Whenever present in sufficient quantity to give a rose color to the sediment or to the precipitate produced by adding barium chloride to the urine, uroerythrin is excreted in increased quantity.

Urobilin, a reddish-brown pigment, occurs normally in very small quantity, but it increases considerably whenever there is great destruction of hæmoglobin in the body (internal hemorrhage, pernicious anæmia, poisoning by antipyrine), in cirrhosis of the liver, and during high fever. When present in excessive quantity urobilin colors the urine a dark brownish-red, and the foam shows a yellow or yellowish-brown color.

It is thought to be usually present in the condition of a chromogen, called urobilinogen, producing the pigment urobilin after being acted upon by light or by an acid.

The presence of urobilin can be demonstrated by the spectroscopic examination of urine to which a small amount of hydrochloric acid has been added. It may be necessary to let this mixture stand a short time, or to dilute it, or to examine the amyl alcohol extract. The characteristic spectrum shows a single band between B. and F. Urine containing urobilin will give a green fluorescence on the addition of 1 per cent. zinc chloride, if it has been previously made alkaline with ammonia and filtered.

Abnormal coloring-matters are chiefly those of blood, bile, and of certain vegetables and drugs.

Blood-pigment is usually present alone as methæmoglobin in hæmoglobinuria, and associated with the red blood-corpuscles in hæmaturia. Bile-pigment will be discussed later.

The ingestion of rhubarb, senna, or santonin produces a bright yellow color in the urine which becomes red on the addition of an alkali. Methylene-blue is excreted by the kidneys and colors the urine blue. Urines which become very dark on standing occur after the ingestion of phenol, in cases of melanotic sarcoma (melanogen), and in alkaptonuria, an unexplained pathological condition in which homogentisic acid and uroleucic acid (alkapton) are excreted by the kidneys.

Odor. The normal odor of fresh urine is characteristic, and is sometimes spoken of as aromatic; it is not known by what substance or substances this odor is caused. The ammoniacal and putrescent odor which urine acquires on standing is due to the products of decomposition formed, chiefly ammonia.

A number of substances taken internally and separated by the kidneys from the blood, cause the urine to assume a characteristic odor; aromatic substances especially impart such odors; oil of turpentine gives an odor reminding of violets, and the odor of cubebs, copaiba, asparagus, garlic, valerian, and other substances is promptly transferred to the urine of persons using these drugs internally. A sweetish smell sometimes attends the presence of large quantities of sugar in urine.

Volume. The amount of urine in twenty-four hours varies greatly under physiological conditions. It is usually between 900 and 1500 c.c. It is influenced very largely by the amount of water ingested, by sweating, by diarrhœa, etc. It is decreased in acute nephritis, increased in chronic nephritis, diabetes mellitus, and diabetes insipidus.

Reaction. This is generally acid in healthy urine which has been recently passed, but may become neutral or alkaline within a short period, by decomposition of urea and formation of ammonium carbonate and carbamate. The acid reaction of urine is due to monosodium ortho-phosphate, NaH_2PO_4, and to free organic acids. These organic acids have not as yet been identified.

While urine shows an acid reaction generally, it may have a neutral or even alkaline reaction. In many cases this alkaline reaction points to decomposition of urea in the bladder, but it may be due also to the elimination of alkali carbonates, derived from food taken or drugs administered.

Thus, the alkali tartrates, citrates, acetates, etc., have (after digestion) a tendency to neutralize the urine, and an excess of them is eliminated as carbonate.

To distinguish between the harmless alkaline reaction caused by fixed alkalies and the alkaline reaction produced by decomposition of urea, a piece of red litmus-paper may be used. If this, after having been moistened with the urine, remains blue on drying (by warming gently) the reaction is due to the fixed alkalies; if the red color reappears, the alkaline is due to ammonia compounds.

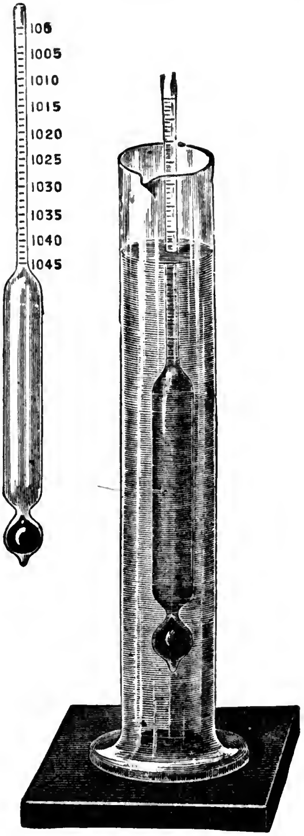
This distinction possesses no importance in urine which has become alkaline on standing.

Urine sometimes is amphoteric in its reaction, *i. e.*, it colors red litmus-paper faintly blue, and blue litmus-paper slightly red. This condition is caused most likely by the simultaneous presence of monosodium orthophosphate, NaH_2PO_4, which has an acid, and of disodium orthophosphate, NaH_2PO_4, which has an alkaline, reaction.

The acidity of the urine is best determined in the following manner (Folin): 25 c.c. of urine are shaken in a flask with 15 to 20 grammes of powdered potassium oxalate, 1 to 2 drops of phenolphthalein ($\frac{1}{2}$ per cent. solution in alcohol) are added, and the mixture titrated at once with $\frac{N}{10}$ sodium hydroxide. The end-reaction is the formation of a distinct pink color. The acidity of the urine is usually expressed in terms of $\frac{N}{10}$ acid or alkali for twenty-four hours.

The oxalate is added to precipitate calcium, and thus avoid the deposition of calcium phosphate as the mixture becomes alkaline. It also reduces the error due to ammonium.

FIG. 73.



Urinometer.

Specific gravity. The normal specific gravity of an average amount of 1500 c.c. of urine passed in twenty-four hours is about 1.020, but it varies, even in health, from 1.012 to 1.030 or more. A specific gravity above 1.030 may indicate the presence of sugar, larger quantities of which may cause the specific gravity to rise to 1.050. Albuminous urine is frequently of low specific gravity, 1.010 to 1.012, especially in chronic nephritis.

It should be remembered that the specific gravity of urine considered separately from the quantity of urine passed in twenty-four hours is of no value, and that in some diseases (for instance in acute nephritis with albuminuria) the specific gravity of albuminous urine may be as high as 1.030, while a diabetic urine may have a specific gravity of 1.025, or less, in consequence of a large volume passed.

The determination of the specific gravity of urine is generally accomplished by the *urinometer*, which is a small hydrometer indicating specific gravity from zero (or 1000) to 60 (or 1060). (See Fig. 73.) As the temperature influences the density of liquids, a urinometer can only give correct results at a certain degree of temperature, which is generally marked upon the instrument.

Composition. Urine is chiefly an aqueous solution of urea and inorganic salts, containing, however, always some uric acid, coloring-, and other organic matters.

Urine also contains gaseous constituents, amounting to about 16 per cent. by volume; these gases are chiefly carbon dioxide (88 per cent.) and nitrogen (11 per cent.), with very little oxygen (1 per cent.).

The quantity of urine passed in a day also varies widely, an adult discharging from 500 to 2300 c.c. in twenty-four hours; a normal average quantity is about 1000 to 1500 c.c. (about 36 to 54 ounces). The quantity of total solids contained in this urine varies from 55 to 60 grammes (840 to 920 grains), and about one-half of this quantity is urea.

As many of the so-called pathological constituents of urine are actually present in minute quantities in normal urine, it is difficult to make an absolute distinction between physiological and pathological constituents. Below is given a working classification of the more important constituents, regarding as normal those whose presence may readily be shown by clinical tests. Accordingly, indican, for example, is placed with the normal bodies, while acetone is placed with the pathological substances, though both are normally present in small amounts.

Normal constituents.

- Nitrogen as
  - Urea.
  - Ammonia.
  - Creatinine.
  - Uric acid.
  - Other bodies
    - Xanthine bases.
    - Allantoin.
    - Hippuric acid.
- Chlorine as chlorides.
- Phosphorus as phosphoric acid.
- Sulphur as
  - Neutral sulphur.
  - Oxidized sulphur = sulphates:
    - (1) Inorganic (K, Na, etc.).
    - (2) Organic (ethereal).
      - Indole (indican).
      - Skatole.
      - Phenol.
- Sodium, Potassium, Calcium, Magnesium, — Combined with acids.
- Oxalic acid.
- Pigments.
- Enzymes.

Pathological constituents.

Proteins:
- Serum albumin.
- Serum globulin.
- Albumose (proteose).
- Peptone.
- Bence-Jones albumin.
- Hæmoglobin.

Carbohydrates:
- Glucose (dextrose).
- Levulose.
- Maltose.
- Lactose.
- Pentose.

Glycuronic acid.

Acetone bodies
- β-oxy-butyric acid.
- Diacetic acid.
- Acetone.

Biliary acids, biliary pigments.
Melanin.
Alkapton.
Unknown body or bodies giving the Ehrlich diazo-reaction.

Determination of total solids. An approximate determination of total solids may be deduced from the specific gravity of the urine, as it has been found that the last two figures of the specific gravity of urine, multiplied by 2.2, correspond to the number of grammes in 1000 c.c. of urine. If, for instance, 1450 c.c. of urine, of a specific gravity of 1.018, have been discharged in twenty-four hours, then the quantity of total solids in 1000 c.c. will be 18 × 2.2, or 39.6 grammes; and in 1450 c.c., 57.42 grammes.

A more exact method of determining the total solids in urine is the evaporation of about 10 c.c. in a weighed platinum dish over a water-bath (or, better, under the receiver of an air-pump over sulphuric acid), until it is found that no more loss in weight ensues on continued exposure of the dish in the drying apparatus. By now reweighing the dish, plus contents, and deducting from the weight that of the empty dish, the weight of total solids is found. This determination has practically no clinical value.

Determination of inorganic constituents. The platinum dish containing the known quantity of total solids is exposed to the action of a non-luminous flame, and the heat continued until all organic matter has been destroyed and expelled. By reweighing now, and deducting the weight of the platinum dish, plus ash, from the weight of the dish, plus total solids, the quantity of total organic matter is determined; and by deducting weight of dish from weight of dish plus ash, the total quantity of inorganic matter is found.

The analysis of the ash is effected by the methods given in connection with the consideration of the various acid and basic constituents themselves. *Chlorine* is determined by precipitating the solution of the ash in nitric acid with silver nitrate, *sulphuric acid* by barium chloride, *phosphoric acid* by ammonium molybdate, *calcium* by ammonium oxalate, *potassium* by chloroplatinic acid, *iron* by potassium ferrocyanide, etc.

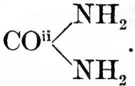
As the methods outlined above are too involved for clinical work, no details are given. Modern methods for quantitative urinary analysis are practically all volumetric, and will be described for the various constituents of the urine.

Nitrogen in the urine. The nitrogen in the urine is derived directly from protein metabolized. As only a small part of the nitrogen is excreted in the feces and sweat, the estimation of the urinary nitrogen is the most commonly used procedure for determining the amount of protein broken down in the body. The total nitrogen varies from 10 to 16 grammes a day, and, as indicated above, varies with the protein metabolism. Thus it is increased with a heavy meat diet, with fever, in diabetes, etc. The approximate distribution of the urinary nitrogen is:

Urea	85 per cent.	
Ammonia	5–6 per cent.	
Creatinine	4 per cent.	
Uric acid	0.5–1 per cent.	
Other nitrogen	3–5 per cent.	(hippuric acid, xanthine bases, etc.).

The estimation of nitrogen alone has little clinical value, but it is frequently done in order to find the percentage of ammonia, which is very valuable. The method used is the customary Kjeldahl method (p. 445), using the Gunning mixture of sulphuric acid, sodium sulphate, and copper sulphate.

Normal nitrogenous constituents of urine. The more important are urea, uric acid, ammonia, creatinine (creatine). Less important are the xanthine bases, hippuric acid, etc.

