The medical student's manual of chemistry.

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THE MEDICAL STUDENT'S

MANUAL

OF

CHEMISTRY

BY

udolph ugust

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Fourth Edition.

NEW YORK
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1893

PREFACE TO THE PRESENT EDITION.

THE arrangement and classification followed in previous editions have been retained.

The rules of orthography adopted by the Chemical Section of the American Association for the Advancement of Science, and by the National Bureau of Education (see Appendix A), have been followed.

That portion of the work treating of the chemistry of the carbon compounds has been much extended and in great part rewritten. The organic substances have been, as in previous editions, classified according to their constitution so far as known, and those alkaloids whose molecular structure has been completely or partially determined have been removed from the miscellaneous position among "alkaloids" to their proper places in the classification. The prominence given to this branch of the subject the author believes to be justified, notwithstanding its intricacy and the consequent difficulty of teaching it satisfactorily to medical students, by reason of the intimate connection of organic chemistry with physiology and with modern pharmacy, and the rapidly increasing use of complex organic products, natural and synthetic, as medicines.

R. A. W.

NEW YORK, September 21st, 1893.

PREFACE TO THE FIRST EDITION.

In venturing to add another to the already long list of chemical text-books, the author trusts that he may find some apology in this, that the work is intended solely for the use of a class of students whose needs in the study of this science are peculiar.

While the main foundations of chemical science, the philosophy of chemistry, must be taught to and studied by all classes of students alike, the subsequent development of the study in its details must be moulded to suit the purposes to which the student will subsequently put his knowledge. And particularly in the case of medical students, in our present defective methods of medical teaching, should the subject be confined as closely as may be to the general truths of chemistry and its applications to medical science.

In the preparation of this Manual the author has striven to produce a work which should contain as much as possible of those portions of special chemistry which are of direct interest to the medical practitioner, and at the same time to exclude so far as possible, without detriment to a proper understanding of the subject, those portions which are of purely technological interest. The descriptions of processes of manufacture are therefore made very brief, while chemical physiology and the chemistry of hygiene, therapeutics, and toxicology have been dwelt upon.

The work has been divided into three parts. In the first part the principles of chemical science are treated of, as well as so much of chemical physics as is absolutely requisite to a proper understanding of that which follows. A more extended study of physics is purposely avoided, that subject being, in the opinion of the author, rather within the domain of physiology than of chemistry.

The second part treats of special chemistry, and in this certain departures from the methods usually followed in chemical text-books are to be noted. The elements are classed, not in metals and metalloids, a classification as arbitrary as unscientific, but into classes and groups according to their *chemical* characters.

In the text the formula of a substance is used in most instances in place of its name, *after it has been described*, with a view to giving the student that familiarity with the notation which can only be obtained by continued use.

In the third part those operations and manipulations which will be of utility to the student and physician are briefly described; not with the expectation that these directions can take the place of actual experience in the laboratory, but merely as an outline sketch in aid thereto.

Although the Manual puts forth no claim as a work upon analytical chemistry, we have endeavored to bring that branch of the subject rather into the foreground so far as it is applicable to medical chemistry. The qualitative characters of each element are given under the appropriate heading, and in the third part, a systematic scheme for the examination of urinary calculi is given. Quantitative methods of interest to the physician are also described in their appropriate places. In this connection the author would not be understood as saying that the methods recommended are in all instances the best known, but simply that they are the best adapted to the limited facilities of the physician.

The author would have preferred to omit all mention of Troy and Apothecaries' weight, but in deference to the opinions of those venerable practitioners who have survived their student days by a half-century, those weights have been introduced in brackets after the metric, as the value of degrees Fahrenheit have been made to follow those Centigrade.

R. A. W.

BUFFALO, N. Y., September 16th, 1883.

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THE MEDICAL STUDENT'S

MANUAL OF CHEMISTRY.

PART I.

INTRODUCTION.

THE simplest definition of chemistry is a modification of that given by Webster: **That branch of science which treats of the composition of substances, their changes in composition, and the laws governing such changes.**

If a bar of soft iron be heated sufficiently it becomes luminous; if caused to vibrate it emits sound; if introduced within a coil of wire through which a galvanic current is passing, it becomes magnetic and attracts other iron brought near it. Under all these circumstances the iron is still iron, and so soon as the heat, vibration, or galvanic current ceases, it will be found with its original characters unchanged; it has suffered no change in **composition.** If now the iron be heated in an atmosphere of oxygen gas, it burns, and is converted into a substance which, although it contains iron, has neither the appearance nor the properties of that metal. The iron and a part of the oxygen have disappeared, and have been converted into a new substance, differing from either; there has been change in **composition,** there has been **chemical action.** Changes wrought in matter by physical forces, such as light, heat, and electricity, are temporary, and last only so long as the force is active; except in the case of changes in the state of aggregation, as when a substance is pulverized or fashioned into given shape. Changes in chemical composition are permanent, lasting until some other change is brought about by another manifestation of chemical action.

However distinct chemical may thus be from physical forces, it is none the less united with them in that grand correlation whose existence was first announced by Grove, in 1842. As, from chemical action, manifestations of every variety of physical force may be obtained: light, heat, and mechanical force from the oxidation of carbon; and electrical force from the action of zinc upon sulfuric acid — so does chemical action have its origin, in many instances, in the physical forces. Luminous rays bring about the chemical decomposition of the salts of silver, and the chemical union of chlorin and hydrogen; by electrical action a decomposition of many compounds into their constituents is instituted, while instances are abundant of reactions, combinations, and decompositions which require a certain elevation of temperature for their production. While, therefore, chemistry in the strictest sense of the term, deals only with those actions which are attended by a change of composition in the material acted upon, yet chemical actions are so frequently, nay universally, affected by existing physical conditions, that the chemist is obliged to give his attention to the science of physics, in so far, at least, as it has a bearing upon chemical reactions, to *chemical physics*—a branch of the subject which has afforded very important evidence in support of theoretical views originating from purely chemical reactions.

General Properties of Matter.

Indestructibility.—The result of chemical action is change in the composition of the substance acted upon, a change accompanied by corresponding alterations in its properties. Although we may cause matter to assume a variety of different forms, and render it, for the time being, invisible, yet in none of these changes is there the smallest particle of matter destroyed. When carbon is burned in an atmosphere of oxygen, it disappears, and, so far as we can learn by the senses of sight or touch, is lost; but the result of the burning is an invisible gas, whose weight is equal to that of the carbon which has disappeared, plus the weight of the oxygen required to burn it.

Impenetrability.—Although one mass of matter may penetrate another, as when a nail is driven into wood, or when salt is dissolved in water; the ultimate particles of which matter is composed cannot penetrate each other, and, in cases like those above cited, the particles of the softer substance are forced aside, or the particles of one substance occupy spaces between the particles of the other. Such spaces exist between the ultimate particles of even the densest substances.

Weight.—All bodies attract each other with a force which is in direct proportion to the amount of matter which they contain. The force of this attraction, exerted upon surrounding bodies by the earth, becomes sensible as weight, when the motion of the attracted body toward the centre of gravity of the earth is prevented.

In chemical operations we have to deal with three kinds of weight: **absolute, apparent,** and **specific.**

The Absolute Weight of a body is its weight in vacuo. It is determined by placing the entire weighing apparatus under the receiver of an air-pump.

The Apparent Weight, or **Relative Weight,** of a body is that which we usually determine with our balances, and is, if the volume of the body weighed be greater than that of the counterpoising weights, less than its true weight. Every substance in a liquid or gaseous medium suffers a loss of apparent weight equal to that of the volume of the medium so displaced. For this reason the apparent weight of some substances may be a minus quantity. Thus, if the air contained in a vessel suspended from one arm of a poised balance be replaced by hydrogen, that arm of the balance to which the vessel is attached will rise, indicating a diminution in weight. (See Weighing; Part III.)

The Specific Weight, or **Specific Gravity,** of a substance is the weight of a given volume of that substance, as compared with the weight of an equal bulk of some substance, accepted as a standard of comparison, under like conditions of temperature and pressure. The sp. gr. of solids and liquids are referred to water; those of gases to air or to hydrogen.* Thus the sp. gr. of sulfuric acid being 1.8, it is, volume for volume, one and eight-tenth times as heavy as water. As, by reason of their different rates of expansion by heat, solids and liquids do not have the same sp. gr. at all temperatures, that at which the observation is made should always be noted, or some standard temperature adopted. The standard temperature adopted by some continental writers and in the U. S. P. is 15° (59° F.). Other standard temperatures are 4° (39°.2 F.), the point of greatest density of water, used by most continental writers, and 15°.6 (60° F.), used in Great Britain and to some extent in this country.

The determination of the specific weight of a substance is frequently of great service. Sometimes it affords a rapid means of distinguishing between two substances similar in appearance; sometimes in determining the quantity of an ingredient in a mixture of two liquids, as alcohol and water; and frequently in determining approximately the quantity of solid matter in solution in a liquid. It is the last object which we have in view in determining the sp. gr. of the urine.

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* As the sp. gr. of pure air (hydrogen = 1) is 14.42, the sp. gr. in terms of air × 14.42 = sp. gr. in terms of hydrogen. Thus, the sp. gr. of hydrochloric acid gas (A = 1) is 1.259. Its sp. gr. (H = 1) is therefore 1.259 × 14.42 = 36.31.

An aqueous solution of a solid heavier than water has a higher sp. gr. than pure water, the variation in sp. gr. following a regular but different rate with each solid. In a simple solution—one of common salt in water, for instance—the proportion of solid in solution can be determined from the sp. gr. In complex solutions, such as the urine, the sp. gr. does not indicate the proportion of solid in solution with accuracy. In the absence of sugar and albumen, a determination of the sp. gr. of urine affords an indication of the amount of solids sufficiently accurate for usual clinical purposes. Moreover, as urea is much in excess over other urinary solids, the oscillations in the sp. gr. of the urine, if the quantity passed in twenty-four hours be considered, and in the absence of albumen and sugar, indicate the variations in the elimination of urea, and consequently the activity of disassimilation of nitrogenous material.

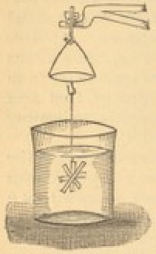
FIG. 1.

To determine the sp. gr. of substances, different methods are adopted, according as the substance is in the solid, liquid, or gaseous state; is in mass or in powder; or is soluble or insoluble in water.

SOLIDS.—*The substance is heavier than water, insoluble in that liquid, and not in powder.*—It is attached by a fine silk fibre or platinum wire to a hook arranged on one arm of the balance, and weighed. A beaker full of pure water is then so placed that the body is immersed in it (Fig. 1), and a second weighing made. By dividing the weight in air by the loss in water, the sp. gr. (water = 1.00) is obtained. Example:

A piece of lead weighs in air........................ 82.0
A piece of lead weighs in water...................... 74.9

Loss in water.................................. 7.1

$$\frac{82.0}{7.1} = 11.55 = \text{sp. gr. of lead.}$$

The substance is in powder, insoluble in water.—The specific gravity bottle (Fig. 3), filled with water, and the powder, previously weighed and in a separate vessel, are weighed together. The water is poured out of the bottle, into which the powder is introduced, with enough water to fill the bottle completely. The weight of the bottle and its contents is now determined. The weight of the powder alone, divided by the loss between the first and second weighings, is the specific gravity. Example:

Weight of iron filings used	6.562
Weight of iron filings and sp. gr. bottle filled with water	148.327
Weight of sp. gr. bottle containing iron filings and filled with water	147.470
Water displaced by iron	0.857

$$\frac{6.562}{0.857} = 7.65 = \text{sp. gr. of iron.}$$

The substance is lighter than water.—A sufficient bulk of some heavy substance, whose sp. gr. is known, is attached to it and the same method followed, the loss of weight of the heavy substance being subtracted from the total loss. Example:

A fragment of wood weighs	4.3946
A fragment of lead weighs	10.6193
Wood with lead attached weighs in air	15.0139
Wood with lead attached weighs in water	5.9295
Loss of weight of combination	9.0844
Loss of weight of lead in water (determined as above)	0.7903
Loss of weight of wood	8.2941

$$\frac{4.3946}{8.2941} = 0.529 = \text{sp. gr. of wood.}$$

The substance is soluble in or decomposable by water.—Its specific gravity, referred to some liquid not capable of acting on it, is determined, using that liquid as water is used in the case of insoluble substances. The sp. gr. so obtained, multiplied by that of the liquid used, is the sp. gr. sought. Example:

A piece of potassium weighs	2.576
A sp. gr. bottle full of naphtha, sp. gr. 0.758, weighs	22.784
	25.360
The bottle with potassium and naphtha weighs	23.103
Loss	2.257

$$\frac{2.576}{2.257} = 1.141 \times 0.758 = 0.865 = \text{sp. gr. of potassium.}$$

Liquids.—The sp. gr. of liquids is determined by the **specific gravity balance,** by the **specific gravity bottle,** sometimes called **picnometer,** or by the **spindle** or **hydrometer.**

By the balance.—The liquid, previously brought to the proper temperature, is placed in the cylinder *a* (Fig. 2), and the plunger immersed in it, and attached to the arm of the balance. The weights are now adjusted, beginning with the largest, until the balance is in equilibrium. The sp. gr. indicated by the balance in Fig. 2 is 1.98.

By the bottle.—An ordinary analytical balance is used. A bottle of thin glass (Fig. 3) is so made as to contain a given volume of water, say 100 c.c., at 15° C., and its weight is determined once for all. To use the picnometer, it is filled with the liquid to be examined and weighed. The weight obtained, minus that of the bottle, is the sp. gr. sought, if the bottle contain 1000 c.c.; 1-10 if 100 c.c., etc. Example: Having a bottle whose weight is 35.35, and which contains 100 c.c.; filled with urine it weighs 137.91, the sp. gr. of the urine is $137.91 - 35.35 = 102.56 \times 10 = 1025.6$—— Water $= 1000$.

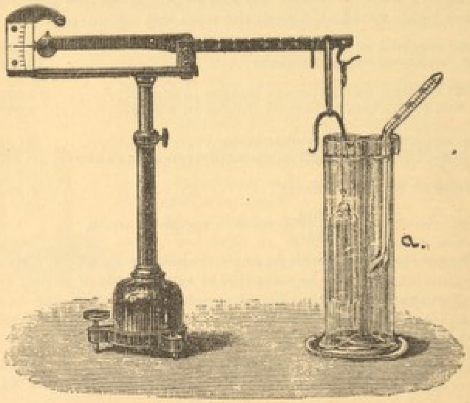

FIG. 2.

By the spindle.—The method by the hydrometer is based upon the fact that a solid will sink in a liquid, whose sp. gr. is greater than its own, until it has displaced a volume of the liquid whose weight is equal to its own; and all forms of hydrometers are simply contrivances to measure the volume of liquid which they displace when immersed. The hydrometer most used by physicians is the urinometer (Fig. 4). It should not be chosen too small, as the larger the bulb, and the thinner and longer the stem, the more accurate are its indications. It should be tested by immersion in liquids of known sp. gr., and the error at different points of the scale should be noted on the box. The most convenient method of using the instrument is as follows: The cylinder, which should have a foot and rim, but no pouring lip, is filled to within an inch of the top; the spindle is then floated and the cylinder completely filled with the liquid under examination (Fig. 4). The reading is then taken at the highest point *a*, where the surface of the liquid comes in contact with the spindle.*

In all determinations of sp. gr. the liquid examined should have the temperature for which the instrument is graduated, as all liquids expand with heat and contract when cooled, and consequently the result obtained will be too low if the urine or other liquid be at a temperature above that at which the instrument is intended to be used, and too high if below that temperature. An accurate correction may be made for temperature in simple solutions. In a complex fluid like the urine, however, this can only be done roughly by allowing 1° of sp. gr. for each 3° C. (5°.4 Fahr.) of variation in temperature.

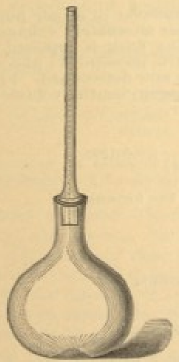

FIG. 3.

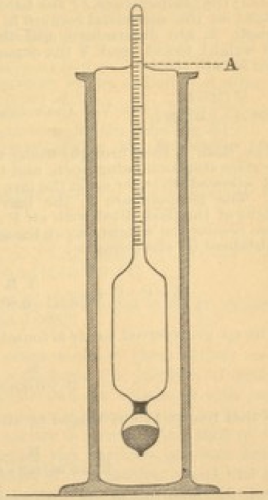

FIG. 4.

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* The advantages of the method described over that usually followed are: Greater facility in reading, less liability to error, the possibility of taking the reading in opaque liquids, and the fact that readings are made upward, not downward.

GASES AND VAPORS.—The specific gravities of gases and vapors are of great importance in theoretical chemistry, as from them we can determine molecular weights, in obedience to the law of Avogadro (p. 33).