Urea, Carbamide, $CO(NH_2)_2$, or  $CO^{ii}\begin{matrix}NH_2\\NH_2\end{matrix}$. 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, the formation of which in the liver has been considered heretofore. Urea has never yet been found as a product of vegetable life, but is found as a normal constituent of the urine of the mammalia, and in smaller quantity in the excrement of birds, fishes, and some reptiles. It occurs in small quantities also in blood, muscular tissue, lymph, perspiration, and many other animal fluids. Pathologically urea may appear in all fluids and tissues.

When pure, urea crystallizes from an aqueous solution in colorless prisms; it is colorless, and has a cooling, bitter taste; it easily dissolves in water, the solution having a neutral reaction; it fuses when heated at 130° C. (266° F.), but decomposes at a higher temperature, giving off ammonia gas and water, while a number of other substances are formed at the same time. 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:

$$CO(NH_2)_2 + 2H_2O = CO_2 + 2NH_3 + H_2O = (NH_4)_2CO_3.$$

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.

Urea forms with acids definite salts, and with certain oxides and salts definite compounds.

Urea is formed artificially by numerous decompositions, as, for instance:

a. By a process similar to the one taking place in the animal system, viz., by limited oxidation of albuminous substances by potassium permanganate.

b. By oxidation of uric acid in the presence of water:

$$\underset{\text{Uric acid.}}{C_5H_4N_4O_3} + H_2O + O = \underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\text{Alloxan.}}{C_4H_2N_2O_4}.$$

c. By the action of caustic alkalies upon creatine:

$$\underset{\text{Creatine.}}{C_4H_9N_3O_2} + H_2O = \underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\text{Sarcosine.}}{C_3H_7NO_2}.$$

d. By the molecular transformation of ammonium cyanate, which takes place when its solution is evaporated and allowed to crystallize:

$$NH_4.CNO = CO(NH_2)_2.$$

e. By the action of carbonyl chloride, $COCl_2$, on ammonia:

$$COCl_2 + 2NH_3 = 2HCl + CO(NH_2)_2.$$

f. By the action of ammonia on ethyl carbonate:

$$(C_2H_5)_2CO_3 + 2NH_3 = 2C_2H_5OH + CO(NH_2)_2.$$

Urea may be obtained from urine by evaporating it to the consistence of a syrup and mixing the cooled residue with an equal volume of nitric acid, when crystals of urea nitrate, $CO(NH_2)_2.HNO_3$, form, which may be decomposed by barium carbonate into urea and barium nitrate:

$$2[CO(NH_2)_2.HNO_3] + BaCO_3 = 2CO(NH_2)_2 + Ba(NO_3)_2 + CO_2 + H_2O.$$

Experiment 95. Evaporate about 200 c.c. of urine to a syrupy consistence, allow to cool, place the vessel containing the syrup in ice and add slowly with stirring a volume of nitric acid equal to that of the evaporated urine. Set aside for twenty-four hours, collect the crystalline mass of urea nitrate on a filter, wash with very little cold water, allow to drain well, dissolve in hot water, and, while the solution boils gently, add small quantities of potassium permanganate until the solution is colorless. To the hot solution add freshly precipitated barium carbonate as long as carbon dioxide escapes. Filter and evaporate the solution to dryness over a water-bath; boil the mass with alcohol, which dissolves the urea, but does not act on the barium nitrate. Allow the urea to crystallize from the alcoholic solution.

Reactions of urea. There are no very characteristic reactions by which urea can be well recognized. From organic mixtures it is separated by digesting them with from 3 to 4 volumes of alcohol in the cold; the filtered liquid is evaporated to dryness and extracted with alcohol, which again is evaporated. The dry residue may be tested for urea as follows:

1. Dissolved in a few drops of water, the addition of an equal quantity of colorless nitric acid causes the formation of white, shining, crystalline plates or prisms of urea nitrate.

2. If a strong solution of oxalic acid is added, instead of nitric acid, rhombic plates of urea oxalate form.

3. The residue (or urea) heated in a test-tube to about 160° C. (320° F.) until no more vapors of ammonia are evolved, leaves a substance termed *biuret*, $C_2H_6N_3O_2$, which, upon the addition of a few drops of potassium hydroxide solution and a drop of cupric sulphate solution, causes the solution of the cupric hydroxide with a reddish-violet color.

Determination of urea. The amount of urea in twenty-four hours is normally from 25 to 35 grammes. The greater part of it is derived from the exogenous protein metabolism, and the total quantity is thereby largely affected by the diet. It is increased by a meat diet, as is the total nitrogen output; it is decreased in fever. In disease of the two organs most concerned with urea elimination, the liver (formation) and the kidney (excretion), it is usually, though not always, decreased.

The quantitative estimation of urea in urine may be effected by various methods, of which but one will be mentioned, because it requires less time and less skill in manipulation than most other methods. This determination is based upon the fact that urea is decomposed by alkali hypobromites into carbon dioxide, water, and nitrogen:

$$CO(NH_2)_2 + 3(NaBrO) = 3NaBr + CO_2 + 2H_2O + 2N.$$

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 prepared freshly by making the following mixture of:

(*a*) 1 volume of a solution containing bromine, 125 grammes; sodium bromide, 125 grammes; water, 1 liter.
(*b*) 1 volume of 22.5 per cent. sodium hydroxide solution.
(*c*) 3 volumes of water.

$$2NaOH + 2Br = NaBr + NaOBr + H_2O.$$

Of the many instruments recommended for the determination of urea, the latest modification of Doremus' apparatus (Fig. 74) is most convenient. The operation is carried out thus: Some urine is poured into *B*, while the stopcock *C* is closed and then opened for a moment so as to fill its lumen. After having washed the tube *A* with water, it is filled with the hypobromite solution. From the tube *B*, previously filled with urine, 1 c.c. (or less if much urea is present) is allowed to mix with the hypobromite solution, and after the reaction is completed the reading is taken. The degrees marked upon the tube *A* indicate directly the number of grammes of urea contained in the quantity of urine employed.

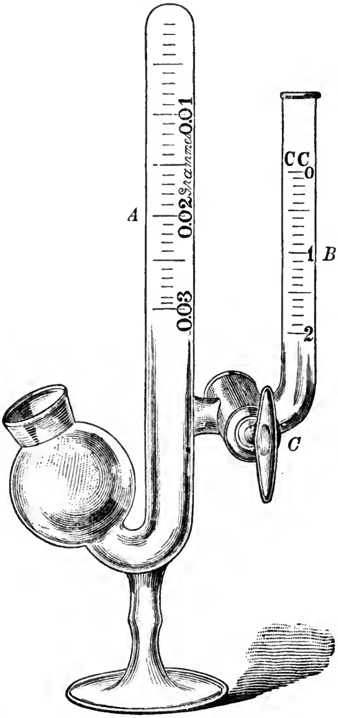
Albumin must be removed, if present, and for careful work the specimen must contain not more than 1 per cent. of urea, which can be readily accomplished by diluting a second specimen.

For careful work this method is not sufficiently accurate, and the Folin method should be used.

Experiment 96. Determine urea in urine by the above-described methods.

Ammonia in the urine. Ammonia is normally present in the urine in small amount, representing about 5 or 6 per cent. of the total nitrogen. The amount seems dependent upon two factors: the ability of the organism to convert the waste nitrogen from the proteins into urea, and the necessity of neutralizing the acid radicals of the urine which are normally in excess of the basic radicals. Accordingly, the urinary ammonia is increased when the urea-forming apparatus is deficient—*i. e.*, in certain disease of the liver. It is likewise increased in the presence of an abnormal excess of acid—*e. g.*, the acidosis of diabetes and of the pernicious type of vomiting in pregnancy. As the absolute amount of ammonia in the urine is greatly modified by the amount of total nitrogen, it is necessary to estimate the amounts of each in order to obtain the important point—the ammonia fraction of the total nitrogen.

Fig. 74.



Doremus' ureometer.

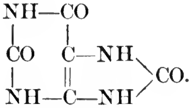
Estimation of ammonia in the urine. The ammonia in a measured amount of urine is set free by the addition of sodium carbonate. By means of a suitable closed system of apparatus and an ordinary suction pump a current of air is carried through this mixture and allowed to bubble up through a measured amount of $\frac{N}{10}$ sulphuric acid. At the end of an hour and a half all of the ammonia will have been carried over, and the excess of acid is titrated with $\frac{N}{10}$ sodium hydroxide with alizarin as an indicator.

Creatinine is normally present in urine to the amount of 1 or 2 grammes in twenty-four hours. It is believed to be derived from the creatine of muscle, and mainly from the body muscle, not the food. Its significance is still much disputed, as an accurate method of estimation has been only comparatively recently devised (Folin, 1905). Creatine is not normally present in urine.

Creatinine is best recognized in the urine by removing the phosphates and coloring-matter by milk of lime, concentrating the filtrate by evaporation, and applying the tests mentioned before. As creatinine is a reducing agent, its presence in urine will influence the tests for sugar based on its deoxidizing power.

Make tests 2 and 3 of Experiment 77, to show the presence of creatinine in urine.

Uric acid, $H_2C_5H_2N_4O_3$. 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 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 gramme.

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 believed that uric acid is derived by oxidation from the purine bodies of the nucleins, and is increased when there is an increase in nuclein metabolism. That coming from the tissue nucleins is termed "endogenous" uric acid; that from the food nucleins is termed "exogenous." While uric acid is formed synthetically in the liver of birds, such a synthesis has not been proved for man. It seems probable that most of the waste nitrogen in birds, as in man, is converted into urea; but is further changed to uric acid for excretion.

The exogenous uric acid is increased on a diet rich in nucleoproteins (sweetbreads); the endogenous uric acid, being derived mainly from the muscles and the leucocytes, is increased after exercise, in leukæmia, etc.

Experiment 97. (*Preparation of uric acid.*) 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 boneblack, 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. (Plate VIII., 4.)

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. Boil with Fehling's solution. A gray precipitate is formed when uric acid, a reddish precipitate when the copper solution, is in excess. (The reaction shows the necessity of exercising judgment in drawing conclusions when testing for sugar in urine with reducing agents.)

4. 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.)

Quantitative estimation of uric acid. Of the many methods described for this purpose, the one which is based on the separation of uric acid and its subsequent titration with potassium permanganate is best adapted for the needs of the physician. It is carried out thus:

Uric acid is precipitated by ammonium sulphate as ammonium urate, which is filtered off and isolated. On the addition of sulphuric acid, uric acid is set free and the amount is titrated with $\frac{N}{20}$ potassium permanganate solution.

Reagents used:

1. Ammonium sulphate, 500; uranium acetate, 5; acetic acid (10 per cent.), 60; water, 650.
2. Ammonium sulphate, 10 per cent. solution.
3. $\frac{N}{20}$ potassium permanganate.

To 100 c.c. of urine add 25 c.c. of reagent 1; let stand until the precipitate has settled (five to ten minutes) and filter through two folded filter-papers. To 100 c.c. of filtrate add 5 c.c. of concentrated ammonia water and let stand for twenty-four hours. Pour off the supernatant fluid through a filter and collect on it the precipitate of ammonium urate with the aid of some 10 per cent. ammonium sulphate; wash with the same solution for a short time. Open the filter and collect the precipitate in a beaker with about 100 c.c. of water. Add 15 c.c. of concentrated sulphuric acid, which will dissolve it. Titrate at once (while hot) with potassium permanganate $\frac{N}{20}$. The end-reaction is the first trace of rose color present throughout the beaker after the addition of *two drops* of the reagent in excess.

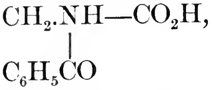
Calculation: As there is used in the titration only $\frac{4}{5}$ of the original amount of urine (taking 100 c.c. of the first filtrate, not the whole 125 c.c.), $\frac{5}{4}$ of the result of the titration is the amount of permanganate which would correspond to 100 c.c. of urine. Each cubic centimeter of the permanganate corresponds to 0.00375 gramme of uric acid from which it is simple to calculate the amount of uric acid present in the urine.

Correction: As ammonium urate dissolves to the extent of 0.003 gramme in 100 c.c., this amount must be added for every 100 c.c. of urine.

Xanthine bodies. The xanthine bodies are normally present in urine in small amount. Those present in largest amount are paraxanthine, heteroxanthine, and methylxanthine, which arise from the similar bodies, caffeine, theobromine, and theophylline, in the food. Otherwise the origin and significance of the purine bodies are thought to be the same as those of uric acid.

Allantoin (glyoxyldiureide), $C_4H_6N_4O_3$, is normally present in minute amounts in adults, more abundantly in the newborn. While it will reduce Fehling's solution, the amount present is never sufficient to give a positive test.

Hippuric acid, $C_9H_9NO_3$ (*Benzoyl-glycocoll, Benzoyl-amino-acetic* *acid*), is a normal constituent of human urine, but is found in much larger quantities in the urine of herbivora. Its constitution is



$$\begin{array}{l} CH_2.NH—CO_2H, \\ \ \ \ \ | \\ C_6H_5CO \end{array}$$

and is the result of the combination of glycocoll and benzoic acid. This synthesis occurs in the kidney. Hay, and especially aromatic herbs, contain benzoic acid, or compounds having a similar composition, and a portion of these compounds is eliminated in hippuric acid. Administration of benzoic acid increases the amount of hippuric acid in urine.

When pure, hippuric acid crystallizes in transparent, colorless, odorless prisms, which have a bitter taste, and are sparingly soluble in water.

Experiment 98. (*Preparation of hippuric acid.*) To 400 c.c. of horse's urine add some milk of lime, heat, filter, evaporate the filtrate to a small volume, and acidify with hydrochloric acid. The calcium hippurate which had been formed is decomposed and the liberated hippuric acid separates either at once or on standing. If too highly colored, dissolve crystals in hot water containing some ammonia, decolorize solution with boneblack, filter, acidify with hydrochloric acid, and recrystallize. Examine crystals microscopically and chemically.

Tests for hippuric acid.

1. Heat in a dry test-tube: a sublimate of benzoic acid is formed and the odor of hydrocyanic acid is noticed.
2. To solution add ferric chloride: a brown precipitate is formed.
3. Heat the dry acid with calcium hydroxide in a test-tube: benzene and ammonia are evolved.
4. Evaporate to dryness with a few drops of nitric acid: an intense odor of nitrobenzene is evolved.

Chlorides in urine. Chlorides are present in larger amount than any other inorganic constituent. As sodium chloride is the most abundant, the total quantity is usually expressed in terms of sodium chloride, and normally amounts to 10 to 15 grammes in twenty-four hours. While the origin of the chlorides is in the ingested food, they bear some relation to the body metabolism, which as yet is not understood. In nephritis there is a retention of chlorides, particularly with the development of œdema. In pneumonia there is a great decrease in the chlorides, with a return to normal amounts at, or even slightly before, the crisis. The significance of these facts is not known.

Qualitative test for chlorides. To a few c.c. of urine, acidified with nitric acid, add a few c.c. of 5 per cent. silver nitrate solution. A white precipitate of silver chloride forms. By comparing the result with that obtained with a known normal urine, a rough estimate can be gotten as to the amount of chlorides present.

Estimation of chlorides. The chlorides in a measured amount of urine are precipitated by the addition of an excess of silver nitrate solution of known strength. The silver chloride is removed and the amount of silver nitrate remaining in solution is determined by the method given on page 427. The following solutions are used: (1) Silver nitrate of such strength that 1 c.c. corresponds to 0.01 gramme of sodium chloride. (2) Potassium sulphocyante of such strength that 1 c.c. corresponds to 1 c.c. of the silver solution. (3) Ammonio-ferric alum, saturated solution.

To 10 c.c. of urine in a 100 c.c. graduated flask add 4 c.c. of concentrated nitric acid and 50 c.c. of distilled water. Add 15 c.c. of the silver solution and dilute the mixture to the 100 c.c. mark, shaking well. Filter off 50 c.c. and titrate with the sulphocyanate solution, after adding 3 c.c. of ammonio-ferric alum. The result multiplied by 2 shows the number of cubic centimeters of silver nitrate which was in excess. The difference between this number and 15 is the number of cubic centimeters of silver nitrate which corresponds to the chloride content of the 10 c.c. of urine.

Phosphoric acid is found in urine, in part (about two-thirds) combined with alkalies, and in part (about one-third) with lime and magnesia. These phosphates have in acid or neutral urine the composition NaH_2PO_4, $CaH_4(PO_4)_2$, $MgH_4(PO_4)_2$; in amphoteric urine, in addition to the above, there occur Na_2HPO_4, $CaHPO_4$, $MgHPO_4$; in alkaline urine compounds of the composition Na_2HPO_4, $CaHPO_4$, $MgHPO_4$, Na_3PO_4, $Ca_3(PO_4)_2$, $Mg_3(PO_4)_2$, $MgNH_4PO_4$ may be present. A small quantity is present as glycerin-phosphoric acid.

The phosphates in urine amount normally to about 3 grammes of P_2O_5 in twenty-four hours. They are derived mainly from the food, and to a much smaller amount from the body protein. They are increased in certain cases of diabetes, and are decreased in most of the fevers. The determination of the phosphatic output has little clinical importance.

On adding any alkali the phosphates of calcium and magnesium (generally termed earthy phosphates) are precipitated; the phosphates of sodium or possibly potassium remain dissolved, and may be precipitated as magnesium ammonium phosphate by the addition of magnesia mixture.

Experiment 99. (*Volumetric determination of phosphoric acid.*) Soluble uranium salts give with phosphates a dirty-white precipitate of uranium phosphate: $Na_2HPO_4 + UO_2(NO_3)_2 = UO_2HPO_4 + 2NaNO_3$. The precipitate is soluble in mineral acids, insoluble in acetic acid. Tincture of cochineal is not affected by uranium phosphate, but is colored greenish by soluble uranium salts. These reactions are used for determining phosphoric acid, thus:

Make up a solution of sodium acetate, 100 grammes; acetic acid (glacial), 30 grammes; and water to make 1000 c.c.

Prepare a volumetric solution of nitrate or acetate of uranium so adjusted that 1 liter is equivalent to 5 grammes of P_2O_5. To 100 c.c. of filtered urine add 5 c.c. of the acetate solution and a few drops of solution of cochineal. Heat to boiling and titrate with uranium solution until the liquid assumes a green color. The number of c.c. required multiplied by 0.005 indicates the quantity of P_2O_5 in the urine used.

Sulphur in the urine. Sulphur is present in the urine in three forms:

Neutral (unoxidized) sulphur; cystine, etc.

Oxidized (acid) sulphur:

a. Inorganic (preformed) sulphates, Na, K, etc.

b. Ethereal (conjugate) sulphates; sulphuric acid in combination with skatole, indole, phenol, etc.

The origin of the urinary sulphur is the protein metabolism, while a small portion may arise from the ingested sulphates. The total amount has little clinical importance. It is increased in fever and with a meat diet. The inorganic sulphates are largely in excess, their amount being about ten times that of the ethereal sulphates.

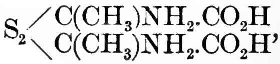
Experiment 100. 1. Demonstrate neutral sulphur by adding HCl to urine with a fragment of zinc; hydrogen sulphide will be evolved and will blacken lead acetate paper.

2. Demonstrate inorganic sulphates by adding barium chloride solution to urine acidified with acetic acid; a white precipitate of barium sulphate will form. Filter this solution; and,

3. Demonstrate ethereal sulphates by adding HCl and barium chloride solution to the filtrate. On boiling the organic sulphates will be broken up and a second precipitate of barium sulphate will form.

Neutral sulphur in the urine. While there is normally present about 10 per cent. of the total sulphur in this form, the bodies which contain it are so far almost unknown. Sulphocyanates are found in small amounts.

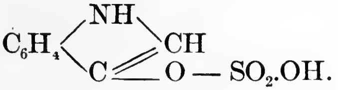
Pathologically the best known body is cystine, which is believed to indicate an inability on the part of the body to completely break down the protein residues.

Cystine, diamino-dithio-dipropionic acid,  $S_2\begin{cases} C(CH_3)NH_2.CO_2H \\ C(CH_3)NH_2.CO_2H \end{cases}$, is secreted by the members of some families, and seems to be without pathological significance, except that it may be deposited in the bladder and form calculi.

Cystine is insoluble in water, alcohol, and ether, but is readily soluble in ammonia-water; boiled with solution of sodium hydroxide a sulphide of sodium is formed which stains silver black. Cystine crystallizes in characteristic regular six-sided tablets, and is best recognized microscopically in the precipitate formed by adding acetic acid to urine. Inorganic sulphates of sodium, potassium, and magnesium are present, but possess no great interest.

Ethereal sulphates. As the conjugated substances (phenol, paracresol, skatole, indole, etc.) are formed in the intestine as putrefaction products of the proteins, and are conjugated (in the liver) merely for excretion, the resulting organic sulphates are increased whenever the intestinal putrefaction is increased. The estimation of these bodies as sulphates is, however, seldom carried out, as the increase is important only when it is marked, and it is simpler to show an increase of the non-sulphate portion. The indican tests are commonly made use of in this connection.

Indican, indoxyl-sulphuric acid, $C_8H_7NSO_4$,



This compound is not identical with the indican found in woad and a few other plants. The vegetable indican is a glucoside, $C_{26}H_{31}NO_7$, yielding by fermentation, among other products, dextrose and indigo-blue, $C_{16}H_{10}N_2O_2$. The latter is identical with the indigo obtained from indoxyl-sulphuric acid, which decomposes into sulphuric acid (or a salt of it), and indoxyl, which latter, by oxidation, yields indigo, thus:

$$\underset{\text{Potassium indoxyl-sulphate.}}{C_8H_6KNSO_4} + H_2O = \underset{\text{Indoxyl.}}{C_8H_7NO} + KHSO_4$$

$$\underset{\text{Indoxyl.}}{2(C_8H_7NO)} + 2O = \underset{\text{Indigo.}}{C_{16}H_{10}N_2O_2} + 2H_2O$$

The source and formation of indican in the body have been mentioned. In urine it occurs normally to the extent of 0.002 per cent., while pathologically the quantity may be much greater. Indican is pale yellow, but is easily converted into indigo-blue, and it is this property which is used for its detection.

Tests for indican.

1. Mix equal volumes of urine and strong hydrochloric acid; then add drop by drop a solution of bleaching-powder until the maximum

of color is attained; add chloroform, which is colored blue. (Care should be taken to add the hypochlorite slowly, as an excess destroys the color; highly colored urine should be decolorized with basic lead acetate; in doubtful cases the mixture of urine, hydrochloric acid, one or two drops of bleaching-powder solution, and chloroform should be set aside for several hours.)

2. *Obermayer's test* depends on the conversion of indican into indigo by ferric chloride; and as this reagent has no further action on indigo, the method has a great advantage over the previous ones. The test is made by following the directions given in the above test, using an equal volume of strong HCl containing 0.2 per cent. of ferric chloride and no bleaching-powder solution.

Indigo-red appears in the urine in the same conditions in which indican is found. It is recognized by Rosenbach's reaction: Urine is boiled, and, while it is still boiling, nitric acid is added drop by drop, when a deep red color appears if indigo-red is present. The foam on shaking the test-tube is bluish red.

Skatole (skatoxyl-sulphuric acid) is rarely present in the urine. Its formation is analogous to that of indole.