Gases.—The specific gravities of gases are obtained as follows: A glass flask of about 300 c.c. capacity, having a neck 20 centimetres long and 6 millimetres in diameter, and fitted with a glass stopcock, is filled with mercury; reversed over mercury; and filled with the gas to just below the stopcock. The stopcock is now closed; the temperature, t; the barometric pressure, H; and the height of the mercurial column in the neck above that in the trough, h, are determined, and the flask weighed. Let P be the weight found, and V the capacity of the flask, determined once for all, then

$$\frac{V\,(H-h)}{760\,(1+0.00366\,t)} = V_0 = \text{the volume of the gas at } 0^\circ \text{ and } 760 \text{ mm.}$$

The flask is then brought under the receiver of an air pump, the glass stopcock being open, and the air alternately exhausted and allowed to enter until the gas in the flask is replaced by air. The temperature t', the barometric pressure H′, and the weight of the flask filled with air P′, are now determined. From these results the weight, K, of the gas occupying the volume V_0 is obtained by the formula:

$$K = P - P' + \frac{V\,H'}{760\,(1+0.00366\,t')} \times 0.001293$$

The sp. gr. referred to air is found by the formula:

$$\frac{K}{V_0 \times 0.001293}$$

and that referred to hydrogen by the formula:

$$\frac{K}{V_0 \times 0.001293 \times 0.06927}$$

Vapors.—The specific gravity of vapors is best determined by Meyer's method, as follows: A small, light glass vessel (Fig. 5) is filled completely with the solid or liquid whose vapor density is to be determined and weighed; from this weight that of the vessel is subtracted; the difference being the weight of the substance P. The small vessel and contents are now introduced into the large branch of the apparatus (Fig. 6), whose weight is then determined. The apparatus is now filled with mercury, the capillary opening at the top of the larger branch is closed by the blow-pipe, and the whole again weighed. The apparatus is suspended by a metallic wire near the bottom of a long tube closed at the bottom, and containing about 50 c.c. of some liquid whose boiling-point is constant and higher than that of the substance experimented on. When the liquid has been heated to active


FIG. 5.

boiling, and the mercury ceases to escape from the small tube, the barometric pressure and the temperature of the air are observed. After the apparatus is cooled, the tube (Fig. 6), with its contents is weighed, and the difference in the level of mercury which existed in the two branches during the heating determined by breaking the capillary point, tilting the apparatus until the smaller branch is completely filled, marking the level of mercury in the larger branch, and afterward measuring the distance from that point to the opening.

By the above process the following factors are determined :

P=weight of substance ;
T=boiling-point of external liquid ;
t=temperature of air ;
H=barometric pressure reduced to 0° ;
h=difference in level of mercury in two branches of tube ;
h'=tension of vapor of mercury at T ;
a=weight of mercury used ;
q=weight of mercury required to fill the tube Fig. 5 ;
r=weight of mercury remaining in the apparatus after heating.

From these the specific gravity, air = 1, is obtained by the equation :

$$D = \frac{P\ 760\ (1+0.00367\ T)\ 13.59}{(H+h+h')\ 0.0012932\ \left[(a+q)\ \left\{1+0.0000303\ (T-t)\right\} - r\ \left\{1+0.00018\ (T-t)\right\}\right]\left[1+0.00018\ t\right]}$$

The sp. gr. in terms of air=1 may be reduced to sp. gr. referred to hydrogen=2, by dividing by 0.06927.

States of Matter.—Matter exists in one of three states ; solid, liquid, and gaseous. In the solid form, the particles of matter are comparatively close together, and are separated with more difficulty than are those of liquid or gaseous matter ; or in other words the cohesion of solid matter is greater than that of the other two forms. In the liquid, the particles are less firmly bound together, and are capable of freer motion about one another. In the gas, the mutual attraction of the particles disappears entirely, and their distance from each other depends upon the pressure to which the gas is subjected.

The term **fluid** applies to both liquids and gases, the former being designated as **incompressible,** from the very slight degree to which their volume can be reduced by pressure. The gases are designated as **compressible fluids,** from the fact that their volume can be reduced by pressure, to an extent limited only by their passage into the liquid form.

It is highly probable that all substances, which are not decomposed when heated, are capable of existing in the three forms of solid, liquid, and gas. There are, however, some substances which are only known in two forms—as alcohol ; or in a single form—as carbon; probably because we are as yet unable to produce artificially a temperature sufficiently low to solidify the one, or sufficiently high to liquefy or volatilize the other.

A **vapor** is an aëriform fluid into which a substance, solid or liquid at the ordinary temperature, is converted by elevation of temperature, or by diminution of pressure. Since the liquefaction of the so-called permanent gases, the distinction between gases and vapors is only one of degree and of convenience. A liquid is said to be **volatile** when, like ether, it is readily converted into vapor. It is said to be **fixed** if, like olive oil, it does not yield a vapor when heated. Certain solids are directly volatile, like camphor, passing from the condition of solid to that of vapor without liquefaction.

FIG. 6.

Divisibility.—All substances are capable of being separated, with greater or less facility, by mechanical means into minute particles. With suitable apparatus, gold may be divided into fragments, visible by the aid of the microscope, whose weight would be $\frac{1}{500000000000}$ of a grain; and it is probable that when a solid is dissolved in a liquid a still greater subdivision is attained.

Although we have no direct experimental evidence of the existence of a limit to this divisibility, we are warranted in believing that matter is not infinitely divisible. A strong argument in favor of this view being that, after physical subdivision has reached the limit of its power with regard to compound substances, these may be further divided into dissimilar bodies by chemical means.

The limit of mechanical subdivision is the **molecule** of the physicist, the smallest quantity of matter with which he has to deal, the smallest quantity that is capable of free existence.

Physical Characters of Chemical Interest.

Crystallization.—Solid substances exist in two forms, **amorphous** and **crystalline.** In the former they assume no definite shape; they conduct heat equally well in all directions; they break irregularly; and, if transparent, allow light to pass through them equally well in all directions. A solid in the crystalline form has a definite geometrical shape; conducts heat more readily in some directions than in others; when broken, separates in certain directions, called **planes of cleavage,** more readily than in others; and modifies the course of luminous rays passing through it differently when they pass in certain directions than when they pass in others.

Crystals are formed in one of four ways: 1.) An amorphous substance, by slow and gradual modification, may assume the crystalline form; as vitreous arsenic trioxid (*q. v.*) passes to the crystalline variety. 2.) A fused solid, on cooling, crystallizes; as bismuth. 3.) When a solid is sublimed it is usually condensed in the form of crystals. Such is the case with arsenic trioxid. 4.) The usual method of obtaining crystals is by the evaporation of a solution of the substance. If the evaporation be slow and the solution at rest, the crystals are large and well-defined. If the crystals separate by the sudden cooling of a hot solution, especially if it be agitated during the cooling, they are small.

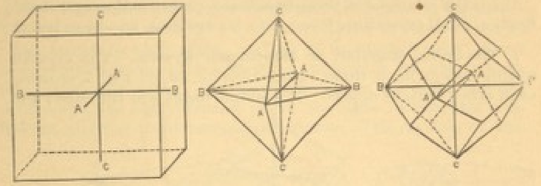

FIG. 7.

Most crystals may be divided by imaginary planes into equal, symmetrical halves. Such planes are called **planes of symmetry.** Thus in the crystals in Fig. 7 the planes *ab ab*, *ac ac*, and *bc bc* are planes of symmetry.

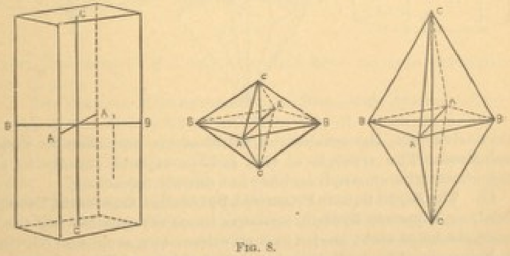

FIG. 8.

When a plane of symmetry contains two or more equivalent linear directions passing through the centre, it is called the **principal plane of symmetry**; as in Fig. 8 the plane *ab ab*, containing the equal linear directions *aa* and *bb*.

Any normal erected upon a plane of symmetry, and prolonged in both directions until it meets opposite parts of the exterior of the crystal, at equal distances from the plane, is called an **axis of symmetry.**

The axis normal to the principal plane is the **principal axis.** Thus in Fig. 8, *aa*, *bb*, and *cc* are axes of symmetry, and *cc* is the principal axis.

Upon the relations of these imaginary planes and axes a classification of all crystalline forms into six **systems** has been based.

I. **The Cubic, Regular, or Monometric System.**—The crystals of this system have three equal axes, *aa*, *bb*, *cc*, Fig. 7, crossing each other at right angles. The simple forms are the **cube;** and its derivatives, the **octahedron, tetrahedron,** and **rhombic dodecahedron.** The crystals of this system expand equally in all directions when heated, and are not doubly refracting.

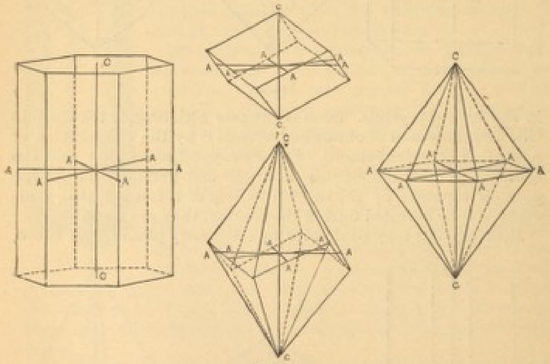

Fig. 9.

II. **The Right Square Prismatic, Pyramidal, Quadratic, Tetragonal,** or **Dimetric System** contains those crystals having three axes placed at right angles to each other—two as *aa* and *bb*, Fig. 8, being equal to each other and the third, *cc*, either longer or shorter. The simple forms are the **right square prism** and the **right square based octahedron.** The crystals of this system expand equally only in two directions when heated. They refract light doubly in all directions except through one axis of single refraction.

III. **The Rhombohedral** or **Hexagonal System** includes crystals having four axes, three of which *aa*, *aa*, *aa*, Fig. 9, are of equal length and cross each other at 60° in the same plane; to which plane the fourth axis, *cc*, longer or shorter than the others, is at right angles. The simple forms are the **regular six-sided prism,** the **regular dodecahedron,** the **rhombohedron,** and the **scalenohedron.** These crystals expand equally in two directions when heated, and refract light singly through the principal axis, but in other directions refract it doubly.

IV. **The Rhombic, Right Prismatic, or Trimetric System.**—The axes of crystals of this system are three in number, all at right angles to each other, and all of unequal length. Fig. 8 represents crystals of this system, supposing *aa*, *bb*, and *cc* to be unequal to each other. The simple forms are the **right rhombic octahedron,** the **right rhombic prism,** the **right rectangular octahedron,** and the **right rectangular prism.** The crystals of this system, like those of the two following, have no true principal plane or axis.

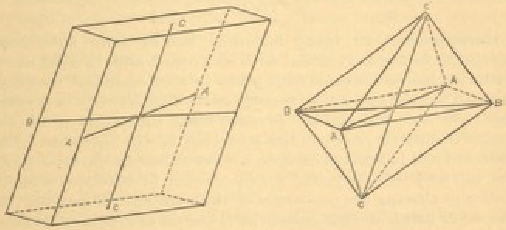

Fig. 10.

V. **The Oblique, Monosymmetric, or Monoclinic System.**—The crystals of this system have three axes, two of which, *aa*, and *cc*, Fig. 10, are at right angles; the third, *bb*, is perpendicular to one and oblique to the other. They may be equal or all unequal in length. The simple forms are the **oblique rectangular** and **oblique rhombic prism** and **octahedron.**

VI. **The Doubly Oblique, Asymmetric, Triclinic,** or **Anorthic System** contains crystals having three axes of unequal length, crossing each other at angles not right angles; Fig. 10, *aa*, *bb*, and *cc* being unequal and the angles between them other than 90°.

The crystals of the fourth, fifth, and sixth systems, when heated, expand equally in the directions of their three axes. They refract light doubly except in two axes.

Secondary Forms.—The crystals occurring in nature or produced artificially have some one of the forms mentioned above, or some modification of those forms. These modifications, or

secondary forms, may be produced by symmetrically removing the angles or edges, or both angles and edges, of the primary forms. Thus, by progressively removing the angles of the cube, the secondary forms shown in Fig. 11 are produced.

It sometimes happens in the formation of a derivative form that alternate faces are excessively developed, producing at length entire obliteration of the others, as shown in Fig. 12. Such crystals are said to be **hemihedral.** They can be developed only in a system having a principal axis.

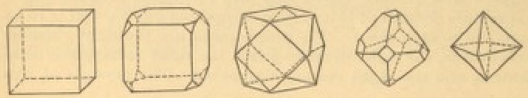

FIG. 11.

Isomorphism.—In many instances two or more substances crystallize in forms identical with each other, and, in most cases, such substances resemble each other in their chemical constitution. They are said to be **isomorphous.** This identity of crystalline form does not depend so much upon the nature of the elements themselves, as upon the structure of the molecule. The protoxid and peroxid of iron do not crystallize in the same form, nor can they be substituted for each other in reactions without radically altering the properties of the resultant compound. On the other hand, all that class of salts known as alums are isomorphous. Not only are their crystals identical in shape, but a crystal of one alum, placed in a saturated solution of another, grows by regular deposition of the second upon its surface. Other alums may be subsequently added to the crystal, a section of which will then exhibit the various salts, layer upon layer.

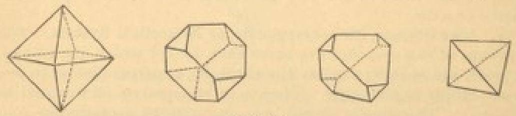

FIG. 12.

Dimorphism.—Although most substances crystallize, if at all, in one simple form, or in some of its modifications, a few bodies are capable of assuming two crystalline forms, belonging to different systems. Such are said to be **dimorphous.** Thus, sulfur, as obtained by the evaporation of its solution in carbon disulfid, forms octahedra, belonging to the fourth system. When obtained by cooling melted sulfur the crystals are oblique prisms belonging to the fifth system. Occasional instances of **trimorphism**, of the formation of crystals belonging to three different systems by the same substance, are also known.

Many substances, on assuming the crystalline form, combine with a certain amount of water which exists in the crystal in a solid combination. Thus nearly half of the weight of crystallized alum is water. This water is called **water of crystallization**, and is necessary to the maintenance of the crystalline form, and frequently to the color. If blue vitriol be heated, it loses its water of crystallization, and is converted into an amorphous, white powder. Some crystals lose their water of crystallization on mere exposure to the air. They are then said to **effloresce.** Usually, however, they only lose their water of crystallization when heated. (See p. 66.)

Allotropy.—Dimorphism apart, a few substances are known to exist in more than one solid form. These varieties of the same substance exhibit different physical properties, while their chemical qualities are the same in kind. Such modifications are said to be **allotropic.** One or more allotropic modifications of a substance are usually crystalline, the other or others amorphous or vitreous. Sulfur, for example, exists not only in two dimorphous varieties of crystals, but also in a third, allotropic form, in which it is flexible, amorphous, and transparent. Carbon exists in three allotropic forms: two crystalline, the diamond and graphite; the third amorphous.

In passing from one allotropic modification to another, a substance absorbs or gives out heat.

Solution.—A solid, liquid, or gas is said to **dissolve,** or form a **solution** with a liquid when the two substances unite to form a homogeneous liquid. Solution may be a purely physical process or a chemical combination.

In **simple** or **physical solution** there is no modification of the properties of the solvent and dissolved substance, beyond the liquefaction. The latter can be regenerated, in its primitive form, by simple evaporation of the former; and the act of solution is usually attended by a *diminution of temperature.*

In **chemical solution** the properties of both solvent and dissolved are more or less modified. The dissolved substance cannot be obtained from the solution by simple evaporation of the solvent, unless the compound formed be decomposable, with formation of the original substance, at the temperature of the evaporation. The act of chemical solution is usually attended by an *elevation of temperature.*

The amount of solid, liquid, or gas which a liquid is capable of dissolving by simple solution depends upon the following conditions:

1. *The nature of the solvent and substance to be dissolved.*—No rule can be given, which will apply in a general way to the solvent power of liquids, or to the solubility of substances. Water is of all liquids the best solvent of most substances. In it some substances are so readily soluble that they absorb a sufficiency from the atmosphere to form a solution; as calcium chlorid. Such substances are said to **deliquesce**. Other substances are insoluble in water in any proportion; as barium sulfate. Elementary substances (with the exception of chlorin) are insoluble, or sparingly soluble, in water. Substances rich in carbon are insoluble in water, but soluble in organic liquids.

2. *The temperature* usually has a marked influence on the solubility of a substance. As a rule, water dissolves a greater quantity of a solid substance as the temperature is increased. This increase in solubility is different in the case of different soluble substances. Thus the increase in solubility of the chlorids of barium and of potassium is directly in proportion to the increase of temperature. The solubility of sodium chlorid is almost imperceptibly increased by elevation of temperature. The solubility of sodium sulfate increases rapidly up to 33° (91°.4 F.), above which temperature it again diminishes.

The solubility of gases, except hydrogen, in water is the greater the lower the temperature, and the greater the pressure.

The amount of a substance that a given quantity of solvent is capable of dissolving at a given temperature is fixed. A solution containing as much of the dissolved substance as it is capable of dissolving is said to be **saturated**. If made at high temperatures it is said to be a *hot saturated*, and if at ordinary temperatures a *cold saturated solution*.

If a hot saturated solution of a salt be cooled, the solid is in most instances separated by crystallization. If, in the case of certain substances, such as sodium sulfate, however, the solution be allowed to cool while undisturbed, no crystallization occurs, and the solution at the lower temperature contains a greater quantity of the solid than it could dissolve at that temperature. Such a solution is said to be **supersaturated.** The contact of particles of solid material with the surface of a supersaturated solution induces immediate crystallization, attended with elevation of temperature.

3. *The presence of other substances already dissolved.*—If to a saturated solution of potassium nitrate, sodium chlorid be added, a further quantity of potassium nitrate may be dissolved. In this case there is double decomposition between the two salts, and the solution contains, besides them, potassium chlorid and sodium nitrate.

4. *The presence of a second solvent.*—If two solvents, *a* and *b*,

incapable of mixing with each other, be brought in contact with a substance which both are capable of dissolving; neither *a* nor *b* takes up the whole of the substance to the exclusion of the other, however greatly the solvent power or bulk of the one may exceed that of the other. The relative quantities taken up by each solvent is in a constant ratio.

Diffusion of Liquids—Dialysis.—If a liquid be carefully floated upon the surface of a second liquid, of greater density, with which it is capable of mixing, two distinct layers will at first be formed. Even at perfect rest, mixture will begin immediately, and progress slowly until the two liquids have **diffused** into each other to form a single liquid whose density is the same throughout.

Substances differ from each other in the rapidity with which they diffuse. Substances capable of crystallization, **crystalloids,** are much more diffusible than those which are incapable of crystallization—**colloids**.