Phenol, C_6H_5OH, and *paracresol,* $C_6H_4.CH_3.OH$, occur in urine in combination with potassium acid sulphate. The combined quantity of the two substances is about 0.002 per cent. The quantity is increased during intestinal putrefaction from all causes (except simple obstruction), when there is absorption of pus from abscess or wounds, and after ingestion of carbolic acid.

Experiment 101. (*Determination of phenol.*)

a. Qualitative determination. Render alkaline 100 c.c. of urine with sodium carbonate, evaporate to a syrup, add 20 c.c. of hydrochloric acid, and distill. To the distillate apply the tests for phenol.

b. Quantitative determination. To 500 c.c. of urine add 25 c.c. of hydrochloric acid and distill 200 c.c. Neutralize distillate with sodium hydroxide, in order to convert benzoic and possibly other acids present into salts, and again distill 200 c.c. Determine the quantity of phenol in the distillate by means of decinormal bromine solution, as directed on page 424.

Pyrocatechin, ortho-dioxybenzene, $C_6H_4(OH)_2$, occurs in urine as pyrocatechin sulphuric acid. It is derived from the putrefaction of vegetable food, and is found in large quantity in urine after taking carbolic acid. Urine containing pyrocatechin turns dark on exposure to air, especially if it is made alkaline.

To show the presence of pyrocatechin, add a little sulphuric acid to the urine, boil, and when cool extract with ether. Evaporate the ether, dissolve the residue in a little water, and apply tests.

Tests for pyrocatechin.

1. Add dilute ferric chloride solution: a green color is evolved. Add a little tartaric acid and then ammonia: the green color changes to violet, but on acidifying with acetic acid the green color reappears.

2. Add sodium hydroxide: the solution turns green, brown, and black.

3. Add lead acetate: pyrocatechin is precipitated as a lead compound.

4. Show that Fehling's solution and ammonio-silver nitrate solution are reduced by pyrocatechin, but that it does not act on alkaline bismuth solution.

Sodium, potassium, calcium, and magnesium occur in the urine mainly as inorganic salts. They are derived from the food. The amount present is not important clinically.

Oxalic acid. The source of this acid in urine is unknown. Many vegetables and fruits contain oxalates, which, after ingestion, are secreted to a great extent unchanged. That oxalic acid occurs as a metabolic product is shown by its excretion during starvation, and also when the diet is exclusively protein and fat. It is believed that the protein, and not the fat, is concerned here. An increased elimination of oxalic acid occurs in diabetes, icterus, and in the condition called oxaluria.

Enzymes in urine. Pepsin has been shown to be present in small amount in normal urine; lipase and a diastase have been found in a few cases.

Pathological constituents. While the normal constituents of urine, and especially the quantity excreted in twenty-four hours, give valuable information in regard to the whole process of metabolism taking place in the body, pathological constituents often show with great precision abnormal conditions existing in the body, and the qualitative or quantitative determination of pathological constituents is therefore a valuable aid in diagnosing disease. Of pathological constituents are of chief interest the proteins (albumin, globulin, albumoses, peptones), sugars, and the constituents of blood or bile. But many other substances occur at times, and should not be overlooked in the examination. To these substances belong acetone, diacetic acid, melanin, a compound giving the diazo-reaction, etc.

Proteins in urine. Albumin in urine is always serum-albumin, and is usually associated with serum-globulin. The pathological condition is termed albuminuria. While transient albuminuria may follow severe muscular or mental strain, cold baths, etc., and leave no permanent effect, it must always be regarded as a pathological condition. The most common cause of continued albuminuria is organic disease of the kidneys, acute and chronic nephritis, or even chronic passive congestion. It occurs in all severe febrile conditions, in blood diseases (pernicious anæmia, leukæmia), after chloroform and ether anæsthesia, and after many poisons (cantharides, phenol, etc.). Albumin is present in all urines containing blood or pus arising from any portion of the urinary tract.

Tests for albumin.

1. *Heat and acid.* Heat to boiling the upper portion of urine in a test-tube. If a cloud appears it is due to albumin or phosphates. The lower cold urine serves as a guide for comparison. If no cloud forms, albumin may or may not be present; in any case add a few drops of 5 per cent. acetic acid until the reaction is acid—boiling again after each drop. A cloud already present, due to phosphates, will disappear; one due to albumin will become more distinct. In case albumin is present, but has not already been coagulated, it will form a cloud on the addition of the acid, showing that there was not sufficient acid present originally, the urine being either neutral or alkaline. The test is made more delicate by the addition of one-eighth of the volume of the urine of saturated salt solution, which should always be done with very dilute urines. It is important to avoid an excess of the acid, as the coagulated albumin may go into solution again. If the test is made with the addition of salt solution, it is extremely delicate and rarely misleading. The acetic acid may be replaced by nitric acid, with which an excess of acid is less to be feared, and $\frac{1}{20}$ to $\frac{1}{10}$ volume of concentrated acid can be added. With nitric acid the urine should not be boiled after the acid has been added.

2. *Nitric acid test.* About 20 c.c. of clear urine are placed in a conical test-glass of about 50 c.c. capacity; from 5 to 10 c.c. of nitric acid are added by means of a pipette in such a manner that the acid flows slowly from the pipette, which is carried to the bottom of the vessel. Operating carefully, two distinct layers of liquid are obtained, and in the presence of albumin a distinct white cloud will appear at

the zone of contact, the extent and intensity of the cloud varying with the quantity of albumin present. Very small quantities of albumin cannot be detected at once, but will appear on standing, the cloudiness extending gradually upward. A distinct ring from 1 to 2 cm. above the zone of contact, and appearing within five to ten minutes after the addition of nitric acid, was formerly thought to be due to uric acid, and was called the urate ring. It is believed now to be in some cases composed of protein material. In urines containing a high percentage of urea, a ring may form at the plane of contact, consisting of urea nitrate, which is distinctly crystalline in appearance. Following the ingestion of turpentine and various balsams, this test may show a precipitate of resinous acids at the junction of urine and acid, which is recognized by its solubility in alcohol or ether. Albumoses produce a ring which dissolves on heating and reappears on cooling.

At the zone of contact a change in color is generally noticed. In normal urine this varies from pale red to intense brick red; in biliary urine a color-play similar to the colors of the rainbow may be noticed, while the presence of indican is indicated by a violet or blue tint. It is important to distinguish between color rings and precipitate rings.

3. *Trichloracetic acid* may be used for the detection of albumin by dropping a fragment into a few cubic centimeters of urine contained in a test-tube. As the acid dissolves, a cloudy ring forms in the presence of albumin, which is not dissolved on warming.

4. *Potassium ferrocyanide test.* 5 to 10 c.c. of cold urine are acidulated with 5 to 10 drops of acetic acid, and to the mixture are added a few drops of solution of potassium ferrocyanide. In the presence of even traces of albumin a turbidity is caused. A precipitate which dissolves on heating is due to albumose. This test is extremely delicate, especially when modified so as to allow a few cubic centimeters of diluted acetic acid, to which a few drops of potassium ferrocynaide solution had been added, to flow down the side of the test-tube containing the urine. A decided turbidity at the point of contact of the two liquids shows albumin.

In case the addition of acetic acid to the cold urine should cause a turbidity (which may be due to mucin or nucleo-albumin) it must be filtered before adding the potassium ferrocyanide.

In the above methods the manipulations and precautions are minutely described, in order to detect small quantities or even traces of albumin. When albumin is abundantly present, there is no difficulty whatever in its detection, as heat will precipitate it in most cases from an acid, neutral, or sometimes even alkaline urine ; the precipitate should, however, always be tested by the addition of a few drops of nitric acid, and the previous addition of a few drops of acetic acid is also advisable.

Quantitative estimation of albumin. The average amount of albumin present in acute cases of albuminuria is 0.1 to 0.5 per cent., rarely over 1 per cent., though it may rise to 4 per cent. An approximate method for the comparative estimation of albumin is to precipitate it (with the precautions above given) in a graduated test-tube by heat and setting aside for twelve (or, better, for twenty-four) hours. At the end of that time the proportion of the coagulated albumin which has collected at the bottom of the fluid is noticed. If the albumin occupy one-fourth, one-sixth, one-tenth of the height of the liquid, there is said to be one-fourth, one-sixth, or one-tenth of albumin in the urine. If, however, at the end of twelve or twenty-four hours scarcely any albumin has collected at the bottom, there is said to be a trace.

The volumes of coagulated albumin indicate the following quantities of dry albumin :

Slight turbidity indicates about	0.01 per cent.
$\frac{1}{20}$ of the tube is filled	0.05 “
$\frac{1}{10}$ “ “	0.10 “
$\frac{1}{4}$ “ “	0.25 “
$\frac{1}{3}$ “ “	0.50 “
$\frac{1}{2}$ “ “	1.00 “
Complete coagulation	2 to 3 “

Esbach's albuminometer (Fig. 75) is a conveniently arranged tube for determining approximately the quantity of albumin. The tube is filled with urine to *U*, and then with the reagent to *R*. The reagent is a solution containing 1 gramme of picric acid and 2 grammes of citric acid in 100 c.c. of water. After having filled the tube it is closed with a stopper, inverted twelve times, and set aside for twenty-four hours. At the end of that time the albumin will have settled down, when the amount pro mille in grammes may be directly read off from the scale.

Tsuchiya's reagent possesses many advantages over Esbach's, and is used in the same manner. It is, Phosphotungstic acid, 1.5 grammes; hydrochloric acid (concentrated), 5 c.c.; alcohol, 95 c.c.

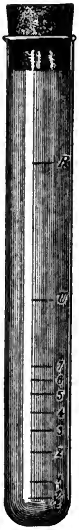
A better method of exactly estimating the amount of albumin is its complete separation and weighing, as described below.

Experiment 102. Acidify 100 c.c. of clear albuminous urine with acetic acid; heat to the boiling-point in a water-bath for half an hour, and filter through a small filter, previously dried at 110° C. (230° F.) and weighed; wash with boiling water to which a little ammonia water has been added (to remove uric acid and urates), then with pure water until the filtrate is not rendered turbid any longer by silver nitrate, next with pure alcohol, and finally with ether. Dry filter and contents at 110° C. (230° F.) and weigh.

As it may happen that the precipitated albumin encloses earthy phosphates, it is well to burn filter with contents in a platinum crucible, and to deduct the weight of the remaining inorganic residue (less the weight of the filter ash) from that of the albumin.

Serum-globulin is detected by rendering the urine alkaline with ammonia water, filtering off the precipitate of phosphates, and adding to the clear filtrate an equal volume of a saturated solution of ammonium sulphate. The appearance of a precipitate indicates globulin.

Fig. 75.



Esbach's albuminometer.

Albumoses answer to the nitric acid test and the potassium ferrocyanide test for albumin; the precipitate formed by these reagents dissolves on heating, but reappears on cooling. Albumoses are further recognized thus: To the urine strongly acidified with hydrochloric acid is added an equal volume of a saturated solution of sodium chloride. On boiling, serum-albumin, if present, is precipitated and filtered off while hot. Albumoses separate from the filtrate on cooling.

The solution, filtered while hot, gives a red biuret reaction. As albumose is frequently present in albuminuria, its demonstration is important only in the absence of albumin. Albumosuria occurs with the absorption of purulent exudates, in acute yellow atrophy of the liver, and in other conditions.

Peptones are not uncommonly present in the urine in albumosuria, but are rarely present alone. Peptonuria exists when it is possible to obtain a red biuret reaction after the careful removal of protein and albumose. Both here and in the case of albumosuria urobilin may mislead one when the biuret reaction is tried. It may be removed by extraction with alcohol.

Bence-Jones body is present in the urine in certain cases of bone disease (multiple myeloma). It is thought to be a unique albumin and not an albumose, as held by the earlier view. It is coagulated in urine acidified with acetic acid on heating to 50° or 60° C., and redissolves as the temperature reaches the boiling-point. It is very rarely present.