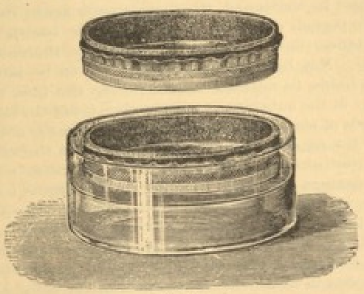
Fig. 13.

If, in place of bringing two solutions in contact with each other, they be separated by a solid or semi-solid, moist, colloid layer, diffusion takes place in the same way through the interposed layer. Advantage is taken of this fact to separate crystalloids from colloids by the process of **dialysis.** The mixed solutions of crystalloid and colloid are brought into the inner vessel of a **dialyser,** Fig. 13, whose bottom consists of a layer of moist parchment paper, while the outer vessel is filled with pure water. Water passes into the inner vessel, and the crystalloid passes into the water in the outer vessel. By frequently changing the water in the outer vessel, solutions of the albuminoids or of ferric hydrate, etc., almost entirely free from crystalloids, may be obtained.

Change of State—Latent Heat.—The passage of a substance from one form to another is always attended by the absorption or liberation of a definite amount of heat. In passing from the solid to the gaseous form, a body absorbs a definite amount of heat with each change of form. If a given quantity of ice at a temperature below the freezing-point of water be heated, its temperature gradually rises until the thermometer marks 0° (32° F.), at which point it remains stationary until the last particle of ice has disappeared. At that time another rise of the thermometer begins, and continues until 100° (212° F.) is reached (at 760 mm. of barometric pressure), when the water boils, and the thermometer remains stationary until the last particle of water has been converted into steam; after which, if the application of heat be continued, the thermometer again rises. During these two periods of stationary thermometer, heat is taken up by the substance, but is not indicated by the thermometer or by the sense. Not being sensible, it is said to be **latent**, a term which is liable to mislead, as conveying the idea that heat is stored up in the substance *as heat;* such is not the case. During the periods of stationary thermometer the heat is not sensible as heat, for the reason that it is being used up in the **work** required to effect that separation of the particles of matter which constitutes its passage from solid to liquid or from liquid to gas.

The amount of heat required to bring about the passage of a given weight of a given substance from the denser to the rarer form is always the same, and the *temperature* indicated by the thermometer during this passage is always the same for that substance, unless in either case a modification be caused by a variation in pressure.

When a solid is liquefied it is said to **fuse**, or to **melt.**

The degree of temperature indicated by the thermometer while a substance is passing from the solid to the liquid state is called its **fusing-point**; that indicated during its passage from the liquid to the solid form, its **freezing-point**; and that indicated during its passage from the liquid to the gaseous form, its **boiling-point.**

The absorption of heat by a volatilizing liquid is utilized in the arts and in medicine for the production of cold (which is simply the absence of heat), in the manufacture of artificial ice, and in the production of local anæsthesia by the ether-spray. The removal of heat from the body in this way, by the evaporation of perspiration from the surface, is an important factor in the maintenance of the body temperature at a point consistent with life.

When a substance passes from a rarer to a denser form it gives out—liberates—an amount of heat equal to that which it absorbed in its passage in the opposite direction. It is for this reason that, while we apply heat to convert a liquid into a vapor, we apply cold (or abstract heat) to reduce a gas to a liquid. As a rule, the thermometrical indication is the same in whichever direction the change of form occurs. Some substances, however, solidify at a temperature slightly different from that at which they fuse.

Usually a solid, when sufficiently heated, passes suddenly into the liquid form, and the fusing-point is sharply defined, and easily determined. Some solids, however, like iron and the fats, when heated to the proper degree, are gradually liquefied, first becoming pasty. Such substances have no true fusing-point, as the thermometer passes through several degrees during their liquefaction.

Most solids, when heated, are first converted into liquids, and these into gases. There are, however, some exceptions to this rule. Most vapors, when condensed, pass into the liquid form, and this in turn into the solid. Some substances, however, are condensed from the form of vapor directly to that of solid, in which case they are said to **sublime.**

Law of Raoult.—When a substance is dissolved in a liquid the freezing point of the latter is lowered and the amount by which it is lowered varies with the nature and quantity of the dissolved substance. Raoult found that the product obtained by multiplying the amount by which the freezing point of a solution containing a fixed quantity of the dissolved substance (1 gram in 100 c.c.), is lowered by the molecular weight of that substance is nearly constant at 18°.5 C. or at 37° C. (See molecular weight, p. 38.) The following are some of the results of Raoult. D.=depression of freezing point in one per cent. solution; M.W.=molecular weight; M.D.=molecular depression.

	M. W.	D.	M. D.
Hydrogen sulfid	34	0.560	19.2
Sulfurous acid	82	0.232	19.1
Nitrous acid	47	0.404	19.0
Hydrocyanic acid	27	0.718	19.4
Acetic acid	60	0.317	19.0
Ammonia	17	1.117	16.9
Methyl alcohol	32	0.541	17.3
Glycerin	92	0.186	17.1
Cane sugar	342	0.054	18.5
Chloral hydrate	165.5	0.114	18.9
Hydrochloric acid	36.5	1.006	36.7
Nitric acid	63	0.568	35.8
Sulfuric acid	98	0.389	38.2
Phosphoric acid	98	0.438	42.9
Sodium hydroxid	40	0.905	36.2
Potassium hydroxid	56	0.630	35.2

Specific Heat.—Equal volumes of different substances at the same temperature contain different amounts of heat. If two equal volumes of the same liquid, of different temperatures, be mixed together, the resulting mixture has a temperature which is the mean between the temperatures of the original volumes. If one litre of water at 4° (39°.2 F.) be mixed with a litre at 38° (100°.4 F.), the resulting two litres will have a temperature of 21° (69°.8 F.). Mixtures of equal volumes of different substances, at different temperatures, do not have a temperature which is the mean of the original temperatures of its constituents. A litre of water at 4° (39°.2 F.), mixed with a litre of mercury at 38° (100°.4 F.), forms a mixture whose temperature is 27° (80°.6 F.). Mercury and water, therefore, differ from each other in their capacity for heat. The same difference exists in a more marked degree between equal *weights* of dissimilar bodies. If a pound of mercury at 4° (39°.2 F.) be agitated with a pound of water at 70° (158° F.), both liquids will have a temperature of 67° (152°.6 F.).

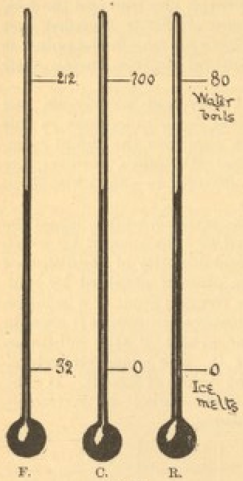

FIG. 14.

The amount of heat required to raise a kilo of water from 0° C. to 1° C. is the unit of heat, and is known as a **calorie.** The **specific heat** of any substance is the amount of heat required to raise one kilo of that substance 1° in temperature, expressed in calories.

Thermometers. — Temperatures below and slightly above the boiling point of mercury are measured by thermometers. The thermometer is usually a glass tube, having a bulb blown at one extremity and closed at the other. The bulb and part of the tube are filled with mercury, or with alcohol, whose contraction or expansion indicates a fall or rise of temperature. The alcoholic thermometer is used for measuring temperatures below the freezing point of mercury (—40°), and the mercurial for temperatures between that point and the boiling point of mercury, 360°(680° F.). Mercurial thermometers are also constructed to read still higher temperatures, the boiling point of the mercury being raised by filling the upper part of the tube with nitrogen under pressure.

In every thermometer there are two **fixed points,** determined by experiment. The **freezing point** is fixed by immersing the instrument in melting ice, and marking the level of the mercury in the tube upon the stem. The **boiling point** is similarly fixed by suspending the instrument in the steam from boiling water. The instrument is graduated according to one of three **scales**: the Celsius or Centigrade, the Fahrenheit, and the Réaumur. The freezing point is marked 0° in the Centigrade and Réaumur scales, and 32° in the Fahrenheit. The boiling point is marked 100° in the Centigrade, 212° in the Fahrenheit, and 80° in the Réaumur (Fig. 14). The space between the fixed points is divided into 100 equal **degrees** in the Centigrade scale, into 180 in the Fahrenheit, and into 80 in the Réaumur. Five degrees Centigrade are therefore equal to nine degrees Fahrenheit.

To convert a thermometric reading in one scale into its equivalent in another the following formulæ are used:

Centigrade into Fahrenheit, $\frac{C\times9}{5}+32=F.$

Fahrenheit into Centigrade, $\frac{(F-32)\times5}{9}=C.$

The Réaumur scale is not used in this country. The Fahrenheit scale is used for unscientific, medical and meteorological purposes, in England and America. The Centigrade scale is used among all nations for all scientific purposes other than those mentioned, and for all uses on the continent of Europe, except in Germany.

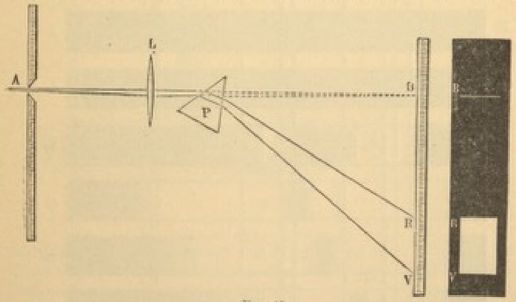

FIG. 15.

Spectroscopy.—A beam of white light, in passing through a prism, is not only **refracted**, or bent into a different course, but is also **dispersed**, or divided into the different colors which constitute the **spectrum** (Fig. 15). The red rays, being the least de-

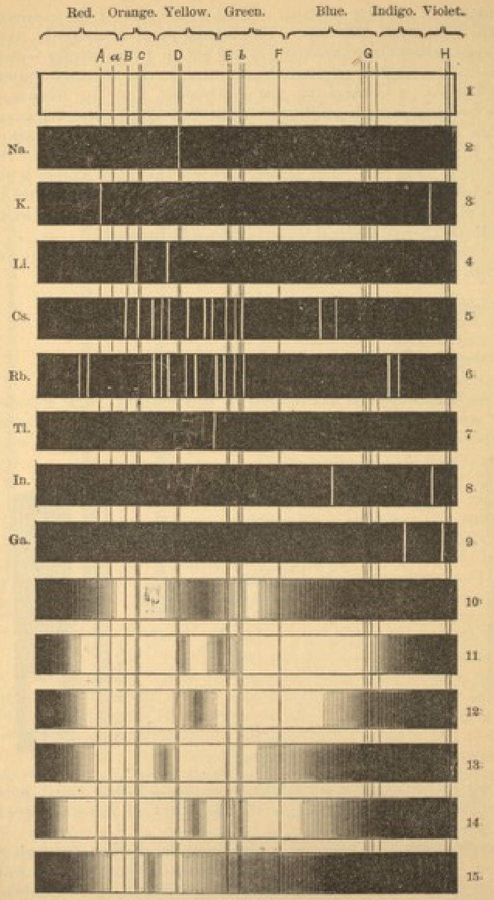
Red.
Orange.
Yellow.
Green.
Blue.
Indigo.
Violet.
A
a
B
C
D
E
b
F
G
H
1
Na.
2
K.
3
Li.
4
Cs.
5
Rb.
6
Tl.
7
In.
8
Ga.
9
10
11
12
13
14
15

FIG. 16.

flected are the **least refrangible**, the violet rays, being the most deflected are the **most refrangible**.

A spectrum is of one of three kinds: 1.) **Continuous**, consisting of a continuous band of colors: red, orange, yellow, green, blue, cyan-blue, and violet. Such spectra are produced by light from white-hot solids and liquids, from gas-light, candle-light, lime-light, and electric light. 2.) **Bright-line spectra**, composed of bright lines upon a dark ground, are produced by glowing vapors and gases. 3.) **Absorption spectra** consist of continuous spectra, crossed by dark lines or bands, and are produced by light passing through a solid, liquid, or gas, capable of absorbing certain rays. Examples of bright-line and absorption spectra are shown in Fig. 16.

The spectrum of sun-light belongs to the third class. It is not continuous, but is crossed by a great number of dark lines, known as **Fraunhofer's lines**, the most distinct of which are designated by letters (No. 1, Fig. 16).

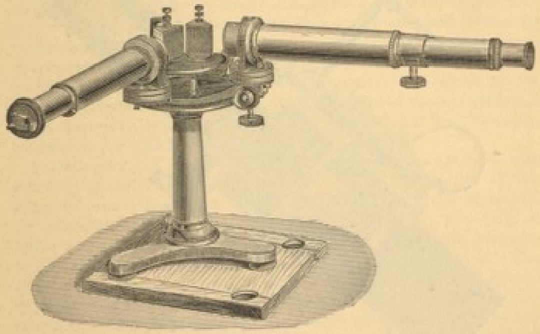

FIG. 17.

The **spectroscope** consists of four essential parts: 1st, the slit, *a*, Fig. 17; a linear opening between two accurately straight and parallel knife-edges. 2d, the colimating lens, *b*; a biconvex lens in whose principal focus the slit is placed, and whose object it is to render the rays from the slit parallel before they enter the prism. 3d, the prism, or prisms, *c*, of dense glass, usually of 60°, and so placed that its refracting edge is parallel to the slit. 4th, an observing telescope, *d*, so arranged as to receive the rays as they emerge from the prisms. Besides these parts spectroscopes are usually fitted with some arbitrary graduation, which serves to fix the location of lines or bands observed.

In direct vision spectroscopes a compound prism is used, so made up of prisms of different kinds of glass that the emerging ray is nearly in the same straight line as the entering ray.

The **micro-spectroscope** (Fig. 18) is a direct vision spectroscope used as the eye-piece of a microscope. With it the spectra of very small bodies may be observed.

As the spectra produced by different substances are characterized by the positions of the lines or bands, some means of fixing their location is required. The usual method consists in determining their relation to the principal Fraunhofer lines. As, however, the relative positions of these lines vary with the nature of the substance of which the prism is made, although their position with regard to the colors of the spectrum is fixed, no two of the arbitrary scales used will give the same reading.

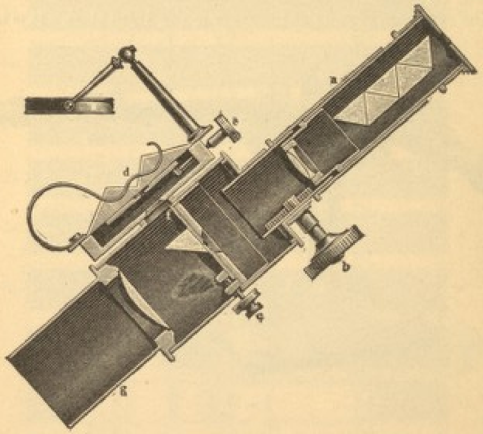

Fig. 18.

The most satisfactory method of stating the positions of lines and bands is in **wave-lengths.** The lengths of the waves of rays of different degrees of refrangibility have been carefully deter-

mined, the unit of measurement being the tenth-metre, of which 10^{10} make a metre. The wave-lengths, $= \lambda$, of the principal Fraunhofer lines, are :

A	7604.00	D	5892.12	G	4307.25
a	7185.00	E	5269.13	H_1	3968.01
B	6867.00	*b*	5172.00	H_2	3933.00
C	6562.01	F	4860.72		

The scale of wave-lengths can easily be used with any spectroscope having an arbitrary scale, with the aid of a curve constructed by interpolation. To construct such a curve, paper is used which is ruled into square inches and tenths. The ordinates are marked with a scale of wave-lengths, and the abscisses with the arbitrary scale of the instrument. The position of each principal Fraunhofer line is then carefully determined in terms of the arbitrary scale, and marked upon the paper with a × at the point where the line of its wave-length and that of its position in the arbitrary scale cross each other. Through these × a curve is then drawn as regularly as possible. In noting the position of an absorption-band, the position of its centre in the arbitrary scale is observed, and its value in wave-lengths obtained from the curve, which, of course, can only be used with the scale and prism for which it has been made.

Polarimetry.—A ray of light passing from one medium into another of different density, at an angle other than 90° to the plane of separation of the two media, is deflected from its course, or **refracted.** Certain substances have the power, not only of deflecting a ray falling upon them in certain directions, but also of dividing it into two rays, which are peculiarly modified. The splitting of the ray is termed **double refraction,** and the altered rays are said to be **polarized.** When a ray of such polarized light meets a mirror held at a certain angle, or a crystal of Iceland spar peculiarly cut (a Nicol's prism), also at a certain angle, it is extinguished. The crystal which produces the polarization is called the **polarizer,** and that which produces the extinction the **analyzer.**

If, when the polarizer and analyzer are so adjusted as to extinguish a ray passing through the former, certain substances are brought between them, light again passes through the analyzer; and in order again to produce extinction, the analyzer must be rotated upon the axis of the ray to the right or to the left. Substances capable of thus influencing polarized light are said to be **optically active.** If, to produce extinction, the analyzer is turned in the direction of the hands of a watch, the substance is said to be **dextrogyrous**; if in the opposite direction, **lœvogyrous.**

The distance through which the analyzer must be turned depends upon the peculiar power of the optically active substance, the length of the column interposed, the concentration, if in solution, and the wave-length of the original ray of light. The **specific rotary power** of a substance is the rotation produced, in degrees and tenths, by one gram of the substance, dissolved in one cubic centimetre of a non-active solvent, and examined in a column one decimetre long. The specific rotary power is determined by dissolving a known weight of the substance in a given volume of solvent, and observing the angle of rotation produced by a column of given length. Then let $p =$ weight in grams of the substance contained in 1 c.c. of solution ; l the length of the column in decimetres ; α the angle of rotation observed ; and $[\alpha]$ the specific rotary power sought, we have

$$[\alpha] = \frac{\alpha}{pl}.$$

In most instruments monochromatic light, corresponding to the D line of the solar spectrum, is used, and the specific rotary power for that ray is expressed by the sign $[\alpha]_D$. The fact that the rotation is right-handed is expressed by the sign +, and that it is left-handed by the sign —.

It will be seen from the above formula that, knowing the value of $[\alpha]_D$ for any given substance, we can determine the weight of that substance in a solution by the formula

$$p = \frac{\alpha}{[\alpha]_D \times l}.$$

The polarimeter or saccharometer is simply a peculiarly constructed polariscope, used to determine the value of α.

Chemical effects of light.—Many chemical combinations and decompositions are much modified by the intensity, and the kind of light to which the reacting substances are exposed. Hydrogen and chlorin gases do not combine, at the ordinary temperature, in the absence of light ; in diffused daylight or gaslight, they unite slowly and quietly ; in direct sunlight, or in the electric light, they unite suddenly and explosively. The salts of silver, used in photography, are not decomposed in the dark, but are rapidly decomposed in the presence of organic matter, when exposed to sunlight.

The chemical activity of the different colored rays of which the solar spectrum is composed is not the same. Those which are the most refrangible possess the greatest chemical activity—the greatest **actinic power.** The visible solar spectrum represents only about one-third of the rays actually emitted from the sun. Two-thirds of the spectrum are invisible as light, and are only recognizable by their heating effects, or by chemical decompositions which they provoke.

Galvanic Electricity.—If two plates, one of pure zinc, the other of pure copper, be immersed in pure, dilute hydrochloric acid, in such a way that the metals are not in contact with each other, there is no action. But if the two metals be connected, outside of the liquid, by a copper wire, the zinc immediately begins to dissolve, and bubbles of hydrogen gas are collected on, and escape from, the surface of the copper, the action continuing so long as the wire connection is maintained, and ceasing so soon as it is interrupted. If a magnetic compass be approached near to the wire, while it is connected with the two plates, the needle will assume a position at right angles to the wire whether the latter be in an east and west position or not. But if the wire be disconnected from either plate, the needle returns to its normal, north and south, position. While the two plates are connected by the wire, an **electrical current** is produced by the chemical action between the zinc and hydrochloric acid, and passes through the liquid and through the wire. A similar electrical current is produced whenever two plates, of different substances, which are conductors of electricity, are connected with each other by a conducting wire, and the free ends dipped into a liquid which has a more intense chemical action upon one plate than upon the other. The plate upon which the greater chemical action is exerted is known as the **negative plate,** or **negative pole,** or **anode,** and, in most batteries consists of zinc. The other plate is called the **collecting plate,** the **positive pole,** or the **cathode,** and usually is made of platinum, carbon or copper. The wires attached to the two plates, as well as any plate, knob or other apparatus in which they terminate are known as the positive and negative **electrodes.** The current is said to pass from the negative to the positive plate in the battery, and from the positive to the negative in the connecting wire, or apparatus outside the battery. The exciting liquid, the two plates, and the connecting wire, with any conducting apparatus that may be interposed in the course of the wire, is called the **circuit.** The circuit is said to be **closed** when the conducting circle is complete. It is **open,** or **broken,** when it is interrupted at one or more points.

Electrolysis.—When a galvanic current of sufficient power passes through a compound liquid, or through a solution of a compound, capable of conducting the current, the compound is decomposed. The decomposition of a compound by this means is called **electrolysis,** and the substance so decomposed is known as the **electrolyte.**

When compounds are subjected to electrolysis the constituent elements are not discharged throughout the mass, although the decomposition occurs at all points between the electrodes. In compounds made up of two elements only, one element is given off at each of the poles, entirely unmixed with the other, and always from the same pole. Thus, if hydrochloric acid be subjected to electrolysis, pure hydrogen is given off at the negative pole and pure chlorin at the positive pole.

In the case of compounds containing more than two elements, a similar decomposition occurs; one element being liberated at one pole and the remaining group of elements separating at the other. This primary decomposition is frequently modified, as to its final products, by intercurrent chemical reactions. Indeed, the group of elements liberated at one pole is rarely capable of separate existence. When, for instance, a solution of potassium sulfate is subjected to electrolysis, the liquid surrounding the positive electrode becomes acid in reaction, and gives off oxygen. At the same time the liquid on the negative side becomes alkaline, and gives off a volume of hydrogen double that of the oxygen liberated. In the first place the potassium sulfate, which consists of potassium, sulfur, and oxygen, is decomposed into potassium, which separates at the negative pole; and sulfur and oxygen, combined together, which go to the positive pole. The potassium liberated at the negative pole immediately decomposes the surrounding water, forming potash, and liberating hydrogen. The sulfur and oxygen group at the positive pole immediately reacts with water to form sulfuric acid and liberate oxygen.

In the electrolysis of chemical compounds the different elements and groups of elements, such as the sulfur and oxygen group in the example given above, known as **residues** or **radicals**, seem to be possessed of definite electrical characters, and are given off at one or the other pole in preference. Those which are given off at the *positive* or platinum pole are supposed to be negatively electrified, and are therefore known as **electro-negative** or **acidulous** elements or residues. Those given off at the *negative* pole, being positively electrified, are known as **electro-positive** or **basylous** elements or residues. The following are the electrical characters of the principal elements and residues:

ELECTRO-NEGATIVE OR ACIDULOUS.

Oxygen,
Sulfur,
Nitrogen,
Chlorin,
Iodin,
Fluorin,
Phosphorus,
Selenium,
Molybdenum,
Tungsten,
Boron,
Carbon,
Antimony,
Tellurium,
Niobium,
Titanium,
Arsenic,
Chromium,
Silicon,
Osmium.

Residues of acids remaining after the removal of a number of hydrogen atoms equal to the basicity of the acid.

Electro-positive or Basylous.

Hydrogen,
Potassium,
Sodium,
Lithium,
Barium,
Strontium,
Calcium,
Magnesium,
Nickel,
Cobalt,
Cerium,
Lead,
Tin,
Bismuth,
Uranium,
Copper,
Glucinium,
Yttrium,
Aluminium,
Zirconium,
Manganese,
Zinc,
Cadmium,
Iron,
Silver,
Mercury,
Palladium,
Platinum,
Rhodium,
Iridium,
Gold,
Alcoholic radicals.

CHEMICAL COMBINATION.

Elements.—The great majority of the substances existing in and upon the earth may be so decomposed as to yield two or more other substances, distinct in their properties from the substance from whose decomposition they resulted, and from each other. If, for example, sugar be treated with sulfuric acid, it blackens, and a mass of charcoal separates. Upon further examination we find that water has also been produced. From this water we may obtain two gases, differing from each other widely in their properties. Sugar is therefore made up of carbon and the two gases, hydrogen and oxygen; but it has the properties of sugar, and not those of either of its constituent parts. There is no method known by which carbon, hydrogen, and oxygen can be split up, as sugar is, into other dissimilar substances.

An element is a substance which cannot by any known means be split up into other dissimilar bodies.

Elements are also called **elementary substances** or **simple substances.**

The number of well-characterized elements at present known is sixty-nine. Of these, either free, or united with each other in varied proportion, and in different ways, all matter is composed.

Laws governing the combination of elements.—The alchemists, Arabian and European, contented themselves in accumulating a store of knowledge of isolated phenomena, without, as far as we know, attempting, in any serious way, to group them in such a manner as to learn the laws governing their occurrence. It was not until the latter part of the last century, 1777, that Wenzel, of Dresden, implied, if he did not distinctly enunciate, what is known as the law of reciprocal proportions. A few years later, Richter, of Berlin, confirming the work of Wenzel, added to it the law of definite proportions, usually called Dalton's first law. Finally, as the result of his investigations from 1804 to 1808, Dalton added the law of multiple proportions, and, reviewing the work of his predecessors, enunciated the results clearly and distinctly.

Considering these laws, not in the order of their discovery, but in that of their natural sequence, we have:

THE LAW OF DEFINITE PROPORTIONS.—**The relative weights of elementary substances in a compound are definite and invariable.** If, for example, we analyze water, we find that it is composed of eight parts by weight of oxygen for each part by weight of hydrogen, and that this proportion exists in every instance, whatever the source of the water. If, instead of decomposing, or

analyzing water, we start from its elements, and by **synthesis**, cause them to unite to form water, we find that, if the mixture be made in the proportion of eight oxygen to one hydrogen by weight, the entire quantity of each gas will be consumed in the formation of water. But if an excess of either have been added to the mixture, that excess will remain after the combination.

Compounds are substances made up of two or more elements united with each other in definite proportions. Compounds exhibit properties of their own, which differ from those of the constituent elements to such a degree that the properties of a compound can never be deduced from a knowledge of those of the constituent elements. Common salt, for instance, is composed of 39.32 per cent. of the light, bluish-white metal, sodium, and 60.68 per cent. of the greenish-yellow, suffocating gas, chlorin.

Compounds made up of two elements only are called **binary** compounds; those consisting of three elements, **ternary** compounds; those containing four elements, **quaternary** compounds, etc.

A mixture is composed of two or more substances, elements or compounds, mingled in any proportion. The characters of a mixture may be predicated from a knowledge of the properties of its constituents. Thus sugar and water may be mixed in any proportion, and the mixture will have the sweetness of the sugar, and will be liquid or solid, according as the liquid or solid ingredient predominates in quantity.

THE LAW OF MULTIPLE PROPORTIONS.—**When two elements unite with each other to form more than one compound, the resulting compounds contain simple multiple proportions of one element as compared with a constant quantity of the other.**

Oxygen and nitrogen, for example, unite with each other to form no less than five compounds. Upon analysis we find that in these the two elements bear to each other the following relations by weight:

In the first, 14 parts of nitrogen to 8 of oxygen.
In the second, 14 parts of nitrogen to $8\times2=16$ of oxygen.
In the third, 14 parts of nitrogen to $8\times3=24$ of oxygen.
In the fourth, 14 parts of nitrogen to $8\times4=32$ of oxygen.
In the fifth, 14 parts of nitrogen to $8\times5=40$ of oxygen.

THE LAW OF RECIPROCAL PROPORTIONS.—**The ponderable quantities in which substances unite with the same substance express the relation, or a simple multiple thereof, in which they unite with each other.** Or, as Wenzel stated it, "the weights b, b', b'' of several bases which neutralize the same weight a of an acid are the same which will neutralize a constant weight a' of another acid; and the weights a, a', a'' of different acids which neutralize the same weight *b* of a base are the same which will neutralize a constant weight of another base *b*′." For example: 71 parts of chlorin combine with 40 parts of calcium, and 16 parts of oxygen also combine with 40 parts of calcium, therefore 71 parts of chlorin combine with 16 parts of oxygen, or the two elements combine in the proportion of some simple multiples of 71 and 16.

The Atomic Theory.—The laws of Wenzel, Richter, and Dalton, given above, are simply generalized statements of certain groups of facts, and, as such, not only admit of no doubt, but are the foundations upon which chemistry as an exact science is based. Dalton, seeking an explanation of the reason of being of these facts, was led to adopt the view held by the Greek philosopher, Democritus, that matter was not infinitely divisible. He retained the name *atom* (ἄτομος = indivisible), given by Democritus to the ultimate particles, of which matter was supposed by him to be composed; but rendered the idea more precise by ascribing to these atoms real magnitude, and a definite weight, and by considering elementary substances as made up of atoms of the same kind, and compounds as consisting of atoms of different kinds.

This hypothesis, the first step toward the atomic theory as entertained to-day, afforded a clear explanation of the numerical results stated in the three laws. If hydrogen and oxygen always unite together in the proportion of one of the former to eight of the latter, it is because, said Dalton, the compound consists of an atom of hydrogen, weighing 1, and an atom of oxygen, weighing 8. If, again, in the compounds of nitrogen and oxygen, we have the two elements uniting in the proportion 14 : 8——14 : 8×2——14 : 8×3——14 : 8×4——14 : 8×5, it is because they are severally composed of an atom of nitrogen weighing 14, united to 1, 2, 3, 4, or 5 atoms of oxygen, each weighing 8. Further, that compounds do not exist in which any fraction of 8 oxygen enters, because 8 is the weight of the indivisible atom of oxygen.

Dalton's hypothesis of the existence of atoms as definite quantities did not, however, meet with general acceptance. Davy, Wollaston, and others considered the quantities in which Dalton had found the elements to unite with each other, as mere *proportional numbers* or *equivalents*, as they expressed it, nor is it probable that Dalton's views would have received any further recognition until such time as they might have been exhumed from some musty tome, had their publication not been closely followed by that of the results of the labors of Humboldt and of Gay Lussac, concerning the *volumes* in which gases unite with each other.

In the form of what are known as Gay Lussac's laws, these results are:

First.—There exists a simple relation between the volumes of gases which combine with each other.

Second.—There exists a simple relation between the sum of the volumes of the constituent gases, and the volume of the gas formed by their union. For example: .

1 volume chlorin unites with 1 volume hydrogen to form 2 volumes hydrochloric acid.
1 volume oxygen unites with 2 volumes hydrogen to form 2 volumes vapor of water.
1 volume nitrogen unites with 3 volumes hydrogen to form 2 volumes ammonia.
1 volume oxygen unites with 1 volume nitrogen to form 2 volumes nitric oxid.
1 volume oxygen unites with 2 volumes nitrogen to form 2 volumes nitrous oxid.

Berzelius, basing his views upon these results of Gay Lussac, modified the hypothesis of Dalton and established a distinction between the *equivalents* and *atoms*. The composition of water he expressed, in the notation which he was then introducing, as being H_2O, and not HO as Dalton's hypothesis called for. As, however, Berzelius still considered the atom of oxygen as weighing 8, he was obliged also to consider the atoms of hydrogen and of certain other elements as double atoms—a fatal defect in his system, which led to its overthrow, and to the re-establishment of the formula HO for water.

It was reserved to Gerhardt to clearly establish the distinction between atom and molecule; to observe the bearing of the discoveries of Avogadro and Ampère upon chemical philosophy; and thus to establish the atomic theory as entertained at present.

As a result of his investigations in the domain of organic chemistry, Gerhardt found that, if Dalton's equivalents be adhered to, whenever carbon dioxid or water is liberated by the decomposition of an organic substance, it is invariably in double equivalents, never in single ones. Always $2CO_2$ or $2HO$, or some multiple thereof, never CO_2 or HO. He further found that if the equivalents $C=6$, $H=1$, and $O=8$ be retained, the formulæ became such that the equivalents of carbon are always divisible by two. In fact, he found the same objections to apply to the notation then in use that had been urged against that of Berzelius.

In 1811, Avogadro, from purely physical researches, had been enabled to state the law which is now known by his name, to the effect that **equal volumes of all gases, under like conditions of temperature and pressure, contain equal numbers of molecules.**

This law is also known as the law of Ampère, the French physicist having enunciated it about the same time as, and independently of, his Italian colaborer.

In the hands of Gerhardt this law, in connection with those of Gay Lussac, became the foundation of what is sometimes called the "new chemistry." Bearing in mind Avogadro's law, we may translate the first three combinations given in the table on p. 33 into the following :

1 molecule chlorin unites with 1 molecule hydrogen, to form 2 molecules hydrochloric acid.
1 molecule oxygen unites with 2 molecules hydrogen, to form 2 molecules vapor of water.
1 molecule nitrogen unites with 3 molecules hydrogen, to form 2 molecules ammonia.

But the ponderable quantities in which these combinations take place are :

35.5 chlorin to .... 1 hydrogen.
16 oxygen to.... .... 2 hydrogen.
14 nitrogen to.......................... 3 hydrogen.

And as single molecules of hydrogen, oxygen, and nitrogen are in these combinations subdivided to form 2 molecules of hydrochloric acid, water, and ammonia, it follows that these molecules must each contain two equal quantities of hydrogen, oxygen, and nitrogen, less in size than the molecules themselves. And, further, as in these instances each molecule contains two of these smaller quantities, or **atoms**, the relation between the weights of the molecules must be also the relation between the weights of the atoms, and we may therefore express the combinations thus :

1 atom chlorin weighing 35.5 unites with 1 atom hydrogen weighing 1 ;
1 atom oxygen weighing 16 unites with 2 atoms hydrogen weighing 2 ;
1 atom nitrogen weighing 14 unites with 3 atoms hydrogen weighing 3 ;

and consequently, if the atom of hydrogen weighs 1, that of chlorin weighs 35.5, that of oxygen 16, and that of nitrogen 14.

Atomic Weight.—The distinction between molecules and atoms may be expressed by the following definitions :

A molecule is the smallest quantity of any substance that can exist in the free state.

An atom is the smallest quantity of an elementary substance that can enter into a chemical reaction.

The molecule is always made up of atoms, upon whose nature, number, and arrangement with regard to each other, the properties of the substance depend. In an elementary substance the atoms composing the molecules are the same in kind, and usually two in number. In compound substances they are dissimilar, and vary in quantity from two in a simple compound, like hydrochloric acid, to hundreds or thousands in more complex substances.

The word atom can only be used in speaking of an elementary body, and that only while it is passing through a reaction. The term molecule applies indifferently to elements and compounds.

The atoms have definite relative weights ; and upon an exact determination of these weights depends the entire science of quantitative analytical chemistry. (See stoichiometry, p. 44.)

They have been determined by repeated and careful analyses of perfectly pure compounds of the elements, and **express the weight of one atom of the element as compared with the weight of one atom of hydrogen,** that being the lightest element known. It is also the weight of a volume of the element, in the form of gas, which would occupy the same volume, under like pressure and temperature, as an amount of hydrogen weighing one. What the *absolute weight* of an atom of any element may be we do not know, nor would the knowledge be of any service did we possess it.

The following table contains a list of the elements at present known, with their atomic weights :

ELEMENTS.