Nucleo-albumin. If the ring occurring in Heller's test some distance above the place of contact becomes more distinct when the urine is diluted, it is believed to be of protein origin, and has been called nucleo-albumin, mucin, euglobulin, Mörner's body, etc. Its true nature is not yet known. The cloud produced by acetic acid in the cold is believed to be due to the same body. As urates may be precipitated in both of these methods, it is important to rule them out by diluting the urine, when the precipitate due to urates will not appear. True nucleo-albuminuria is rare.

Blood. The presence of blood in urine manifests itself generally, unless the amount be too slight, by a blood-red or brownish color with a bluish, smoky, or greenish tint, and deposits a red or reddish-brown sediment after standing. As a general rule, all constituents of blood, including the corpuscles, are present (hæmaturia), but in some cases only hæmoglobin (methæmoglobin) is found (hæmoglobinuria).

The tests for blood depend either on the microscope, spectroscope, or on chemical changes. By the microscope is examined the deposit which forms on standing; almost unaltered blood-corpuscles may be found, or they may be much swollen, decolorized, and deformed.

Hæmaturia is common and occurs in diseases of the kidney (acute nephritis, stone, tuberculosis, trauma); similar conditions of the ureters and bladder; general conditions (malignant forms of smallpox, malaria, etc.; hæmophilia).

Hæmoglobinuria occurs occasionally in severe fevers (scarlet fever, yellow fever); after severe burns or exposure to cold; in certain poisonings (potassium chlorate, carbon monoxide). It is always preceded by hæmoglobinæmia, *i. e.*, the presence of free hæmoglobin in the circulating blood. The spectroscope shows the absorption-bands of the blood-pigments, for which see Fig. 72.

Tests for blood in urine.

1. Render alkaline with sodium hydroxide and boil. In the presence of blood coloring-matter the precipitate of phosphates produced is colored red. In a urine containing other coloring-matters (bile-pigments, etc.) the test may be misleading; in such cases, filter off the precipitate, wash, and dissolve it in acetic acid. In the presence of blood-pigment the solution becomes red, but the color gradually disappears on exposure to air.

2. Allow a mixture of freshly prepared tincture of guaiacum and

ozonized oil of turpentine to flow down the side of a test-tube in such a manner as to form a distinct layer above the urine. A white ring, gradually turning blue, will appear at the surface of contact. (Ozonized oil of turpentine is oil which has been exposed to air for some time; in place of it may be used peroxide of hydrogen or a mixture of this compound with ether.)

3. Add a little of a solution of egg-albumin to 100 c.c. of urine, heat to boiling, and filter off the coagulum, which has taken up the hæmatin. Mix the precipitate in a mortar with 20 c.c. of absolute alcohol and a few drops of sulphuric acid, transfer to a flask, heat to boiling, and filter. After cooling, render alkaline with sodium hydroxide, reduce with ammonium sulphide, and examine spectroscopically for reduced hæmatin. (Fig. 72.)

The direct spectroscopic examination of urine is generally unsatisfactory, because it often contains a number of substances giving absorption spectra.

Carbohydrates in urine. Dextrose (glucose) in urine is normally present in minute amount. When the amount is sufficient to give the customary reduction tests, the condition is spoken of as glycosuria. If dextrose be eaten in large amount the body is unable to burn all of it, and a temporary glycosuria results. This is called alimentary glycosuria and is not a serious condition. The amount of sugar, the "assimilation limit," which can be ingested without the appearance of the sugar in the urine, differs for the different sugars and differs in different individuals. A more serious condition, persistent glycosuria, exists in diabetes when the body is unable to carry on the normal sugar metabolism. In this disease the amount of dextrose in the urine may be very large, and frequently dextrose is present, even when the patient is on a carbohydrate-free diet. In both of these conditions the glycosuria is secondary to an increase in the dextrose content of the blood, while in experimental "phloridzin diabetes" the change is in the kidneys, and there is no increase in the dextrose of the blood.

There are many tests by which dextrose can be detected. They depend chiefly on the following properties of dextrose, viz.: 1, to act as a deoxidizing or reducing agent upon certain metallic oxides (copper, bismuth, silver, mercury) in the presence of alkalies; 2, to produce a yellow or brown color when in contact with alkalies, slowly in the cold, rapidly on heating; 3, to ferment with yeast; 4, to unite with phenyl-hydrazine to a crystalline compound; 5, to have the power of rotating the plane of polarization to the right.

Tests.

1. *Trommer's test.* A few drops (2–4) of a 5 per cent. solution of cupric sulphate are added to about 5 to 8 c.c. of urine in a test-tube and then an equal volume of potassium (or sodium) hydroxide solution is added. The alkaline hydroxide precipitates both earthy phosphates and cupric hydroxide, the latter, however, dissolving (especially if sugar be present) in the excess of the alkali, producing a beautiful blue transparent liquid. (If no sugar is present, the color is less blue, but more of a greenish hue.) The liquid is now heated, when, if sugar be present, a yellow precipitate of cuprous hydroxide is formed which subsequently loses its water and becomes the red cuprous oxide, which falls to the bottom or adheres to the sides of the test-tube. (Plate VIII., 5.)

In drawing conclusions from the above test, it should be remembered that a change of color does not indicate sugar; that a precipitate of earthy phosphates must not be mistaken for cuprous oxide; and that substances other than sugar may deoxidize cupric oxide at the temperature of 100° C. (212° F.).

A disadvantage of Trommer's test is the formation of black cupric oxide whenever too much copper solution is used in proportion to the sugar present. The formation of the black oxide, which may mask a small quantity of cuprous oxide, is avoided in the next test.

2. *Fehling's test* differs from Trommer's test in merely using a previously mixed reagent instead of producing this reagent, as it were, in the urine by adding to it cupric sulphate and an alkaline hydroxide successively. This reagent, known as *Fehling's solution*, or as *alkaline cupric tartrate volumetric solution*, is made by mixing exactly equal volumes of the below-mentioned copper solution and the Rochelle salt solution at the time required.

Copper solution:

Crystallized cupric sulphate	34.64 grammes.
Water, sufficient quantity to make	500 c.c.

Rochelle salt solution:

Potassium sodium tartrate	173 grammes.
Potassium hydroxide	125 "
Water, sufficient quantity to make	500 c.c.

Both solutions are preserved in small well-stoppered bottles, and mixed only at the time needed, because the mixture is apt to decompose when kept some time.

The addition of sodium-potassium tartrate in Fehling's solution prevents the precipitation of cupric hydroxide by the alkaline hydroxide. This action is analogous to the formation of the soluble scale compounds of iron, where the precipitation of ferric hydroxide is also prevented by tartaric or other organic acids.

The test is made by heating in a test-tube 10 c.c. of Fehling's solution which has been diluted with 2 to 5 volumes of water and adding drop by drop the suspected urine; if the latter contains larger quantities of sugar, a yellow or red precipitate of cuprous hydroxide and oxide will be produced very readily; if but small quantities are present, the reaction will appear only on standing for some time.

Haines' test is a modification of Fehling's test. The reagent is as follows: "Dissolve 30 grains of cupric sulphate in ½ ounce of water, add ½ ounce of glycerin and then 5 fluidounces of liquor potassæ." The advantage of the reagent is that it is very stable. It should be used by boiling about 1 drachm in a test-tube, adding 8 to 10 drops of the suspected urine, and again bringing to a boil. In the presence of sugar a precipitate of cuprous oxide is thrown down.

3. *Bötger's bismuth test* consists in adding to a mixture of equal volumes of urine and potassium (or sodium) hydroxide solution a few grains of subnitrate of bismuth and boiling for half a minute. If sugar be present, a gray or dark-brown, finally black, precipitate of bismuthous oxide, Bi_2O_2, or of metallic bismuth is formed. If but very little sugar is present, the undecomposed excess of bismuthic nitrate (or bismuthic hydroxide) mixes with the metallic bismuth, imparting to it a gray color; the test should then be repeated with a smaller amount of the bismuth salt. (Plate VIII., 6.)

The above test may be advantageously modified by using a bismuth solution instead of the powder. The solution known as *Nylander's reagent* is made by dissolving 2 grammes of bismuth subnitrate, 4 grammes of Rochelle salt, and 10 grammes of sodium hydroxide in 90 c.c. of water, and filtering. One-half c.c. of this solution is heated with about 5 c.c. of urine, when, in the presence of sugar, a brown or black precipitate will form after a few minutes' boiling.

If the urine contains hydrogen disulphide (sometimes produced by decomposition of certain urinary constituents), black bismuth sulphide will be formed, which may be mistaken for metallic bismuth; albumin itself may be the cause of the formation of alkaline sulphides: the previous complete separation of albumin is therefore indispensable.

4. *Moore's* or *Heller's test* is made by heating urine with about one-fourth its volume of solution of potassium hydroxide. In the presence of sugar the color of the mixture will deepen to a dark yellow or brown, and the depth of color is a fair indication of the quan-

tity of sugar present. In case but a slight change takes place in color, it is well to compare it with that of an unchanged specimen of the urine.

5. *Fermentation test.* This is based upon the decomposition of dextrose by yeast with the generation of carbon dioxide. A piece of yeast about the size of a pea is ground up in urine and the mixture used to fill a fermentation tube. The tube is then kept for twenty-four hours at a fairly constant temperature of 22° to 28° C. If dextrose be present, fermentation will commence within twelve hours and will manifest itself by the formation of carbon dioxide gas, which will collect at the upper end of the long arm of the tube.

The urine and the fermentation apparatus should be sterilized by heat to destroy any gas-producing bacteria present. For a control of the test, two more fermentation tubes should be prepared, one with a mixture of a glucose solution and yeast (to determine that the yeast is efficient), and another with sterilized water and yeast (to show that the yeast itself does not generate gas).

The disadvantages of this process are the length of time required for its performance, the unreliability of the ferment, and the fact that small quantities of sugar (less than 0.5 per cent.) evolve so little carbon dioxide that a doubt may be felt as to the presence of sugar at all.

6. *The phenyl-hydrazine test.* To 10 c.c. of urine in a test-tube, add phenyl-hydrazine hydrochloride, 0.4 gramme and sodium acetate, 1 gramme, warm until dissolved, adding water, if necessary, and keep in a boiling water-bath for half an hour. Filter while hot, and allow to cool slowly. The presence of dextrose will be shown by the deposition of yellow crystals, which are seen with the microscope to be needles arranged in sheaves. This precipitate is an osazone (phenyl-dextrosazone) and melts at 205° C. Pentoses and maltose give similar osazones, as do lactose and glycuronic acid. The latter are rarely present in sufficient amount to give a positive test with the urine directly. The melting-points are of value in recognizing the different osazones.

7. *Polariscopic test.* Before urine can be examined by the polariscope it should be freed from proteins and from the greater part of coloring-matters by precipitation with neutral lead acetate. The sensitiveness of the test depends on the construction of the instrument, but even the best polarimeters do not show traces of sugar, for which reason it is generally useless to apply the test unless sugar has been indicated by other tests.

The following table shows the tests for distinguishing dextrose from other reducing agents occurring in the urine:

	Fehling's test.	Bismuth test.	Fermentation test.	Phenyl-hydrazine test.	Polariscopic test.
Dextrose	Reduction	Reduction	Positive	Positive	Dextro-rotatory
Pentoses	Reduction	Reduction	Negative	Positive	Dextro-rotatory
Lactose	Reduction	Reduction	Negative	Positive	Dextro-rotatory
Lævulose	Reduction (partial)	Reduction	Positive	Positive	Lævo-rotatory
Glycuronic acid	Reduction	Reduction	Negative	Positive	Lævo-rotatory in urine
Alkaptonic acids	Reduction	Negative	Negative	Negative	Inactive
Uric acid	Reduction	Negative	Negative	Negative	Inactive
Creatinine	Reduction	Negative	Negative	Negative	Inactive
Pyrocatechin	Reduction	Negative	Negative	Negative	Inactive
Allantoin	Reduction	Negative	Negative	Negative	Inactive

Quantitative estimation of sugar. By far the best method is the decomposition of a copper solution of a known strength, and Fehling's solution prepared as stated above, answers this purpose well.