NAME.	A. Symbol.	B. Atomic Weight.	NAME.	A. Symbol.	B. Atomic Weight.
Aluminium ...	Al.	27.02	Mercury	Hg.	199.7
Antimony.....	Sb.	120	Molybdenum..	Mo.	95.5
Arsenic	As.	74.9	Nickel	Ni.	58
Barium........	Ba.	136.8	Nitrogen......	N.	14.044
Bismuth	Bi.	206.5	Osmium......	Os.	198.5
Boron..........	Bo.	11	Oxygen........	O.	16
Bromin	Br.	79.952	Palladium	Pd.	105.7
Cadmium	Cd.	111.8	Phosphorus...	P.	31
Cesium	Cs.	132.6	Platinum......	Pt.	194.4
Calcium.......	Ca.	40	Potassium	K.	39.137
Carbon	C.	11.974	Rhodium	Rh.	104.1
Cerium	Ce.	141	Rubidium.....	Rb.	85.3
Chlorin	Cl.	35.457	Ruthenium....	Ru.	104.2
Chromium....	Cr.	52.4	Samarium	Sm.	150
Cobalt	Co.	58.9	Scandium.....	Sc.	44
Columbium...	Cb.	94	Selenium......	Se.	78.8
Copper.	Cu.	63.2	Silicon.........	Si.	28
Davyium......	Da.	154	Silver..........	Ag.	107.675
Didymium....	D.	144.78	Sodium	Na.	22.998
Erbium	E.	165.9	Strontium.....	Sr.	87.4
Fluorin	F.	19	Sulfur	S.	31.984
Gallium........	Ga.	68.8	Tantalum......	Ta.	182
Germanium...	Gr.	72.32	Tellurium......	Te.	128
Glucinum.	Gl.	9	Thallium	Tl.	203.7
Gold	Au.	196.2	Thorium.......	Th.	233
Hydrogen.....	H.	1	Tin	Sn.	117.7
Indium........	In.	113.4	Titanium	Ti.	49.85
Iodin	I.	126.85	Tungsten	W.	183.6
Iridium	Ir.	192.7	Uranium......	U.	238.5
Iron...........	Fe.	55.9	Vanadium....	V.	51.3
Lanthanium ..	La.	138.5	Ytterbium	Yb.	172.7
Lead...........	Pb.	206.92	Yttrium.	Y.	89.8
Lithium.......	Li.	7	Zinc	Zn.	64.9
Magnesium....	Mg.	24	Zirconium.....	Zr.	89.6
Manganese	Mn.	54			

In some cases the results of analyses are such as would agree with two values as the atomic weight of an element equally well. In this case we can decide which is the correct value by the **law of Dulong and Petit.** These observers found that while the atomic weights of the elements vary greatly from each other, the specific heats (see p. 19) differ from each other in an opposite manner, and to such an extent that the product obtained by multiplying the two together does not vary much from 6.4. This product is known as the **atomic heat.** When it is not possible to determine by analysis which of two numbers is the correct atomic weight of an element, that one is selected which, when multiplied by the specific heat, gives a result most nearly approaching 6.4.

The atomic heats of boron, carbon, silicon, sulfur, and phosphorus are subject to great variations, as is shown in the following table :

		Specific Heat.	Atomic Heat.
BORON.			
Crystallized	at − 39.6°	0.1915	2.11
Crystallized	at + 76.7°	0.2737	3.01
Crystallized	at + 233.2°	0.3663	3.99
Amorphous		0.255	2.81
CARBON.			
Diamond	at − 50.5°	0.0635	0.76
Diamond	at + 140°	0.2218	2.66
Diamond	at + 985°	0.4589	5.51
Graphite	at − 50.3°	0.1138	1.37
Graphite	at + 138.5°	0.2542	3.05
Graphite	at + 977.9°	0.4670	5.60
Wood charcoal		0.2415	2.90
SILICON.			
Crystallized	at − 39.8°	0.1360	3.81
Crystallized	at + 128.7°	0.1964	5.50
Crystallized	at + 232.4°	0.2029	5.68
Fused	at + 100°	0.175	4.90
SULFUR.			
Orthorhombic	at + 45°	0.163	5.22
Orthorhombic	at + 99°	0.1776	5.68
Liquid	at + 150°	0.234	7.49
Recently fused	at + 98°	0.20259	6.48

PHOSPHORUS.		Specific Heat.	Atomic Heat.
Yellow	at − 78°	0.174	5.39
Yellow	at + 36°	0.202	6.26
Liquid	at + 100°	0.212	6.57
Amorphous	at + 98°	0.170	5.27

It will be observed that, as the temperature of the *solid* element is increased, the atomic heat more nearly approaches 6.4. It will further be noticed that those elements with which the perturbations occur are those which are capable of existing in two or more allotropic forms (see p. 15). As in the passage of an element from one allotropic condition to another, absorption or liberation of heat always takes place, as the result of "interior work;" it is probable that these perturbations are due to a constant tendency of the element to pass from one allotropic condition to another.

The atomic heats of those elementary gases which have only been liquefied by enormous cold and pressure are tolerably constant at about 2.4.

Molecular Weight.—The molecular weight of a substance is the weight of its molecule as compared with the weight of an atom of hydrogen. It is also, obviously, the sum of the weights of all the atoms making up the molecule.

A very ready means of determining the molecular weight of a gaseous substance or of one which may be converted into vapor, is based upon Avogadro's law. The sp. gr. of a gas is the weight of a given volume as compared with that of an equal volume of hydrogen. But these equal volumes contain equal numbers of molecules (p. 33), and therefore, in determining the sp. gr. of a gas, we obtain the weight of its molecule as compared with that of a molecule of hydrogen; and, as the molecule contains two atoms of hydrogen, while one atom of hydrogen is the unit of comparison, it follows that **the specific gravity of a gas compared with hydrogen, multiplied by two, is its molecular weight.**

For example, the gas acetylene and the liquid benzene each contain 92.31 per cent. of carbon, and 7.69 per cent. of hydrogen; which is equivalent to 24 parts, or two atoms of carbon; and 2 parts, or two atoms of hydrogen. The sp. gr. of acetylene, referred to hydrogen=2, is 13; its molecular weight is, therefore, 26, and its molecule contains two atoms of carbon and two atoms of hydrogen. The sp. gr. of vapor of benzene is 39; its molecular weight is, therefore, 78, and its molecule contains six atoms of carbon and six atoms of hydrogen.

When a substance is not capable of being volatilized, its molecular weight may be obtained by determining its percentage composition by analysis, and selecting that value which is nearest in obedience to the **law of Raoult** (see p. 19).

The vapor densities of comparatively few elements are known :

	Vapor Density.	Atomic Weight.	Molecular Weight.
Hydrogen	1	1	2
Oxygen	16	16	32
Sulfur	32	32	64
Selenium	82	79	164
Tellurium	130	128	260
Chlorin	35.5	35.5	71
Bromin	80	80	160
Iodin	127	127	254
Phosphorus	63	31	124
Arsenic	150	75	300
Nitrogen	14	14	28
Potassium	39.	39	78
Cadmium	56	112	112
Mercury	100	200	200

The atomic weight being, in most of the above instances, equal to the vapor density, and to half the molecular weight, it may be inferred that *the molecules of these elements consist of two atoms.* Noticeable discrepancies exist in the case of four elements. The molecular weights of phosphorus and arsenic, as obtained from their vapor densities, are not double, but four times as great as their atomic weights. The molecules of phosphorus and arsenic are, therefore, supposed to contain four atoms. Those of cadmium and mercury contain but one atom.

Valence or Atomicity.—It is known that the atoms of different elements possess different powers of combining with and of replacing atoms of hydrogen. Thus :

One atom of chlorin combines with one atom of hydrogen.

One atom of oxygen combines with two atoms of hydrogen.

One atom of nitrogen combines with three atoms of hydrogen.

One atom of carbon combines with four atoms of hydrogen.

The valence, atomicity, or equivalence of an element is the saturating power of one of its atoms as compared with that of one atom of hydrogen.

Elements may be classified according to their valence into—

Univalent elements, or monads	Cl'
Bivalent elements, or dyads	O''
Trivalent elements, or triads	B'''
Quadrivalent elements, or tetrads	C^{iv}
Quinquivalent elements, or pentads	P^{v}
Sexvalent elements, or hexads	W^{vi}

Elements of even valence, *i. e.*, those which are bivalent, quadrivalent, or sexvalent, are sometimes called **artiads** ; those of uneven valence being designated as **perissads.**

In notation the valence is indicated, as above, by signs placed to the right and above the symbol of the element.

But the valence of the elements is not fixed and invariable. Thus, while chlorin and iodin each combine with hydrogen, atom for atom, and in those compounds are consequently univalent, they unite with each other to form two compounds—one containing one atom of iodin and one of chlorin, the other containing one atom of iodin and three of chlorin. Chlorin being univalent, iodin is obviously trivalent in the second of these compounds. Again, phosphorus forms two chlorids, one containing three, the other five atoms of chlorin to one of phosphorus.

In view of these facts, we must consider, either: 1, that the valence of an element is that which it exhibits in its most saturated compounds, as phosphorus in the pentachlorid, and that the lower compounds are non-saturated, and have free valences; or 2, that the valence is variable. The first supposition depends too much upon the chances of discovery of compounds in which the element has a higher valence than that which might be considered the maximum to-day. The second supposition—notwithstanding the fact that, if we admit the possibility of two distinct valences, we must also admit the possibility of others—is certainly the more tenable and the more natural. *In speaking, therefore, of the valence of an element, we must not consider it as an absolute quality of its atoms, but simply as their combining power in the particular class of compounds under consideration.* Indeed, compounds are known in whose molecules the atoms of one element exhibit two distinct valences. Thus, ammonium cyanate contains two atoms of nitrogen: one in the ammonium group is quinquivalent, one in the acid radical is trivalent.

When an element exhibits different valences, these differ from each other by two. Thus, phosphorus is trivalent or quinquivalent: platinum is bivalent or quadrivalent.

Symbols—Formulæ—Equations.—**Symbols** are conventional abbreviations of the names of the elements, whose purpose it is to introduce simplicity and exactness into descriptions of chemical actions. They consist of the initial letter of the Latin name of the element, to which is usually added one of the other letters. If there be more than two elements whose names begin with the same letter, the single-letter symbol is reserved for the commonest element. Thus, we have nine elements whose names begin with C; of these the commonest is Carbon, whose symbol is C; the others have double-letter symbols, as Chlorin, Cl; Cobalt, Co; Copper, Cu (Cuprum), etc.

These symbols do not indicate simply an indeterminate quantity, but represent one atom of the corresponding element.

When more than one atom is spoken of, the number of atoms which it is desired to indicate is written either before the symbol or, in small figures, after and below it. Thus, H indicates one atom of hydrogen; 2Cl, two atoms of chlorin; C_4, four atoms of carbon, etc.

What the symbol is to the element, the **formula** is to the compound. By it the number and kind of atoms of which the molecule of a substance is made up are indicated. The simplest kind of formulæ are what are known as **empirical formulæ**, which indicate only the kind and number of atoms which form the compound. Thus, HCl indicates a molecule composed of one atom of hydrogen united with one atom of chlorin; $5H_2O$, five molecules, each composed of two atoms of hydrogen and one atom of oxygen, the number of molecules being indicated by the proper numeral placed before the formula, in which place it applies to all the symbols following it. Sometimes it is desired that a numeral shall apply to a part of the symbols only, in which case they are enclosed in parentheses; thus, $Al_2(SO_4)_3$ means twice Al and three times SO_4.

For other varieties of formulæ, see pp. 50–52.

Equations are combinations of formulæ and algebraic signs so arranged as to indicate a chemical reaction and its results. The signs used are the plus and equality signs; the former being equivalent to "and," and the second meaning "have reacted upon each other and have produced." The substances entering into the reaction are placed before the equality sign, and the products of the reaction after it; thus, the equation

$$2KHO+H_2SO_4=K_2SO_4+2H_2O$$

means, when translated into ordinary language: two molecules of potash, each composed of one atom of potassium, one atom of hydrogen, and one atom of oxygen, *and* one molecule of sulfuric acid, composed of one atom of sulfur, four atoms of oxygen, and two atoms of hydrogen, *have reacted upon each other and have produced* one molecule of potassium sulfate, composed of one atom of sulfur, four atoms of oxygen, and two atoms of potassium, *and* two molecules of water, each composed of two atoms of hydrogen and one atom of oxygen.

As no material is ever lost or created in a reaction, the number of each kind of atom occurring before the equality sign in an equation must always be the same as that occurring after it. In writing equations they should always be proved by examining whether the half of the equation before the equality sign contains the same number of each kind of atom as that after the equality sign. If it do not the equation is incorrect.

Acids, Bases, and Salts.—All ternary and quaternary mineral substances have one of three **functions.**

The **function** of a substance is its chemical character and relationship, and indicates certain general properties, reactions and decompositions which all substances possessing the same function possess or undergo alike. Thus, in mineral chemistry we have **acids, bases,** and **salts**; in organic chemistry alcohols, aldehydes, ketones, ethers, etc.

An acid is a compound of an electro-negative element or residue with hydrogen; which hydrogen it can part with in exchange for an electro-positive element without formation of a base. An acid may also be defined as a **compound body which evolves water by its action upon pure caustic potash or soda.**

No substance which does not contain hydrogen can, therefore, be called an acid.

The basicity of an acid is the number of replaceable hydrogen atoms contained in its molecule.

A **monobasic** acid is one containing a single replaceable atom of hydrogen, as nitric acid, HNO_3; a **dibasic** acid is one containing two such replaceable atoms, as sulfuric acid, H_2SO_4; a **tribasic** acid is one containing three replaceable hydrogen atoms, as phosphoric acid, H_3PO_4. **Polybasic** acids are such as contain more than one atom of replaceable hydrogen.

Hydracids are acids containing no oxygen; **oxacids** or **oxyacids** contain both hydrogen and oxygen.

The term **base** is regarded by many authors as applicable to any compound body capable of neutralizing an acid. It is, however, more consistent with modern views to limit the application of the name to such **compound substances as are capable of entering into double decomposition with acids to form salts and water.** They may be considered as one or more molecules of water in which one-half of the hydrogen has been replaced by an electro-positive element or radical; or as compounds of such elements or radicals with one or more groups, OH. Being thus considered as derivable from water, they are also known as hydroxids. They have the general formula, $Mn(OH)n$. They are **monatomic, diatomic, triatomic,** etc., according as they contain one, two, three, etc., groups **oxhydryl** (OH).

A double decomposition is a reaction in which both of the reacting compounds are decomposed to form two new compounds.

Sulfobases, or hydrosulfids, are compounds in all respects resembling the bases, except that in them the oxygen of the base is replaced by sulfur.

Salts are substances formed by the substitution of basylous radicals or elements for a part or all of the replaceable hydrogen of an acid. They are always formed, therefore, when bases and acids enter into double decomposition. They are not, as was formerly supposed, formed by the union of a metallic with a non-metallic oxid, but, as stated above, by the substitution of one or more atoms of an element or radical for the hydrogen of the acid. Thus, the compound formed by the action of sulfuric acid upon quicklime is not SO_3CaO, but $CaSO_4$, formed by the interchange of atoms:

and not

it is, therefore, **calcium sulfate,** and not **sulfate of lime.**

The term **salt,** as used at present, applies to the compounds formed by the substitution of a basylous element for the hydrogen of *any* acid; and indeed, as used by some authors, to the acids themselves, which are considered as salts of hydrogen. It is probable, however, that eventually the name will be limited to such compounds as correspond to acids whose molecules contain more than two elements. Indeed, from the earliest times of modern chemistry a distinction has been observed between the **haloid salts,** *i.e*, those the molecules of whose corresponding acids consist of hydrogen, united with one other element, on the one hand; and **the oxysalts,** the salts of the oxacids, *i.e.*, those into whose composition oxygen enters, on the other hand. This distinction, however, has gradually fallen into the background, for the reason that the methods and conditions of formation of the two kinds of salts are usually the same *when the basylous element belongs to that class usually designated as metallic.*

There are, however, important differences between the two classes of compounds. There exist compounds of all of the elements corresponding to the hydracids, binary compounds of chlorin, bromin, iodin, and sulfur. There is, on the other hand, a large class of elements the members of which are incapable of forming salts corresponding to the oxacids. No salt of an oxacid with any one of the elements usually classed as metalloids (excepting hydrogen) has been obtained.

Haloid salts may be formed by direct union of their constituent elements; oxysalts are never so produced.

Action of Acids and Bases on Salts, and of Salts on each other. —If an acid be added to a solution of a salt whose acid it nearly equals in chemical activity, the salts of both acids and the free acids themselves will probably exist in the solution, provided both acids and salts are soluble. Thus:

$$\underset{\text{Sulfuric acid.}}{2H_2SO_4} + \underset{\text{Potassium nitrate.}}{3KNO_3} = \underset{\text{Potassium sulfate.}}{K_2SO_4} + \underset{\text{Potassium nitrate.}}{KNO_3} + \underset{\text{Sulfuric acid.}}{H_2SO_4} + \underset{\text{Nitric acid.}}{2HNO_3}$$

If an acid be added to a solution of a salt whose acid it greatly exceeds in activity, the salt is decomposed, with formation of the salt of the stronger acid and liberation of the weaker acid; both acids and salts being soluble:

$$\underset{\text{Sulfuric acid.}}{H_2SO_4} + \underset{\text{Sodium acetate.}}{2C_2H_3O_2Na} = \underset{\text{Sodium sulfate.}}{Na_2SO_4} + \underset{\text{Acetic acid.}}{2C_2H_3O_2H}$$

If to a solution of a salt whose acid is insoluble in the solvent used, an acid be added capable of forming a soluble salt with the basylous element, such soluble salt is formed and the acid is deposited:

$$\underset{\text{Sulfuric acid.}}{H_2SO_4} + \underset{\text{Sodium stearate.}}{2C_{18}H_{35}O_2Na} = \underset{\text{Sodium sulfate.}}{Na_2SO_4} + \underset{\text{Stearic acid.}}{2C_{18}H_{35}O_2H}$$

If to a salt whose acid is volatile at the existing temperature, an acid capable of forming with the basylous element a salt fixed at the same temperature be added, the fixed salt is formed and the volatile acid expelled. Thus, with the application of heat:

$$\underset{\text{Sulfuric acid.}}{H_2SO_4} + \underset{\text{Sodium nitrate.}}{2NaNO_3} = \underset{\text{Sodium sulfate.}}{Na_2SO_4} + \underset{\text{Nitric acid.}}{2HNO_3}$$

If to a solution of a salt an acid be added which is capable of forming an insoluble salt with the base, such insoluble salt is formed and precipitated:

$$\underset{\text{Sulfuric acid.}}{H_2SO_4} + \underset{\text{Barium nitrate.}}{Ba(NO_3)_2} = \underset{\text{Barium sulfate.}}{BaSO_4} + \underset{\text{Nitric acid.}}{2HNO_3}$$

If to a solution of a salt whose basylous element is insoluble a soluble base is added, capable of forming a soluble salt with the acid, such soluble salt is formed, with precipitation of the insoluble base:

$$\underset{\text{Cupric sulfate.}}{CuSO_4} + \underset{\text{Potassium hydroxid.}}{2KHO} = \underset{\text{Potassium sulfate.}}{K_2SO_4} + \underset{\text{Cupric hydroxid.}}{CuH_2O_2}$$

If a base be added to a solution of a salt with whose acid it is capable of forming an insoluble salt, such insoluble salt is formed and precipitated, and the base of the original salt, if insoluble, is also precipitated:

$$\underset{\text{Barium hydroxid.}}{BaH_2O_2} + \underset{\text{Potassium sulfate.}}{K_2SO_4} = \underset{\text{Barium sulfate.}}{BaSO_4} + \underset{\text{Potassium hydroxid.}}{2KHO}$$

$$\underset{\text{Barium hydroxid.}}{BaH_2O_2} + \underset{\text{Silver sulfate.}}{Ag_2SO_4} = \underset{\text{Barium sulfate.}}{BaSO_4} + \underset{\text{Silver hydroxid.}}{2AgHO}$$

When solutions of two salts, the acids of both of which form soluble salts with both bases, are mixed, the resultant liquid contains the four salts :

$$\underset{\text{Potassium sulfate.}}{3K_2SO_4} + \underset{\text{Sodium nitrate.}}{3NaNO_3} = \underset{\text{Potassium sulfate.}}{2K_2SO_4} + \underset{\text{Sodium sulfate.}}{Na_2SO_4} + \underset{\text{Potassium nitrate.}}{2KNO_3} + \underset{\text{Sodium nitrate.}}{NaNO_3}$$

or in some other proportion.

If solutions of two salts, the acid of one of which is capable of uniting with the base of the other to form an insoluble salt, are mixed, such insoluble salt is precipitated :

$$\underset{\text{Barium nitrate.}}{Ba(NO_3)_2} + \underset{\text{Sodium sulfate.}}{Na_2SO_4} = \underset{\text{Barium sulfate.}}{BaSO_4} + \underset{\text{Sodium nitrate.}}{2NaNO_3}$$

Stoichiometry (*στοιχεῖον* = an element; *μέτρον* = a measure)—in its strict sense refers to the law of definite proportions, and to its applications. In a wider sense, the term applies to the mathematics of chemistry, to those mathematical calculations by which the quantitative relations of substances acting upon each other, and of the products of such reactions are determined.

A chemical reaction can always be expressed by an equation, which, as it represents not only the nature of the materials involved, but also the number of molecules of each, is a quantitative as well as a qualitative statement.

Let it be desired to determine how much sulfuric acid will be required to completely decompose 100 parts of sodium nitrate, and what will be the nature and quantities of the products of the decomposition. First the equation representing the reaction is constructed :

$$\underset{\text{Sulfuric acid.}}{H_2SO_4} + \underset{\text{Sodium nitrate.}}{2NaNO_3} = \underset{\text{Disodic sulfate.}}{Na_2SO_4} + \underset{\text{Nitric acid.}}{2HNO_3}$$

which shows that one molecule of sulfuric acid decomposes two molecules of sodium nitrate, with the formation of one molecule of sodium sulfate and two of nitric acid. The quantities of the different substances are, therefore, represented by their molecular weights, or some multiple thereof, which are in turn obtained by adding together the atomic weights of the constituent atoms :

$$\begin{array}{rcrcrcr} H_2SO_4 & + & 2NaNO_3 & = & Na_2SO_4 & + & 2HNO_3 \\ 1\times2=\ 2 & & 23\times1=23 & & 23\times2=46 & & 1\times1=\ 1 \\ 32\times1=32 & & 14\times1=14 & & 32\times1=32 & & 14\times1=14 \\ 16\times4=\underline{64} & & 16\times3=\underline{48} & & 16\times4=\underline{64} & & 16\times3=\underline{48} \\ 98 & & 85\times2=170 & & 142 & & 63\times2=126 \end{array}$$

Consequently, 98 parts H_2SO_4 decompose 170 parts $NaNO_3$, and produce 142 parts Na_2SO_4 and 126 parts HNO_3. To find the result as referred to 100 parts $NaNO_3$, we apply the simple proportion :

$$\begin{array}{l}
170 : 100 :: 98 : 57.64\text{—}57.64 = \text{parts } H_2SO_4 \text{ required.} \\
170 : 100 :: 142 : 83.53\text{—}83.53 = \text{ `` } \; Na_2SO_4 \text{ produced.} \\
170 : 100 :: 126 : 74.11\text{—}74.11 = \text{ `` } \; HNO_3 \quad \text{``}
\end{array}$$

As in writing equations (see p. 40), the work should always be proved by adding together the quantities on each side of the equality sign, which should equal each other : $98+170=268=142+126=268$ or $57.64+100=157.64=83.53+74.11=157.64$.

In determining quantities as above, regard must be had to the purity of the reagents used, and, if they be crystallized, to the amount of water of crystallization (see p. 15) they contain.

Let it be desired to determine how much crystallized cupric sulfate can be obtained from 100 parts of sulfuric acid of 92% strength. As cupric sulfate crystallizes with five molecules of water of crystallization the reaction occurs according to the equation :

$$\begin{array}{ccccccc}
\underset{\text{Sulfuric acid.}}{H_2SO_4} & + & \underset{\text{Cupric oxid.}}{CuO} & + & \underset{\text{Water.}}{4H_2O} & = & \underset{\text{Cupric sulfate.}}{CuSO_4 5Aq.} \\
 & & 63 & & 1\times2=2 & & 63\times1=63 \\
1\times2=2 & & 16 & & 16\times1=16 & & 32\times1=32 \\
32\times1=32 & & & & & & 16\times4=64 \\
16\times4=\underline{64} & & & & & & 18\times5=\underline{90} \\
98 & & \overline{79} & & \overline{18}\times4=72 & & 249
\end{array}$$

$$98+79+72=249.$$

98 parts of 100% H_2SO_4 will produce, therefore, 249 parts of crystallized cupric sulfate. But as the acid liquid used contains only 92 parts of true H_2SO_4 in 100 ; 100 parts of such acid will yield 233.75 parts of crystallized sulfate, for 98 : 92 : : 249 : 233.75.

In gravimetric quantitative analysis the substance whose quantity is to be determined is converted into an insoluble compound, which is then purified, dried, and weighed (see Part III.), and from this weight the desired result is calculated.

Let the problem be to determine what percentage of silver is contained in a silver coin. Advantage is taken of the formation of the insoluble silver chlorid. A piece of the coin is then chipped off and weighed : Weight of coin used = 2.5643 grams. The chip is then dissolved in nitric acid, forming a solution of silver nitrate. From this solution the silver is precipitated as chlorid, by the addition of hydrochloric acid, according to the equation :

$AgNO_3$	+	HCl	=	$AgCl$	+	HNO_3
Silver nitrate.		Hydrochloric acid.		Silver chlorid.		Nitric acid.
108×1=108		1		108		1×1= 1
14×1= 14		35.5		35.5		14×1=14
16×3= 48						16×3=48
170		36.5		143.5		63

$$170 + 36.5 = 206.5 = 143.5 + 63.$$

The silver chlorid is collected, dried, and weighed :

Weight of coin used....................2.5643 grams.
Weight of AgCl obtained...............3.0665 "

∴ 143.5 grams AgCl contain 108 grams Ag—143.5 : 108 : : 3.0665 : 2.3078—2.5643 grams of the coin contain 2.3078 grams of silver, or 90%—2.5643 : 100 : : 2.3078 : 8.

Nomenclature.—The names * of the elements are mostly of Greek derivation, and have their origin in some prominent property of the substance. Thus, *phosphorus*, φῶς, *light*, and φέρειν, *to bear*. Some are of Latin origin, as *silicon*, from *silex*, flint ; some of Gothic origin, as *iron*, from *iarn ;* and others are derived from modern languages, as *potassium* from *pot-ash*. Very little system has been followed in naming the elements, beyond applying the termination *ium* to the metals, and *in* or *on* to the metalloids ; and even to this rule we find such exceptions as a metal called *manganese* and a metalloid called *sulfur*.

The names of *compound substances* were formerly chosen upon the same system, or rather lack of system, as those of the elements. So long as the number of compounds with which the chemist had to deal remained small, the use of these fanciful appellations, conveying no more to the mind than perhaps some unimportant quality of the substances to which they applied, gave rise to comparatively little inconvenience. In these later days, however, when the number of compounds known to exist, or whose existence is shown by approved theory to be possible, is practically infinite, some systematic method of nomenclature has become absolutely necessary.

The principle of the system of nomenclature at present used is that the name shall convey the composition and character of the substance.

Compounds consisting of two elements, or of an element and a radical only, *binary compounds*, are designated by compound names made up of the name of the more electro-positive, followed by that of the more electro-negative, in which the termination *id* has been substituted for the termination, *in*, *on*, *ogen*, *ygen*,

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* For rules governing orthography and pronunciation of chemical terms see Appendix A.

orus, *ium*, and *ur*. For example: the compound of potassium and chlorin is called potassium chlor*id*, that of potassium and oxygen, potassium ox*id*, that of potassium and phosphorus, potassium phosph*id*.

In a few instances the older name of a compound is used in preference to the one which it should have under the above rule, for the reason that the substance is one which is typical of a number of other substances, and therefore deserving of exceptional prominence. Such are *ammonia*, NH_3; *water*, H_2O.

When, as frequently happens, two elements unite with each other to form more than one compound, these are usually distinguished from each other by prefixing to the name of the element varying in amount the Greek numeral corresponding to the number of atoms of that element, as compared with a *fixed* number of atoms of the other element.

Thus, in the series of compounds of nitrogen and oxygen, most of which contain two atoms of nitrogen, N_2 is the standard of comparison, and consequently the names are as follows:

N_2O = Nitrogen *mon*oxid.
NO $(=N_2O_2)$ = Nitrogen *di*oxid.
N_2O_3 = Nitrogen *tri*oxid.
NO_2 $(=N_2O_4)$ = Nitrogen *tetr*oxid.
N_2O_5 = Nitrogen *pent*oxid.

Another method of distinguishing two compounds of the same two elements consists in terminating the first word in *ous*, in that compound which contains the less proportionate quantity of the more electro-negative element, and in *ic* in that containing the greater proportion; thus:

SO_2 = Sulfur*ous* oxid.
SO_3 = Sulfur*ic* oxid.

Hg_2Cl_2 (2Hg : 2Cl) = Mercur*ous* chlorid.
$HgCl_2$ (2Hg : 4Cl) = Mercur*ic* chlorid.

This method, although used to a certain extent in speaking of compounds composed of two elements of Class II. (see p. 54), is used chiefly in speaking of binary compounds of elements of different classes.

In naming the *oxacids* the word *acid* is used, preceded by the name of the electro-negative element other than oxygen, to which a prefix or suffix is added to indicate the degree of oxidation. If there be only two, the least oxidized is designated by the suffix *ous*, and the more oxidized by the suffix *ic*, thus:

HNO_2 = Nitr*ous* acid.
HNO_3 = Nitr*ic* acid.

If there be more than two acids, formed in regular series, the least oxidized is designated by the prefix *hypo* and the suffix *ous*; the next by the suffix *ous*; the next by the suffix *ic*; and the most highly oxidized by the prefix *per* and the suffix *ic*; thus:

$HClO$ = *Hypo*chlor*ous* acid.
$HClO_2$ = Chlor*ous* acid.
$HClO_3$ = Chlor*ic* acid.
$HClO_4$ = *Per*chlor*ic* acid.

Certain elements, such as sulfur and phosphorus, exist in acids which are derived from those formed in the regular way, and which are specially designated.

The names of the oxysalts are derived from those of the acids by dropping the word *acid*, changing the termination of the other word from *ous* into *ite*, or from *ic* into *ate*, and prefixing the name of the electro-positive element or radical; thus:

HNO_2 Nitr*ous* acid.	KNO_2 Potassium nitr*ite*.
HNO_3 Nitr*ic* acid.	KNO_3 Potassium nitr*ate*.
$HClO$ Hypochlor*ous* acid.	$KClO$ Potassium hypochlor*ite*.

Acids whose molecules contain more than one atom of replaceable hydrogen are capable of forming more than one salt with electro-positive elements, or radicals, whose valence is less than the basicity of the acid. Ordinary phosphoric acid, for instance, contains in each molecule three atoms of basic hydrogen, and consequently is capable of forming three salts by the replacement of one, two, or three of its hydrogen atoms, by one, two, or three atoms of a univalent metal. To distinguish these the Greek prefixes *mono*, *di*, and *tri* are used, the termination *ium* of the name of the metal being changed to *ic*, thus:

H_2KPO_4 = *Mono*potass*ic* phosphate.
HK_2PO_4 = *Di*potass*ic* phosphate.
K_3PO_4 = *Tri*potass*ic* phosphate.

The first is also called *dihydro*potass*ic* phosphate, and the second, *hydrodi*potass*ic* phosphate.

In the older works, salts in which the hydrogen has not been entirely displaced are sometimes called **bisalts** (bicarbonates), or **acid salts**; those in which the hydrogen has been entirely displaced being designated as **neutral salts.**

Some elements, such as mercury, copper, and iron, form two distinct series of salts. These are distinguished, in the same way as the acids, by the use of the suffix *ous* in the names of those containing the less proportion of the electro-negative group, and the suffix *ic* in those containing the greater proportion, *e.g.:*

$(Cu_2)_2SO_4$ . . . . $(1SO_4 : 4Cu)$ = Cupr*ous* sulfate.
Cu_2SO_4 . . . . $(2SO_4 : 4Cu)$ = Cupr*ic* sulfate.

$FeSO_4$ . . . . $(2SO_4 : 2Fe)$ = Ferr*ous* sulfate.
$(Fe_2)(SO_4)_3$. . . . . $(3SO_4 : 2Fe)$ = Ferr*ic* sulfate.

The names, **basic salts, subsalts,** and **oxysalts** have been applied indifferently to salts, such as the lead subacetates, which are compounds containing the normal acetate and the hydrate or oxid of lead; and to salts such as the so-called bismuth subnitrate, which is a nitrate, not of bismuth, but of the univalent radical $(Bi'''O'')'$.

By **double salts** are meant such as are formed by the substitution of different elements or radicals for two or more atoms of replaceable hydrogen of the acid, such as ammonio-magnesian phosphate, $PO_4Mg''(NH_4)'$.

Radicals.—Many compounds contain groups of atoms which pass from one compound to another, and, in many reactions, behave like elementary atoms. Such groups are called **radicals**, or **compound radicals.**

Marsh gas has the composition CH_4. By acting upon it in suitable ways we can cause the atom of carbon, accompanied by three of the hydrogen atoms, to pass into a variety of other compounds, such as: $(CH_3)Cl$; $(CH_3)OH$; $(CH_3)_2O$; $C_2H_3O_2(CH_3)$. Marsh gas, therefore, consists of the radical (CH_3) combined with an atom of hydrogen: $(CH_3)'H$.

It is especially among the compounds of carbon that the existence of radicals comes into prominent notice. They, however, occur in inorganic substances also. Thus the nitric acid molecule consists of the radical NO_2, combined with the group OH.

Like the elements, the radicals possess different valences, depending upon the number of unsatisfied valences which they contain. Thus the radical (CH_3) is univalent, because three of the four valences of the carbon atom are satisfied by atoms of hydrogen, leaving one free valence. The radical (PO) of phosphoric acid is trivalent, because two of the five valences of the phosphorus atom are satisfied by the two valences of the bivalent oxygen atom, leaving three free valences.

In notation the radicals are usually enclosed in brackets, as above, to indicate their nature. The names of radicals terminate in *yl* or in *gen;* thus: (CH_3) = methyl; (CN) = cyanogen.

The terms *radical* and *residue*, although sometimes used as synonyms, are not such in speaking of electrical decompositions (see p. 27). Thus the radical of sulfuric acid is SO_2; but when sulfuric acid is electrolyzed it is decomposed into hydrogen and the residue SO_4.

Composition and Constitution.—The characters of a compound depend not only upon the kind and number of its atoms, but also upon the manner in which they are attached to each other. There are, for instance, two substances, each having the **empirical formula** $C_2H_4O_2$, one of which is a strong acid, the other a neutral ether. As the molecule of each contains the same number and kind of atoms, the differences in their properties must be due to differences in the manner in which the atoms are linked together.

The composition of a compound is the number and kind of atoms contained in its molecule; and is shown by its empirical formula.

The constitution of a compound is the number and kind of atoms and their relations to each other, within its molecule; and is shown by its typical or graphic formula.

In the system of **typical formulæ** all substances are considered as being so constituted that their rational formulæ may be referred to one of three classes or types, or to a combination of two of these types. These three classes, being named after the most common substance occurring in each, are expressed thus:

The hydrogen type.	The water type.	The ammonia type.
$\left.\begin{matrix}H\\H\end{matrix}\right\}$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$
$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}$	$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2$
etc.,	etc.,	etc.,

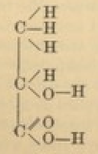
it being considered that the formula of any substance of known constitution can be indicated by substituting the proper element, or radical, for one or more of the atoms of the type, thus:

$\left.\begin{matrix}Cl\\H\end{matrix}\right\}$	$\left.\begin{matrix}(C_2H_5)'\\H\end{matrix}\right\}O$	$\left.\begin{matrix}(C_2H_5)'\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}Cl_2\\Ca\end{matrix}\right\}$	$\left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}(CO)''\\H_2\\H_2\end{matrix}\right\}N_2$
Hydrochloric acid.	Alcohol.	Ethylamin.	Calcium chlorid.	Sulfuric acid.	Urea.