1000 c.c. of Fehling's solution, containing 34.64 grammes of crystallized cupric sulphate, $CuSO_4.5H_2O$, are decomposed by 5 grammes of grape-sugar, or 1 c.c. of solution by 0.005 of grape-sugar.

To make the quantitative determination, operate as follows: 10 c.c. of Fehling's solution are poured into a porcelain dish of about 200 c.c. capacity, placed over a flame. The copper solution is diluted with about 40 c.c. of water, and heated to boiling; to the boiling liquid, urine (which has been previously diluted with 9 parts of water) is added from a burette very gradually, until the blue color of the solution has disappeared, and there remains, upon subsidence of the cuprous oxide, an almost colorless, clear liquid. A filtered portion of this liquid, acidified with hydrochloric acid, should not give a reddish-brown precipitate with potassium ferrocyanide (a precipitate would show that all copper had not been precipitated, and that more urine was needed), while a second portion of the filtered fluid should not produce a red precipitate on boiling with a few drops of Fehling's solution (a precipitate would indicate that too much urine had been added, in which case the operation has to be repeated).

The calculation of the amount of sugar present is easily made. 10 c.c. of Fehling's solution are decomposed by 0.05 gramme of sugar; this quantity must, therefore, be contained in the number of c.c. of urine used. Suppose 30 c.c. of urine, diluted with 9 parts of water, or 3 c.c. of pure urine, have been required to decompose the 10 c.c. of Fehling's solution, then 3 c c. of urine contain of grape-sugar 0.05 gramme, or 100 c.c. of urine 1.666 grammes, according to the proportion :

$$3 : 0.05 :: 100 : x$$
$$x = 1.666.$$

If the urine contains but very little sugar, it may be used directly without diluting it, or instead of diluting it with 9 parts of water, it may be diluted with 4 volumes or with an equal volume of water.

In using Fehling's solution for the volumetric estimation of lactose, it should be remembered that 1 c.c. of solution is decomposed by 0.0067 gramme of lactose.

Modified Fehling method (Rudisch and Celler). The only change is in diluting the 10 c.c. of Fehling solution with 40 c.c. of 50 per cent. potassium sulphocyanate instead of with 40 c.c. of water. The end-reaction here is the same, *i. e.*, the disappearance of the blue. As there is no precipitate to obscure the end-point, the estimation is readily made and the method is an improvement over the original procedure. As the same amount of Fehling's solution is used, the calculation is carried out in the same way.

Harvey G. Beck has devised the following method :

The apparatus used consists of a suitable beaker; four centrifugal tubes graduated at 2 c.c.; a pipette of 2 c.c. capacity, graduated into twentieths c.c., and a wire tube-holder to support the tubes when placed in the beaker. A centrifuge will greatly facilitate the work.

The procedure is as follows: The beaker, one-third full of water, is placed over a Bunsen flame, and the four centrifugal tubes, after being filled to the graduation mark (2 c.c.) with standard Fehling's solution, are placed in the tube-holder and suspended in the beaker. The tubes are numbered respectively 1, 2, 3, and 4, according to their position in the tube-holder. The urine is added from the pipette in quantities of twentieths c.c., as follows: $\frac{4}{20}$ to No. 1, $\frac{5}{20}$ to No. 2, $\frac{6}{20}$ to No. 3, and $\frac{7}{20}$ to No. 4. The tubes, after being thoroughly shaken, are suspended in boiling water for at least three minutes, when they are removed and either set aside in the tube-stand until the cupric oxide is precipitated, or centrifugalized in order to hasten precipitation. If all the tubes still show a blue color, the urine is increased to $\frac{8}{20}$, $\frac{9}{20}$, $\frac{10}{20}$, and $\frac{11}{20}$ respectively, by adding $\frac{4}{20}$ c.c. to each tube, and the foregoing steps are repeated. This process is continued until one, or more, of the tubes is completely decolorized. The first tube in the series in which the blue color has entirely disappeared is noted; the number of twentieths c.c. required to reduce it, divided into twenty, gives the percentage of sugar present.

Estimation by fermentation can be readily done, using specially graduated tubes, which can be read directly in percentages of dextrose.

Estimation by means of the polariscope furnishes the quickest method; the details cannot be given here.

Other carbohydrates in urine. **Lævulose** is rarely present in the urine; in almost all of the cases dextrose is also presen t(diabetes). Lævulosuria should be suspected when a urine reduces copper solutions, rotates polarized light to the left or not at all, and shows no lævorotation after being fermented.

Lævulose reduces copper and bismuth solutions, ferments with yeast, is lævorotatory, and forms the same osazone with phenyl-hydrazine as is formed by dextrose.

Maltose is very rarely present in urine. Such urines show a higher percentage of sugar with the polariscope than with Fehling's solution.

Lactose occurs in the urine of lactating women, and occasionally in the urine of persons on an exclusive milk diet. It gives a delayed and incomplete Fehling test, reduces Nylander's solution, does not ferment with yeast, rotates polarized light to the right. While it forms a yellow osazone with phenyl-hydrazine, the amount present in the urine is rarely sufficient to give a positive test.

Pentoses, $C_5H_{10}O_5$, occur in many fruits and vegetables as complex carbohydrates, known as *pentosanes.* When taken into the body the pentosanes are split and pentose is excreted in the urine. Considerable pentose is found in the urine of persons addicted to the use of morphine. Pentoses owe their chief importance to the similarity of their reactions to those of glucose. Normally, the quantity of pentose in the urine is not such as to interfere with the reactions for sugar.

Pentoses reduce Fehling's and bismuth solutions; they are dextrorotatory; with phenyl-hydrazine they form a crystalline compound, melting between 153° and 158° C. (307° and 317° F.). Pentoses do not ferment with yeast, and are characterized by responding to *Tollen's orcin reaction.* This is made by adding 3 c.c. of a saturated solution of orcin in hydrochloric acid to 5 c.c. of urine previously decolorized with boneblack. In the presence of pentose a green color develops on heating, beginning at the top and gradually extending through the mixture.

Glycuronic acid, $CHO.(CHOH)_4.CO_2H$. Glycuronic acid occurs in normal urine in minute amount. It is an oxidation product of glucose, and is usually present in the form of the conjugated glycuronates, *i. e.*, glycuronic acid linked to aromatic bodies (phenol, cresol, etc.). It is increased after the taking of camphor, chloral, menthol, and other substances, which produce aromatic substances in the urine to which the glycuronic acid is linked. The amount usually present is not sufficient to reduce Fehling's solution, unless the boiling is continued for a long time. The conjugate glycuronates are lævorotatory.

Glycuronic acid reduces Fehling's and bismuth solutions, forms an osazone melting at 115° C. (239° F.), does not ferment with yeast, and is dextrorotatory. 5 c.c. of urine containing glycuronic acid when decolorized with boneblack, mixed with an equal volume of hydrochloric acid and 0.025 phloroglucin, develops a deep-red color on heating. (This reaction is also shown by pentoses; glycuronic acid does not give the orcin reaction.)

Acetone, diacetic and β-oxy-butyric acids. These substances, commonly called the "acetone bodies," are believed to be due to an abnormal metabolism of fat, though the protein metabolism may also be concerned. As can be seen from the following reactions acetone is derived from diacetic acid, and diacetic acid from β-oxy-butyric acid:

$$\underset{\beta\text{-oxy-butyric acid.}}{CH_3CH(OH).CH_2.COOH} + O = \underset{\text{Diacetic acid.}}{CH_3.CO.CH_2COOH} + H_2O$$

$$CH_3.CO.CH_2.COOH = \underset{\text{Acetone.}}{CH_3.CO.CH_3} + CO_2$$

As oxy-butyric acid and diacetic acid are unstable, acetone is the first of these bodies to appear in the urine, and it is only as the pathological conditions increase that diacetic and finally oxy-butyric acid are found. Acetone is, indeed, normally present in minute amounts, and is always increased in the presence of the other two. As these bodies have the same origin, their presence has the same significance, the higher members showing merely a graver aspect.

They are increased in many conditions: with a carbohydrate-free diet, in any cachectic condition, in many types of fever. They are markedly increased in diabetes.

The more severe cases of acetonuria are also referred to as *acidosis* (acid intoxication). The term emphasizes, of course, not the acid excreted in the urine, but the acid remaining in the system. In order to neutralize this abnormal acidity without using the fixed alkali of the body the organism converts less nitrogen into urea than is normally done, and uses it as an alkali in the form of ammonia. Thus the proportion of the urinary nitrogen in the form of ammonia is increased in acidosis, becoming even 40 per cent., the normal being 5 or 6 per cent. This percentage is the best index of the severity of the condition.

Acidosis is most common in diabetes and pernicious vomiting of pregnancy, and indicates the danger of coma.

Legal's test for acetone. To 25 c.c. of urine add an equal volume of a strong, freshly-made solution of sodium nitroprusside, and then a few drops of sodium hydroxide solution. In the presence of acetone a red color develops, which, on addition of an excess of acetic acid, becomes darker red. (Compare Weyl's reaction for creatinine.)

Acetone may also be recognized in the following manner: 500 c.c. of urine are acidified with a few drops of hydrochloric acid and distilled. To the distillate a few drops of iodine solution (1 iodine, 2 potassium iodide, 100 water) and of potassium hydroxide are added. If acetone is present, a characteristic yellowish-white precipitate of iodoform is formed.

Diacetic acid is recognized by adding to the urine drop by drop a fairly strong solution of ferric chloride, filtering off any precipitate of phosphate, and adding more ferric chloride, when in the presence of diacetic acid a deep-red color is produced, which disappears on boiling. The test should also be made with an ethereal extract, obtained by shaking urine previously acidified with sulphuric acid with ether; the ferric chloride solution, on being agitated with the ethereal extract, becomes red. (As salicylic acid and a number of other substances give a red or violet color with ferric chloride, care must be taken not to confound diacetic acid with these substances.)

The detection of β-oxy-butyric acid is difficult, and is rarely done in clinical work. Its presence is probable when urine, after being fermented, still contains a lævorotatory body.

Bile may be present in the urine in any case of jaundice.

Detection of bile-pigment. The presence of bile in urine is generally indicated by a decided color, which varies from a deep brownish-red to a dark brown; the foam of such urine (produced by shaking) has a distinct yellow color, and a piece of filtering-paper or a piece of linen dipped into the urine assumes a yellow color, which does not disappear on drying.

The further detection of bile depends upon the reactions of the biliary coloring-matters or biliary acids.

Tests for bile.

1. *Gmelin's test* for biliary coloring-matters has been considered, and may be applied to urine either by allowing a small quantity of nitric acid, containing some nitrous acid, to flow down the sides of a test-tube (containing the urine) in such a manner that the two fluids do not mix, or by placing upon a porcelain plate a few drops of the urine, near it a few drops of nitric acid, to which one drop of sulphuric acid has been added, and allowing the two liquids to approach gradually. In both cases (if bile-pigment is present) a play of

color is seen at the point of union between the two fluids, the colors changing from green to blue, violet-red, and yellow or yellowish-green. While the appearance of the green at the beginning is indispensable to prove the presence of bile, the presence of all the other colors is not essential. (Plate VIII., 7.)

The above test may be made in a somewhat modified form by mixing the urine with a concentrated solution of sodium nitrate, and pouring down the sides of the test-tube concentrated sulphuric acid in such a manner as to form two distinct layers; the colors are seen at the point of contact as above.

If the urine be very dark in color, it should be diluted with water before applying the above tests.