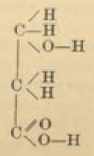
Typical formulæ are of great service in the classification of compound substances, as well as to indicate, to a certain degree, their nature and the method of the reactions into which they enter. Thus in the case of the two substances mentioned above, as both having the composition $C_2H_4O_2$, we find on examination that one contains the group $(CH_3)'$, while the other contains the group $(C_2H_3O)'$. The difference in their constitution at once becomes apparent in their typical formulæ, $\left.\begin{array}{r}(CHO)'\\(CH_3)'\end{array}\right\}O$ and $\left.\begin{array}{r}(C_2H_3O)'\\H\end{array}\right\}O$, indicating differences in their properties, which we find upon experiment to exist. The first substance is neutral in reaction and possesses no acid properties ; it closely resembles a salt of an acid having the formula $\left.\begin{array}{r}(CHO)\\H\end{array}\right\}O$. The second substance, on the other hand, has a strongly acid reaction, and markedly acid properties, as indicated by the oxidized radical and the extra-radical hydrogen. It is capable of forming salts by the substitution of an atom of a univalent, basylous element for its single replaceable atom of hydrogen : $\left.\begin{array}{r}(C_2H_3O)'\\Na\end{array}\right\}O$.

Although typical formulæ have been and still are of great service, many cases arise, especially in treating of the more complex organic substances, in which they do not sufficiently indicate the relations between the atoms which constitute the molecule, and thus fail to convey a proper idea of the nature of the substance. Considering, for example, the ordinary lactic acid, we find its composition to be $C_3H_6O_3$, which, expressed typically, would be $\left.\begin{array}{r}(C_3H_4O)''\\H_2\end{array}\right\}O_2$, a constitution supported by the fact that the radical $(C_3H_4O)''$ may be obtained in other compounds, as $\left.\begin{array}{r}(C_3H_4O)''\\Cl_2\end{array}\right\}$. This constitution, however, cannot be the true one, because in the first place, lactic acid is not dibasic, but monobasic ; and in the second place, there is another acid, called paralactic acid, having an identical composition, yet differing in its products of decomposition. These differences in the properties of the two acids must be due to a different *arrangement* of atoms in their molecules, a view which is supported by the sources from which they are obtained and the nature of their products of decomposition.

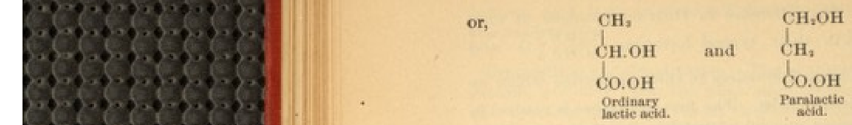
To express the constitution of such bodies **graphic formulæ** are used, in which the position of each atom in relation to the others is set forth. The constitution of the two lactic acids would be expressed by graphic formulæ in this way :



and



or,



$$\begin{array}{c} CH_3 \\ | \\ CH.OH \\ | \\ CO.OH \end{array} \quad \text{and} \quad \begin{array}{c} CH_2OH \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

Ordinary lactic acid. Paralactic acid.

It must be understood that these graphic formulæ are simply intended to show the relative attachments of the atoms, and are in nowise intended to convey the idea that the molecule is spread out upon a flat surface, with the atoms arranged as indicated in the diagram.

Great care and much labor are required in the construction of these graphic formulæ, the positions of the atoms being determined by a close study of the methods of formation, and of the products of decomposition of the substance under consideration. Naturally, in a matter of this nature, there is always room for differences of opinion—indeed, the entire atomic theory is open to question, as is the theory of gravitation itself. But whatever may be advanced, two facts cannot be denied: first, that chemistry owes its advancement within the past half-century to the atomic theory, which to-day is more in consonance with observed facts than any substitute which can be offered; second, that without the use of graphic formulæ it is impossible to offer any adequate explanation of the reactions which we observe in dealing with the more complex organic substances.

In chemistry, as in other sciences, a sharp distinction must always be made between facts and theories: the former, once observed, are immutable additions to our knowledge; the latter are of their nature subject to change with our increasing knowledge of facts. We have every reason for believing, however, that the supports upon which the atomic theory rests are such that, although it may be modified in its details, its essential features will remain unaltered.

Classification of the Elements.—Berzelius was the first to divide all the elements into two great classes, to which he gave the names **metals** and **metalloids.** The metals, being such substances as are opaque, possess what is known as metallic lustre, are good conductors of heat and electricity, and are electro-positive; the metalloids, on the other hand, such as are gaseous, or, if solid, do not possess metallic lustre, have a comparatively low power of conducting heat and electricity, and are electro-negative.

This division, based upon purely physical properties, which, in many cases, are ill-defined, has become insufficient. Several elements formerly classed under the above rules with the metals, resemble the metalloids in their chemical characters much more closely than they do any of the metals. Indeed, by the characters mentioned above, it is impossible to draw any line of demarcation which shall separate the elements distinctly into two groups.

The classification of the elements should be such that each group shall contain elements whose *chemical* properties are similar—the *physical* properties being considered only in so far as they are intimately connected with the chemical. The arrangement of elements into groups is not equally easy in all cases. Some groups, as the chlorin group, are sharply defined, while the members of others differ from each other more widely in their properties. The positions of most of the more recently discovered elements are still uncertain, owing to the imperfect state of our knowledge of their properties.

The method of classification which we will adopt, and which we believe to be more natural than any hitherto suggested, is based upon the chemical properties of the oxids and upon the valence of the elements. We abandon the division into metals and metalloids, and substitute for it a division into four great classes, according to the nature of the oxids and the existence or non-existence of oxysalts. In the first of these classes hydrogen and oxygen are placed together, for the reason that, although they differ from each other in many of their properties, they together form the basis of our classification, and may, for this and other reasons, be regarded as **typical elements**. They both play important parts in the formation of acids, and neither would find a suitable place in either of the other classes. Our primary division would then be as follows:

Class I.—Typical elements.

Class II.—Elements whose oxids unite with water to form acids, never to form bases. Which do not form oxysalts.

This class contains all the so-called metalloids except hydrogen and oxygen.

Class III.—Elements whose oxids unite with water, some to form bases, others to form acids. Which form oxysalts.

Class IV.—Elements whose oxids unite with water to form bases; never to form acids. Which form oxysalts.

In this class are included the more strongly electro-positive metals.

Within the classes a further subdivision is made into groups, each group containing those elements within the class which have equal valences, which form corresponding compounds, and whose *chemical characters* are otherwise similar.

For the sake of convenience the term **metal** is retained to apply to the members of Classes III. and IV. ; the term **non-metal** being used for those belonging to Class II.

Class I.

GROUP I.—Hydrogen.
GROUP II.—Oxygen.

Class II.

GROUP I.—Fluorin, chlorin, bromin, iodin.
GROUP II.—Sulfur, selenium, tellurium.
GROUP III.—Nitrogen, phosphorus, arsenic, antimony.
GROUP IV.—Boron.
GROUP V.—Carbon, silicon.
GROUP VI.—Vanadium, columbium, tantalium.
GROUP VII.—Molybdenum, tungsten, osmium (?).

Class III.

GROUP I.—Gold.
GROUP II.—Cromium, manganese, iron.
GROUP III.—Glucinium, aluminium, scandium, gallium, indium.
GROUP IV.—Uranium.
GROUP V.—Lead.
GROUP VI.—Bismuth.
GROUP VII.—Titanium, zirconium, tin.
GROUP VIII.—Palladium, platinum.
GROUP IX.—Rhodium, ruthenium, iridium.

Class IV.

GROUP I.—Lithium, sodium, potassium, rubidium, cesium, silver.
GROUP II.—Thallium.
GROUP III.—Calcium, strontium, barium.
GROUP IV.—Magnesium, zinc, cadmium.
GROUP V.—Nickel, cobalt.
GROUP VI.—Copper, mercury.
GROUP VII.—Yttrium, cerium, ytterbium, lanthanium, didymium, erbium.
GROUP VIII.—Thorium.

PART II.

SPECIAL CHEMISTRY.

CLASS I.

TYPICAL ELEMENTS.

HYDROGEN—OXYGEN.

ALTHOUGH, in a strict sense, hydrogen is regarded by most chemists as the one and only type-element—that whose atom is the unit of atomic and molecular weights—the important part which oxygen plays in the formation of those compounds whose nature forms the basis of our classification, its acid-forming power in organic compounds, and the differences existing between its properties and those of the elements of the sulfur group, with which it is usually classed, warrant us in separating it from the other elements and elevating it to the position it here occupies.

HYDROGEN.

Symbol=**H**—*Univalent—Atomic weight* = 1—*Molecular weight* = 2—*Sp. gr.* = 0.06926A[*]—*One litre weighs* 0.0896 *gram*[†]—100 *cubic inches weigh* 2.1496 *grains*[‡]—1 *gram measures* 11.16 *litres*[†]—1 *grain measures* 46.73 *cubic inches*[‡]—*Name derived from* ὕδωρ = *water, and* γεννάω = *I produce—Discovered by Cavendish in* 1766.

Occurrence.—Occurs free in volcanic gases, in fire-damp, occluded in meteorites, in the gases exhaled from the lungs, and in those of the stomach and intestine. In combination in water, hydrogen sulfid, ammoniacal compounds, and in many organic substances.

Preparation.—(1.) By electrolysis of water, H is given off at the negative pole. Utilized when pure H is required.

---

[*] Air = 1. When the sp. gr. is referred to H = 1, A is replaced by H.
[†] At 0° C. and 760 mm. barometric pressure.
[‡] At 60° F. and 30 inches bar. pressure.

(2.) By the disassociation of water at very high temperatures.

(3.) By the decomposition of water by certain metals. The alkali metals decompose water at the ordinary temperature:

$$\underset{\text{Sodium.}}{Na_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Sodium hydroxid.}}{2NaHO} + \underset{\text{Hydrogen.}}{H_2}$$

Some other metals, such as iron and copper, effect the decomposition only at high temperatures:

$$\underset{\text{Iron.}}{3Fe_2} + \underset{\text{Water.}}{8H_2O} = \underset{\text{Triferric tetroxid.}}{2Fe_3O_4} + \underset{\text{Hydrogen.}}{8H_2}$$

(4.) By decomposition of water, passed over red-hot coke:

$$\underset{\text{Carbon.}}{C} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Carbon dioxid.}}{CO_2} + \underset{\text{Hydrogen.}}{2H_2}$$

or at a higher temperature:

$$\underset{\text{Carbon.}}{2C} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Carbon monoxid.}}{2CO} + \underset{\text{Hydrogen.}}{2H_2}$$

(5.) By decomposition of mineral acids, in the presence of water, by zinc and certain other metals:

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Sulfuric acid.}}{H_2SO_4} + \underset{\text{Water.}}{xH_2O} = \underset{\text{Zinc sulfate.}}{ZnSO_4} + \underset{\text{Hydrogen.}}{H_2} + \underset{\text{Water.}}{xH_2O}$$

The water serves to dissolve the zinc sulfate. Chemically pure zinc, or zinc whose surface has been covered with an alloy of zinc and mercury, does not decompose the acid unless it forms part of a galvanic battery whose circuit is closed. The zincs of galvanic batteries are therefore covered with the alloy mentioned—are amalgamated—to prevent waste of zinc and acid.

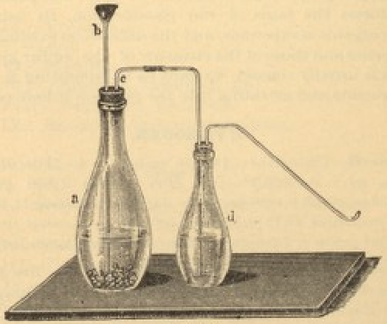


FIG. 19.

This is the method usually resorted to for obtaining H. The gas so obtained is, however, contaminated with small quantities of other gases, hydrogen phosphid, sulfid, and arsenid.

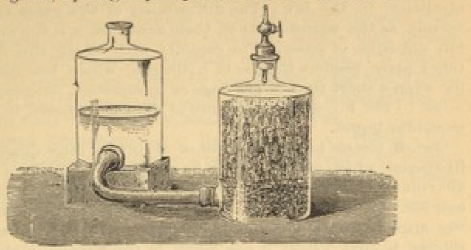


Fig. 20.

Hydrogen, carbon dioxid, hydrogen sulfid, and other gases produced by the action of a liquid upon a solid at ordinary temperatures, are best prepared in one of the forms of apparatus shown in Figs. 19, 20, and 21.

The solid material is placed in the larger bottle (Fig. 19), or, over a layer of broken glass about five centimetres thick, in the bottle A (Fig. 20). The liquid reagent is from time to time introduced by the funnel tube, Fig. 19; or the bottle B, Fig. 20, is filled with it. The wash-bottles are partially filled with water to arrest any liquid or solid impurity. The apparatus, Figs. 20 and 21, have the advantage of being always ready for use. When the stopcock is open the gas escapes. When it is closed the internal pressure depresses the level of the liquid in A into the layer of broken glass, and the action is arrested. Kipp's apparatus, Fig. 21, is another convenient form of constant apparatus. The solid reagent is placed in the central bulb.

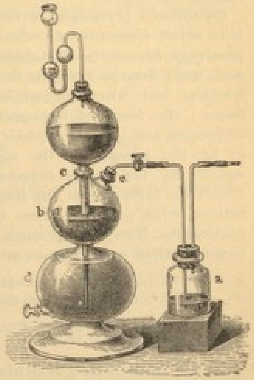


Fig. 21.

(6.) By heating together a mixture of zinc dust and dry slacked lime:

$$\begin{array}{ccccccccc} Zn & + & CaH_2O_2 & = & ZnO & + & CaO & + & H_2 \\ \text{Zinc.} & & \text{Calcium hydroxid.} & & \text{Zinc oxid.} & & \text{Calcic monoxid.} & & \text{Hydrogen.} \end{array}$$

Properties.—*Physical.*—Hydrogen is a colorless, odorless, tasteless gas; 14.47 times lighter than air, being the lightest substance known. The weight of a litre, 0.0896 gram, is called a **crith** (κριθή = barleycorn). It is almost insoluble in water and alcohol. It conducts heat and electricity better than any other gas. In obedience to the law: **The diffusibility of two gases varies inversely as the square roots of their densities,** it is the most rapidly diffusible of gases. The rapidity with which this diffusion takes place renders the use of hydrogen, which has been kept for even a short time in gas-bags or gasometers, dangerous. At −140° (−229° F.), under a pressure of 650 atmospheres, it forms a steel-blue liquid.

Certain metals have the power of absorbing large quantities of hydrogen, which is then said to be **occluded.** Palladium absorbs 376 volumes at the ordinary temperature; 932 vols. at 90° (194° F.) and 526 vols. at 245° (473° F.). The occluded gas is driven off by the application of heat, and possesses great chemical activity, similar to that which it has when in the nascent state. This latter quality, and the fact that heat is liberated during the occlusion, would seem to indicate that the gas is contained in the metal, not in a mere physical state of condensation, but in chemical combination.

Chemical.—Hydrogen exhibits no great tendency to combine with other elements at ordinary temperatures. It combines explosively, however, with chlorin under the influence of sunlight, and with fluorin even in the dark. It does not support combustion, but, when ignited, burns with a pale blue and very hot flame; the result of the combination being water. Mixtures of hydrogen and oxygen explode violently on the approach of flame, or by the passage of the electric spark, the explosion being caused by the sudden expansion of the vapor of water formed, under the influence of the heat of the reaction. Hydrogen also unites with oxygen when brought in contact with spongy platinum. Many compounds containing oxygen give up that element when heated in an atmosphere of hydrogen:

$$\underset{\text{Cupric oxid.}}{CuO} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Copper.}}{Cu} + \underset{\text{Water.}}{H_2O}$$

The removal of oxygen from a compound is called a reduction or deoxidation.

At the instant that H is liberated from its compounds it has a deoxidizing power similar to that which ordinary H possesses only at elevated temperatures, and its tendency to combine with other elements is greater than under other conditions. The greater energy of H, and of other elements as well, in this **nascent state,** may be thus explained. Free H exists in the form of molecules, each one of which is composed of two atoms, but at the instant of its liberation from a compound, it is in the form of individual atoms, and that portion of force required to split up the molecule into atoms, necessary when free H enters into reaction, is not required when the gas is in the nascent state.

In its physical and chemical properties, this element more closely resembles those usually ranked as metals than it does those forming the class of metalloids, among which it is usually placed. Its conducting power, its appearance in the liquid form, as well as its relation to the acids, which may be considered as salts of H, tend to separate it from the metalloids.

Analytical Characters.—(1.) Burns with a faintly blue flame, which deposits water on a cold surface brought in contact with it; (2.) Mixed with oxygen, explodes on contact with flame, producing water.

OXYGEN.

Symbol = **O**—*Bivalent—Atomic weight* = 16; *molecular weight* = 32—*Sp. gr.* = 1.10563 A (*calculated* = 1.1088); 15.95 H; *sp. gr. of liquid* = 0.9787—*One litre weighs* 1.4300 *grams* = 16 *criths*—100 *cubic inches weigh* 34.27 *grains—Name derived from* ὀξύς = *acid, and* γεννάω = *I produce—Discovered by Mayow in* 1674; *re-discovered by Priestley in* 1774.

Occurrence.—Oxygen is the most abundant of the elements. It exists free in atmospheric air; in combination in a great number of substances, mineral, vegetable, and animal.