2. Add a few drops of sodium carbonate solution to the urine until it has a distinct alkaline reaction, then add calcium chloride and shake well. The precipitated calcium carbonate carries down the pigments and leaves the urine nearly colorless or of its normal color. Collect the precipitate on a filter, wash, and transfer it with alcohol to a test-tube. Dissolve by the addition of hydrochloric acid and boil the clear solution, when it turns green. Allow to cool and add nitric acid, when the green solution turns blue, violet, and red. (This test may show the presence of biliary coloring-matters when Gmelin's test fails to do so, and is recommended when the urine contains a large amount of indican.)

While bile acids are always present with bile-pigment in urine, their demonstration is usually difficult.

Pettenkofer's test for biliary acids is made by dissolving a few grains of cane-sugar in urine contained in a test-tube, and allowing concentrated sulphuric acid to trickle down the side of the inclined test-tube; a purple band is seen at the upper margin of the acid, and on slightly shaking the liquid becomes at first turbid, then clear, and almost simultaneously it turns yellow, then pale cherry-red, dark carmine-red, and finally a beautiful purple violet. The temperature must not be allowed to rise much above 38° C. (100° F.).

As many substances (other than biliary acids) show a similar reaction, it is often necessary to separate the bile acids by the process described in connection with the consideration of bile itself.

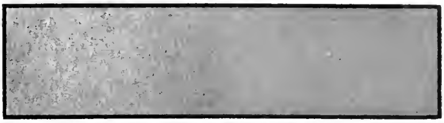
In case the quantity of biliary constituents is so small that they cannot be noticed by the tests mentioned, the urine should be shaken with about one-fourth of its volume of chloroform, which dissolves the biliary matters. Some of this solution is dropped upon blotting paper, and after evaporation a drop of red fuming nitric acid is

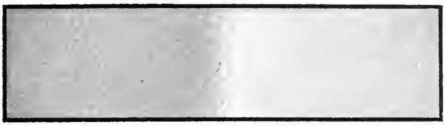
PLATE VIII.

PHYSIOLOGICAL REACTIONS.

1

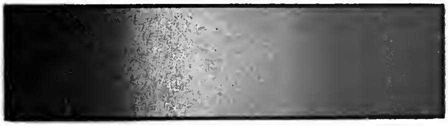
Xanthoproteic Reaction.

2

Biuret Reaction. Most albumins sho the color on the left, peptones that on th right.

3

Indican Reaction.

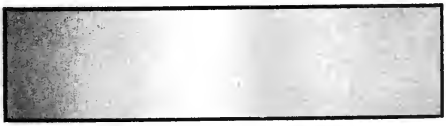
4

Murexid Test for uric acid.

5

Fehling's Test for sugar.

6

Bötger's bismuth Test for sugar.

7

Gmelin's Test for biliary colorin matters.

8

Diazo Reaction.

A. Hoen & Co. Lith. Baltimore, Md.

For explanation of reactions see page in Index.

placed in the centre of the remaining stain, when concentric color rings appear. The second portion of chloroform solution is evaporated and the residue used for making the reactions, as described above.

Melanin (melanogen), the black pigment of the skin of the negro, has been found in the urine of persons suffering from melanotic cancer and certain wasting diseases. Urine containing melanin darkens on standing, turns black on the addition of either nitric or chromic acid, and forms with bromine-water a yellow precipitate rapidly turning dark.

Alkaptonic acids. Two of these acids occur in the urine of certain otherwise healthy persons, and seem to be without clinical significance. The acids are: *homogentisic acid*, dioxphenyl-acetic acid, $C_6H_3(OH)_2.CH_2.CO_2H$, and *uroleucic acid*, dioxyphenyl-lactic acid, $C_6H_3(OH)_2.C_2H_3.OH.CO_2H$.

Both acids reduce Fehling's solution, as also ammoniacal silver nitrate solution, but not bismuth solution; they are optically inactive, do not form an osazone, and do not ferment with yeast.

To test for alkaptonic acids, the urine should be acidified with hydrochloric acid and then extracted with ether. The ethereal solution is evaporated, the residue dissolved in water, and heated with Millon's reagent. In the presence of alkaptonic acids a purple-red color is observed.

Diazo-reaction. Some abnormal constituent (which has not yet been isolated) is found in the urine of certain diseases. The presence of this unknown substance is indicated by a very characteristic reaction with diazo-benzene-sulphonic acid, which compound is produced by the action of nitrous acid on sulphanilic acid. Two solutions are required: *a.* 5 grammes of sulphanilic acid dissolved in a mixture of 50 c.c. of hydrochloric acid and 1000 c.c. of water; *b.* a 0.5 per cent. solution of sodium nitrite. To perform the reaction 50 parts of *a* and 1 part of *b* are mixed, and equal volumes of the reagent and of urine are mixed in a test-tube and saturated with ammonia. In those cases in which the reaction is positive the solution assumes a carmine-red color, which, on shaking, must also be visible in the foam. If the test-tube is allowed to stand twenty-four hours, a greenish precipitate is formed. Normal urine, thus treated, shows a deep-yellow or orange to orange-red color; the precipitated phosphates as well as the foam are colorless. On Plate VIII., 8, the color of the diazo-reaction is represented. Normal urine may show the orange-red on the left, but the carmine-red on the right is characteristic of the diazo-reaction.

If, instead of mixing the urine and reagent with ammonia water, the latter be allowed to float on the mixture, a carmine-red ring will form at the zone of contact, when the reaction is positive.

It was formerly held that this test is pathognomonic of typhoid fever. Later work has, however, shown that it usually is present in typhoid fever and measles; it is frequently present in erysipelas, pneumonia, scarlet fever, diphtheria, and pulmonary tuberculosis; it is rarely present in acute rheumatic fever and cerebrospinal meningitis.

It is, however, of much value in the diagnosis of typhoid fever, and is thought to indicate a bad prognosis in pulmonary tuberculosis.

Functional tests of the kidney. Many attempts have been made to find a substance which, when injected into the body, would be excreted by the kidney in such a manner that examination of the urine would show the ability of the kidneys to carry on their function of excretion. Among the substances tried are methylene-blue, salicylic acid, and phloridzin. By far the most suitable substance has recently been found in phenolsulphonephthalein (Geraghty-Rowntree). This substance has no poisonous action, and is excreted very rapidly by normal kidneys. It produces a red color in alkaline solution, and its amount may thus be readily estimated by noting the extent to which a standard solution must be diluted to produce the same depth of color. It is somewhat more accurate to use a special instrument, a colorimeter. After the injection of this drug (0.006 gramme) the unchanged drug will, under normal conditions, appear in the urine in from five to eleven minutes, 50 per cent. is excreted during the first hour, and from 60 to 80 per cent. during the first and second hour together.

In diseases of the kidneys the initial appearance is delayed and the hourly output is decreased.

Urinary deposits (*sediments*). Normal urine is always clear, but occasionally, and particularly in abnormal conditions, it is turbid.

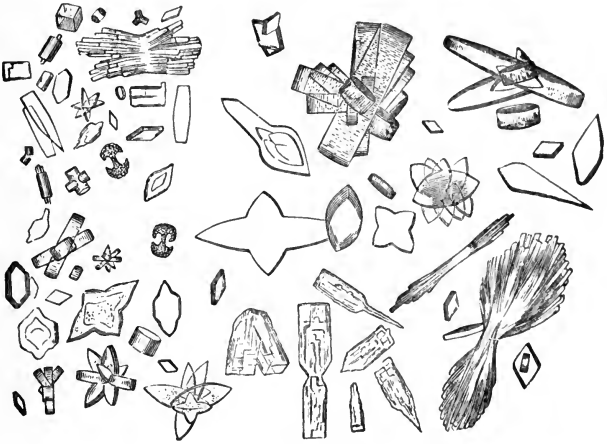
Urine may be turbid when passed, and this indicates an excess of mucus, or the presence of renal epithelium, pus, blood, chyle, semen, bile, fat-globules, or phosphates or urate of sodium in excess, etc. A turbidity subsequent to the passage of the urine is generally due to the precipitation of phosphates or urates, or it may result from fermentation or decomposition. Either of the substances named will form a deposit on standing.

When such a deposit is to be examined, a few ounces of the urine should be set aside for several hours in a tall, narrow, cylindrical glass or whirled in the centrifuge for a few minutes; when the sediment has collected at the bottom the supernatant urine may be decanted, or the sediment may be taken out by means of a pipette for examination.

Sediments are either organized or unorganized. To the first belong: mucus, blood, pus, fat, urinary casts, epithelium, spermatozoids, fungi, infusoria, etc.; to the second belong: uric acid, urates, calcium oxalate, phosphate, or carbonate, magnesium-ammonium phosphate, cystine, hippuric acid, etc.

The chemical examination of any urinary sediment should always be preceded by a microscopical examination, which latter is in many cases the only way of determining the nature of the sediment, especially of the organized substances.

FIG. 76.



Various forms of uric acid crystals. (Finlayson.)

Organized sediments. *Red blood-corpuscles* appear under the microscope as reddish, circular disks, sometimes laid together in strings. If seen in profile, they appear biconcave.

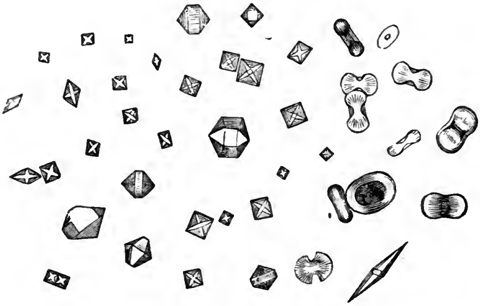
Pus cells (leucocytes) appear as round granular cells, in which the nucleus frequently is not made out until dilute acetic acid is added.

Epithelial cells, from the urinary tubules, ureter, bladder, vagina, etc. Their place of origin is frequently difficult to determine.

Casts. Hyaline, waxy, finely granular, coarsely granular, pus casts, blood casts, epithelial casts.

Unorganized sediments. (*a*) In acid urine. *Uric acid* is deposited in colored crystals from acid urine; it is not dissolved by heat, nor by acetic or hydrochloric acid, but dissolves on the addition of caustic potash and burns on platinum foil without leaving a residue; it is recognized by the murexide test. Uric acid crystallizes in many forms, usually in rhombs with rounded corners, the so-called "whetstone crystals." The crystals are usually brown. The sediment has a red crystalline appearance ("brick-dust"), and occurs in any concentrated, strongly acid urine.

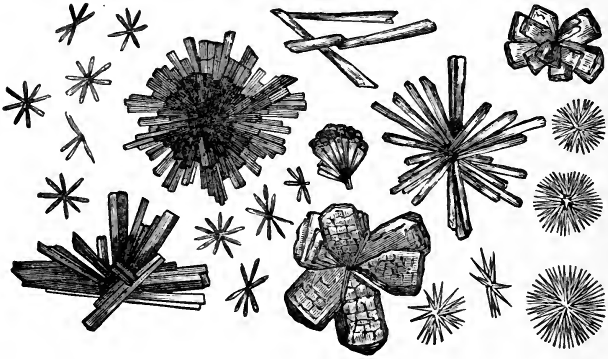
FIG. 77.



Calcium oxalate crystals. (Finlayson.)

Acid urates (Na, K) form a voluminous sediment, amorphous under the microscope, of a yellowish-brown or reddish color. This is the only sediment which dissolves on heating.

FIG. 78.



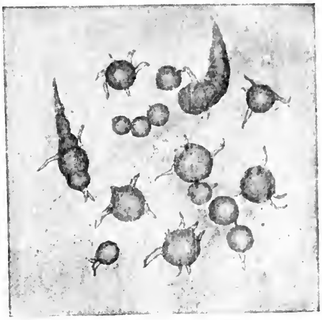
Crystalline phosphates. (Finlayson.)

Calcium oxalate is rarely found in more than microscopic amounts. The crystals are peculiarly clear, and have a double envelope, or sometimes a dumb-bell appearance.

Magnesium-ammonium phosphate, or triple phosphate, $MgNH_4$.-$PO_4.6H_2O$, is found generally in triangular prisms with bevelled ends, but sometimes also in star-shaped, feathery crystals, due to the partial dissolving of the first type. These crystals are most abundant in alkaline urine, but are also present in faintly acid urines. They dissolve in acetic acid.

(*b*) In alkaline urine. *Ammonium-magnesium phosphate* (*vide supra*).

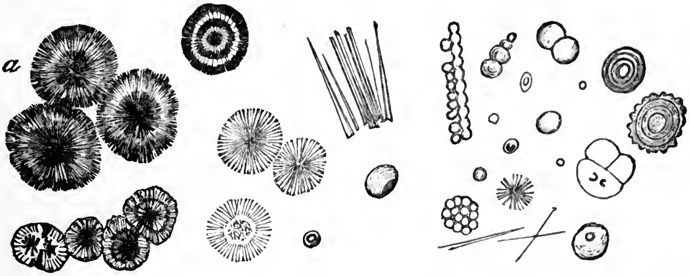
FIG. 79.



Ammonium urate crystals. (C. E. Simon.)

Calcium and magnesium phosphates. These are basic phosphates. They form the commonest sediment in alkaline urine, are amorphous, dissolve with acetic acid, but not with heat.

FIG. 80.



Crystals of leucine (different forms). (Crystals of creatinine-zinc chloride resemble the leucine crystals depicted at *a*.) The crystals figured to the right consist of comparatively impure leucine. (Charles.)

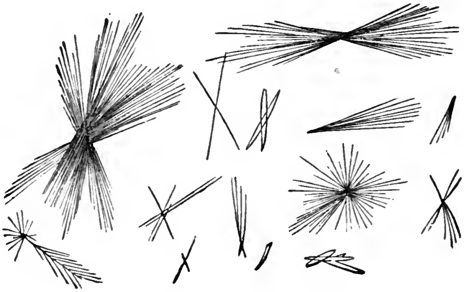
(*c*) In ammoniacal urine. *Ammonium-magnesium phosphate* (*vide supra*).

Ammonium urate is found, generally associated with amorphous or crystalline phosphates, in urine which has become ammoniacal. The crystalline globules are generally covered with spinous excrescences, which give them the characteristic "thorn-apple" appearance, and have a yellow color. They are soluble in acetic acid.

The following crystals occur only in abnormal urines:

Leucine, or amino-caproic acid, $C_6H_{11}(NH_2)O_2$, and *Tyrosine*, $C_9H_{11}NO_3$, are but rarely met with in urinary deposits. Leucine is found either as rounded lumps, showing but little crystalline structure, or as spherical masses, exhibiting fine radial striation. Tyrosine appears generally in fine, long, silky needles, forming bundles or rosettes.

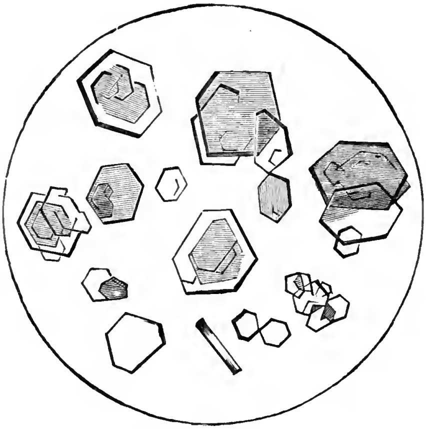
Fig. 81.



Tyrosine crystals. (Charles.)

Cystine occurs occasionally as a grayish, crystalline deposit, forming transparent six-sided plates; it also occurs in calculi. The latter may be recognized by the chemical properties mentioned below, or by dissolving a little in hydrochloric acid and neutralizing with ammonia, when cystine is reprecipitated and shows the characteristic six-sided plates under the microscope.

Fig. 82.



Crystals of cystine spontaneously voided with urine. (Roberts.)

Urinary calculi are solid deposits of various sizes formed from the urine within the kidney, ureter, bladder, and urethra. They may contain all the constituents of urine which occur as sediments, and also certain pathological constituents deposited around an organic framework.

Calculi are called *primary* when formed in unchanged urine, and *secondary* when they are formed in urine which has undergone decomposition. Uric acid, calcium oxalate, calcium carbonate, xanthine, and cystic calculi are primary formations, while ammonium urate, phosphatic and urostealith calculi are secondary.

During the development of a calculus the original deposit may be covered by a layer of a different material, which in turn may be covered by another substance. For this reason a simple stone may be converted into a compound one. In this way a primary stone, by irritation of the bladder producing cystitis, accompanied by alkaline fermentation, causes a deposition of phosphates, and is converted into a secondary calculus. The further action of the alkaline urine may dissolve the primary calculus, replacing it with phosphates.

In examining calculi it is necessary to make a section through the centre of the calculus and scrape off a little from each layer, the portions being examined separately. They may be found to be alike (simple calculi) or unlike (compound or mixed calculi) in composition. The following scheme serves for a qualitative examination of calculi. Heat some of the powdered calculus on platinum foil, when the material will either burn and char without a flame (A), or burn with a flame (B), or will not burn at all (C). (It should be remembered that a calculus generally contains a little organic matter, so that slight carbonization is always to be expected on heating it.)

A. To the material burning without a distinct flame apply the murexide test. If affirmative, uric acid or urates are indicated. Heat some powder with potassium hydroxide; a strong odor of ammonia proves the calculus to consist of *ammonium urate;* a negative result shows it to be *uric acid.* If the murexide test was negative, test for *xanthine.* The powder will dissolve in nitric acid without effervescence, leave on evaporation a yellow residue, turning orange with alkali and red on heating.

B. Material burning with a distinct flame may either be soluble in alcohol and ether (urostealith) or insoluble in these solvents, but soluble in potassium hydroxide solution on heating (fibrin), or soluble both in hydrochloric acid and in caustic alkalies (cystine). *Urostealith* burns with a yellow flame and emits the odor of burning resin. *Fibrin* burns also with a yellow flame, but emits odor of burnt feathers. *Cystine* burns with a pale-blue flame, emitting a peculiar sharp odor. On evaporation of its solution in ammonia it separates in characteristic six-sided plates.

C. Material which does not burn may consist of calcium carbonate, calcium oxalate, or phosphates. *Calcium carbonate* shows effervescence with all acids, and the solution, after being neutralized, is precipitated by ammonium oxalate. *Calcium oxalate* does not effervesce with hydrochloric acid directly, but does so after being heated, when carbonate is formed and is tested for as such. The presence of phosphates is indicated by the presence of a yellow precipitate, produced in the solution in nitric acid by ammonium molybdate. When the phosphates, on heating with caustic potash, evolve ammonia gas, *magnesium ammonium phosphate* is present; when the test is negative the calculus consists of *calcium phosphate*, which can be verified by dissolving the powder in hydrochloric acid, neutralizing with ammonia, redissolving the precipitate in acetic acid, and adding ammonium oxalate, when a white precipitate is formed.

Most common are calculi of uric acid; often met with are those of urates, phosphates, and oxalates; rarely, however, those of xanthine, cystine, fibrin, and urostealith.

QUESTIONS.—What is urine, where and by what process is it formed in the animal body, and what is its function? Mention the general physical and chemical properties of urine. Give the composition of human urine, and state by what conditions the composition is influenced. State the composition and properties of urea. By what process is urea formed in the animal body, and how can it be obtained artificially? Describe a process by which urea may be estimated quantitatively in urine. In what forms is uric acid found in urine, and what are its properties? Describe the murexide test. How can uric acid be determined quantitatively in urine? What is hippuric acid, and by what tests may it be recognized? What points are to be considered, and what substances determined, in the analysis of normal and abnormal urine? What is the color of urine, and what are the chief causes influencing the color? What is the specific gravity of healthy urine, how is it determined, and how is the total amount of solids approximately calculated from the specific gravity? Describe the different tests by which albumin may be recognized, and state the precautions necessary in making these tests. How may the quantity of albumin in urine be determined approximately, and also accurately? Describe the various tests for sugar. On what principles are they based, and how can sugar be distinguished from other reducing substances occurring in urine? How is sugar determined quantitatively? By what tests are biliary pigments and acids recognized in urine? What is the nature of urinary sediments, and by what means are they recognized? What are urinary calculi generally composed of, and by what simple tests can their nature be determined?

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.

TABLE OF ELEMENTS AND ATOMIC WEIGHTS.

On the basis H = 1 (U. S. P., VIII.) and O = 16 (International Weights, 1912).

Name.	Symbol.	Atomic weights.	
		H = 1	O = 16
Aluminum	Al	26.9	27.1
Antimony	Sb	119.3	120.2
Argon	A	39.6	39.88
Arsenic	As	74.4	74.96
Barium	Ba	136.4	137.37
Bismuth	Bi	206.9	208
Boron	B	10.9	11
Bromine	Br	79.36	79.92
Cadmium	Cd	111.6	112.4
Cæsium	Cs	131.9	132.81
Calcium	Ca	39.8	40.07
Carbon	C	11.91	12
Cerium	Ce	139.2	140.25
Chlorine	Cl	35.18	35.46
Chromium	Cr	51.7	52
Cobalt	Co	58.56	58.97
Columbium[1]	Cb	93.3	93.5
Copper	Cu	63.1	63.57
Erbium	Er	164.8	167.7
Fluorine	F	18.9	19
Gadolinium	Gd	155.8	157.3
Gallium	Ga	69.5	69.9
Germanium	Ge	71.9	72.5
Glucinum[2]	Gl	9.03	9.1
Gold	Au	195.7	197.2
Helium	He	3.99	3.99
Hydrogen	H	1.00	1.008
Indium	In	113.1	114.8
Iodine	I	125.9	126.92
Iridium	Ir	191.5	193.1
Iron	Fe	55.5	55.84
Krypton	Kr	81.2	82.92
Lanthanum	La	137.9	139
Lead	Pb	205.35	207.1
Lithium	Li	6.98	6.94
Magnesium	Mg	24.18	24.32
Manganese	Mn	54.6	54.93
Mercury	Hg	198.5	200.6
Molybdenum	Mo	95.3	96
Neodymium	Nd	142.5	144.3
Neon	Ne	19.9	20.2
Nickel	Ni	58.3	58.68
Nitrogen	N	13.93	14.07
Osmium	Os	189.6	190.9
Oxygen	O	15.88	16
Palladium	Pd	105.7	106.7
Phosphorus	P	30.77	31.04
Platinum	Pt	193.3	195.2
Potassium	K	38.86	39.1
Praseodymium[3]	Pr	139.4	143.6
Radium	Ra	223	226.4
Rhodium	Rh	102.2	102.9
Rubidium	Rb	84.8	85.45
Ruthenium	Ru	100.9	101.7
Samarium	Sm	148.9	150.4
Scandium	Sc	43.8	44.1
Selenium	Se	78.6	79.2
Silicon	Si	28.2	28.3
Silver	Ag	107.12	107.88
Sodium	Na	22.88	23
Strontium	Sr	86.94	87.63
Sulphur	S	31.83	32.07
Tantalum	Ta	181.6	181.5
Tellurium	Te	126.6	127.5
Terbium	Tb	158.8	159.2
Thallium	Tl	202.6	204
Thorium	Th	230.8	232.4
Thulium	Tm	169.7	168.5
Tin	Sn	118.1	119
Titanium	Ti	47.7	48.1
Tungsten	W	182.6	184
Uranium	U	236.7	238.5
Vanadium	V	50.8	51
Xenon	Xe	127	130.2
Ytterbium	Yb	171.7	172
Yttrium	Yt	88.3	89
Zinc	Zn	64.9	65.37
Zirconium	Zr	89.9	90.6

[1] Also called Niobium, Nb.

[2] Also called Beryllium, Be.

[3] Also called Didymium, Di.

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