Preparation.—(1.) By heating certain oxids:

$$\underset{\text{Mercuric oxid.}}{2HgO} = \underset{\text{Mercury.}}{2Hg} + \underset{\text{Oxygen.}}{O_2}$$

This was the method used by Priestley. 100 grams of mercuric oxid produce 5.16 litres of oxygen:

$$\underset{\text{Manganese dioxid.}}{3MnO_2} = \underset{\text{Trimanganic tetroxid.}}{Mn_3O_4} + \underset{\text{Oxygen.}}{O_2}$$

The black oxid of manganese is heated to redness in an iron or clay retort (Scheele, 1775); and 100 grams yield 8.51 litres of oxygen.

(2.) By the electrolysis of water, acidulated with sulfuric acid, O is given off at the positive pole.

(3.) By the action of sulfuric acid upon certain compounds rich in O: manganese dioxid, potassium dichromate, and plumbic peroxid:

$$\underset{\text{Manganese dioxid.}}{2MnO_2} + \underset{\text{Sulfuric acid.}}{2H_2SO_4} = \underset{\text{Manganous sulfate.}}{2MnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{O_2}$$

100 grams of manganese dioxid produce 12.82 litres of O.

(4.) By decomposing H_2SO_4 at a red heat, $2H_2SO_4 = 2SO_2 + 2H_2O + O_2$.

(5.) By the decomposition by heat of certain salts rich in O: alkaline permanganates, nitrates, and chlorates.

The best method, and that usually adopted, is by heating a mixture of potassium chlorate and manganese dioxid in equal parts, moderately at first and more strongly toward the end of the reaction. The chlorate gives up all its O (27.33 litres from 100 grams of the salt), according to the equation:

$$\underset{\text{Potassium chlorate.}}{2KClO_3} = \underset{\text{Potassium chlorid.}}{2KCl} + \underset{\text{Oxygen.}}{3O_2}$$

At the end of the operation the manganese dioxid remains, apparently unchanged. The most probable explanation of its action is that potassium permanganate and free chlorin are first produced, while a part of the oxygen is liberated:

$$\underset{\substack{\text{Potassium}\\\text{chlorate.}}}{4KClO_3} + \underset{\substack{\text{Manganese}\\\text{dioxid.}}}{2MnO_2} = \underset{\substack{\text{Potassium}\\\text{permanganate.}}}{K_2Mn_2O_8} + \underset{\substack{\text{Potassium}\\\text{chlorid.}}}{2KCl} + \underset{\text{Chlorin.}}{Cl_2} + \underset{\text{Oxygen.}}{4O_2}$$

that the permanganate so formed is decomposed at a comparatively low temperature, according to the equation:

$$\underset{\substack{\text{Potassium}\\\text{permanganate.}}}{K_2Mn_2O_8} = \underset{\substack{\text{Potassium}\\\text{manganate.}}}{K_2MnO_4} + \underset{\substack{\text{Manganese}\\\text{dioxid.}}}{MnO_2} + \underset{\text{Oxygen.}}{O_2}$$

and, finally, that the manganate so formed is decomposed by the chlorin produced in the first reaction, according to the equation:

$$\underset{\substack{\text{Potassium}\\\text{manganate.}}}{K_2MnO_4} + \underset{\text{Chlorin.}}{Cl_2} = \underset{\substack{\text{Potassium}\\\text{chlorid.}}}{2KCl} + \underset{\substack{\text{Manganese}\\\text{dioxid.}}}{MnO_2} + \underset{\text{Oxygen.}}{O_2}$$

A small quantity of free chlorin usually exists in the gas produced by this reaction. If the oxygen is to be used for inhalation, the chlorin should be removed by allowing the gas to stand over water for 24 hours.

When heat is required for the generation of gases the operation is conducted in retorts of glass or metal, or in the apparatus shown in Fig. 22. If the gas be collected over water the disengagement tube must be withdrawn from the water, before the source of heat is removed. Neglect of this precaution will cause an explosion, by the entrance of water into the hot flask, by the contraction of the gas contained in it, on partial cooling.

(6.) By the mutual decomposition of potassium permanganate and hydrogen peroxid, in the presence of sulfuric acid:

$$\underset{\substack{\text{Hydrogen}\\\text{peroxid.}}}{H_2O_2} + \underset{\substack{\text{Potassium}\\\text{permanganate.}}}{K_2Mn_2O_8} + \underset{\substack{\text{Sulfuric}\\\text{acid.}}}{3H_2SO_4} = \underset{\substack{\text{Potassium}\\\text{sulfate.}}}{K_2SO_4} + \underset{\substack{\text{Manganous}\\\text{sulfate.}}}{2MnSO_4} + \underset{\text{Water.}}{4H_2O} + \underset{\text{Oxygen.}}{3O_2}$$

One kilo H_2O_2 (3%) and 500 cc. dilute H_2SO_4 (1:5) are placed in the generating flask and 56 grams $K_2Mn_2O_8$, dissolved in H_2O, are gradually added. With these quantities 20 litres O are obtained.

(7.) By the action of dilute hydrochloric acid upon a mixture of 2 parts barium peroxid, 1 part manganese dioxid, and 1 part plaster of Paris, compressed into cubes about 1½ cent. square.

Methods 6 and 7 have the advantage that heat is not required, and the forms of apparatus, Figs. 19, 20, and 21, may be used.

Properties.—*Physical.*—Oxygen is a colorless, odorless, tasteless gas, soluble in water in the proportion of 7.08 cc. in 1 litre of water at 14°.8 (58°.6 F.), somewhat more soluble in absolute alcohol. It liquefies at −140° (−220° F.) under a pressure of 300 atmospheres. Liquid oxygen boils at −187°.4 (−294°.5 F.) at the ordinary pressure.

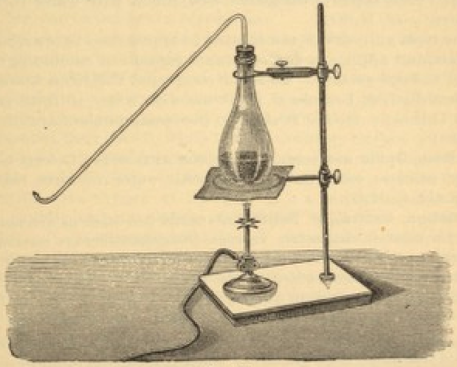


Fig. 22.

Chemical.—Oxygen is characterized, chemically, by the strong tendency which it exhibits to enter into combination with other elements. It forms binary compounds with all elements except fluorin and bromin. With most elements it unites directly, especially at elevated temperatures. In many instances this union is attended by the appearance of light, and always by the extrication of heat. The luminous union of O with another element constitutes the familiar phenomenon of **combustion**, and is the principal source from which we obtain so-called artificial heat and light. A body is said to be **combustible** when it is capable of so energetically combining with the oxygen of the air as to liberate light as well as heat. Gases are said to be **supporters of combustion,** when combustible substances will unite with them, or with some of their constituents, the union being attended with the appearance of heat and light. The distinction between combustible substances and supporters of combustion is, however, one of mere convenience. The action taking place between the two substances, one is as much a party to it as the other. A jet of air burns in an atmosphere of coal-gas as readily as a jet of coal-gas burns in air.

The compounds of oxygen—the **oxids**—are divisible into three groups:

1. **Anhydrids**—oxids capable of combining with water to form *acids.* Thus *sulfuric anhydrid,* SO_3, unites with water to form *sulfuric acid,* H_2SO_4.

The term anhydrid is not limited in application to *binary* compounds, but applies to any substance capable of combining with water to form an acid. Thus the compound $C_4H_6O_3$ is known as acetic anhydrid, because it combines with water to form acetic acid: $C_4H_6O_3 + H_2O = 2C_2H_4O_2$. (See compounds of arsenic and sulfur.)

2. **Basic Oxids** are such as combine with water to form bases. Thus, calcium oxid, CaO, unites with water to form calcium hydroxid, CaH_2O_2.

3. **Saline, neutral, or indifferent oxids** are such as are neither acid nor basic in character. In some instances they are essentially neutral, as in the case of the protoxid of hydrogen, or water. In other cases they are formed by the union of two other oxids, one basic, the other acid in quality, such as the red oxid of lead, Pb_3O_4, formed by the union of a molecule of the acidulous peroxid, PbO_2, with two of the basic protoxid, PbO. It is to oxids of this character that the term "saline" properly applies.

The process of respiration is very similar to combustion, and as oxygen gas is the best supporter of combustion, so, in the diluted form in which it exists in atmospheric air, it is not only the best, but the only supporter of animal respiration. (See carbon dioxid.)

Analytical Characters.—1.) A glowing match-stick bursts into flame in free oxygen. 2.) Free O, when mixed with nitrogen dioxid, produces a brown gas.

Ozone.—*Allotropic oxygen.*—Air through which discharges of static electricity have been passed, and oxygen obtained by the decomposition of water (if electrodes of gold or platinum be used), have a peculiar odor, somewhat resembling that of sulfur, which is due to the conversion of a part of the oxygen into ozone.

Ozone is produced: 1.) By the decomposition of water by the battery. 2.) By the slow oxidation of phosphorus in damp air. 3.) By the action of concentrated sulfuric acid upon barium dioxid. 4.) By the passage of silent electric discharges through air or oxygen.

In the preparation of ozonized oxygen the best results are obtained by passing a slow current of oxygen through an apparatus made entirely of glass and platinum, cooled by a current of cold water, and traversed by the invisible discharge of an induction coil.

Pure, liquid ozone has been obtained by subjecting ozonized oxygen to the temperature of liquid oxygen at the atmospheric pressure. It is a dark blue liquid, almost opaque in layers 2 mm. thick, which is not decomposed at the ordinary temperature, but converted into a blueish gas.

When oxygen is ozonized it contracts slightly in volume, and when the ozone is removed from ozonized oxygen by mercury or potassium iodid the volume of the gas is not diminished. These facts, and the great chemical activity of ozone, have led chemists to regard it as condensed oxygen; the molecule of ozone being represented thus (OOO), while that of ordinary oxygen is (OO).

Ozone is very sparingly soluble in water, insoluble in solutions of acids and alkalies. In the presence of moisture it is slowly converted into oxygen at 100° (212° F.), a change which takes place rapidly and completely at 237° (459° F.). It is a powerful oxidant; it decomposes solutions of potassium iodid with formation of potassium hydroxid, and liberation of iodin; it oxidizes all metals except gold and platinum, in the presence of moisture; it decolorizes indigo and other organic pigments, and acts rapidly upon rubber, cork, and other organic substances.

Analytical Characters.—1.) Neutral litmus paper, impregnated with solution of potassium iodid, is turned blue when exposed to air containing ozone. The same litmus paper without iodid is not affected. 2.) Manganous sulfate solution is turned brown by ozone. 3.) Solutions of thallous salts are colored yellow or brown by ozone. 4.) Paper impregnated with fresh tincture of natural (unpurified) guaiacum is colored blue by ozone. 5.) Paper impregnated with solution of manganous sulfate, or lead hydroxid, or palladium chlorid is colored dark brown or black by ozone. 6.) Metallic silver is blackened by ozone.

When inhaled, air containing 0.07 gram of ozone per litre causes intense coryza and hæmoptysis. It is probable that ozone is by no means as constant a constituent of the atmosphere as was formerly supposed. (See Hydrogen dioxid.)

Compounds of Hydrogen and Oxygen.

Two are known—hydrogen oxid or water, H_2O ; hydrogen peroxid or oxygenated water, H_2O_2.

Water.

H_2O—*Molecular weight*=18—*Sp. gr.*=1—*Vapor density*=0.6218 A ; *calculated*=0.6234—*Composition discovered by Priestley in* 1780.

Occurrence.—In unorganized nature H_2O exists in the gaseous form in atmospheric air and in volcanic gases ; in the liquid form very abundantly ; and as a solid in snow, ice, and hail.

As **water of crystallization** it exists in definite proportion in certain crystals, to the maintenance of whose shape it is necessary.

In the organized world H_2O forms a constituent part of every tissue and fluid.

Formation.—Water is formed : 1. By union, brought about by elevation of temperature, of one vol. O with two vols. H.

2. By burning H, or substances containing it, in air or in O.

3. By heating organic substances containing H to redness with cupric oxid, or with other substances capable of yielding O. This method of formation is utilized to determine the amount of H contained in organic substances.

4. When an acid and a hydroxid react upon each other to form a salt:

$$\underset{\text{Sulfuric acid.}}{H_2SO_4} + \underset{\text{Potassium hydroxid.}}{2KHO} = \underset{\text{Potassium sulfate.}}{K_2SO_4} + \underset{\text{Water.}}{2H_2O}$$

5. When a metallic oxid is reduced by hydrogen :

$$\underset{\text{Cupric oxid.}}{CuO} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Copper.}}{Cu} + \underset{\text{Water.}}{H_2O}$$

6. In the reduction and oxidation of many organic substances.

Pure H_2O is not found in nature. When required pure it is separated from suspended matters by filtration, and from dissolved substances by distillation.

Properties.—*Physical.*—With a barometric pressure of 760 mm. H_2O is solid below 0° (32° F.) ; liquid between 0° (32° F.) and 100° (212° F.) ; and gaseous above 100° (212° F.). When H_2O is enclosed in capillary tubes, or is at complete rest, it may be cooled to − 15° (5° F.) without solidifying. If, while at this temperature, it be agitated, it solidifies instantly, and the temperature suddenly rises to 0° (32° F.). The melting-point of ice is lowered 0.0075° (0.0135° F.) for each additional atmosphere of pressure.

The boiling-point is subject to greater variations than the freezing-point. It is the lower as the pressure is diminished, and the higher as it is increased. Advantage is taken of the reduced boiling-point of solutions in vacuo for the separation of substances, such as cane sugar, which are injured at the temperature of boiling H_2O. On the other hand, the increased temperature that may be imparted to liquid H_2O under pressure is utilized in many processes, in the laboratory and in the arts, for effecting solutions and chemical actions which do not take place at lower temperatures. The boiling-point of H_2O holding solid matter in solution is higher than that of pure H_2O, the degree of increase depending upon the amount and nature of the substance dissolved. On the other hand, mixtures of H_2O with liquids of lower boiling-point boil at temperatures less than 100° (212° F.). Although the conversion of water into water-gas takes place most actively at 100° (212° F.), water and ice evaporate at all temperatures.

Water is the best solvent we have, and acts in some instances as a simple solvent, in others as a chemical solvent.

Vapor of water is colorless, transparent, and invisible. Sp. gr. 0.6234 A or 9 H. A litre of vapor of water weighs 0.8064. The latent heat of vaporization of water is 536.5; that is, as much heat is required to vaporize 1 kilo. of water at 100° as would suffice to raise 536.5 kilos. of water 1° in temperature. In passing from the liquid to the gaseous state, water expands 1,696 times in volume.

Chemical.—Water may be shown to consist of 1 vol. O and 2 vols. H, or 8 by weight of O and 1 by weight of H, either by analysis or synthesis.

Analysis is the reducing of a compound to its constituent elements.

Synthesis is the formation of a compound from its elements. A partial synthesis is one in which a complex compound is produced from a simpler one, but not from the elements.

Water may be resolved into its constituent gases: 1st. By electrolysis of acidulated water; H being given off at the negative and O at the positive pole. 2d. By passing vapor of H_2O through a platinum tube heated to whiteness, or through a porcelain tube heated to about 1,100°. 3d. By the action of the alkali metals. Hydrogen is given off, and the metallic hydroxid remains in solution in an excess of H_2O. 4th. By passing vapor of H_2O over red-hot iron. Oxid of iron remains and H is given off.

Water combines with oxids to form new compounds, some of which are acids and others bases, known as **hydroxids.**

A hydroxid is a compound formed by the replacement of half of the hydrogen of water by a metal.

A hydrate is a compound containing chemically combined water.

The hydrates of the electro-negative elements and radicals are **acids**; most of those of the electro-positive elements and radicals are **basic hydroxids.**

Certain substances, in assuming the crystalline form, combine with a definite proportion of water, which is known as **water of crystallization,** and whose presence, although necessary to the maintenance of certain physical characters, such as color and crystalline form, does not modify their chemical reactions. In many instances a portion of the water of crystallization may be driven off at a comparatively low temperature, while a much higher temperature is required to expel the remainder. This latter is known as **water of constitution.**

The symbol Aq (Latin, *aqua*) is frequently used to designate the water of crystallization, the water of constitution being indicated by H_2O. Thus $MgSO_4,H_2O+6$ Aq represents magnesium sulfate with one molecule of water of constitution and six molecules of water of crystallization. We consider it preferable, however, as the distinction between water of crystallization and water of constitution in many salts is only one of degree and not of kind, to use the symbol Aq to designate the sum of the two; thus, $MgSO_4+7$ Aq.

Water decomposes the chlorids of the second class of elements (those of carbon only at high temperatures and under pressure); while the chlorids of the elements of the third and fourth classes are either insoluble, or soluble without decomposition.

Natural Waters.—Water, as it occurs in nature, always contains solid and gaseous matter in solution and frequently solids in suspension.

Natural waters may be classified, according to the nature and quantity of foreign matters which they contain, into **potable** and **unpotable** waters. To the first class belong rain-water, snow- and ice-water, spring-water (fresh), river-water, lake-water, and well-water. To the second class belong stagnant waters, sea-water, and the waters of mineral springs.

Rain-water is usually the purest of natural waters, so far as dissolved solids are concerned, containing very small quantities of the chlorids, sulfates, and nitrates of sodium and ammonium. Owing to the large surface exposed during condensation, rain-water contains relatively large quantities of dissolved gases—oxygen, nitrogen, and carbon dioxid; and sometimes hydrogen sulfid and sulfur dioxid. The absence of carbonates and the presence of nitrates and oxygen render rain-water particularly prone to dissolve lead, when in contact with that metal. In summer, rain-water is liable to become charged with vegetable organic matter suspended in the atmosphere.

Ice-water contains very small quantities of dissolved solids or gases, which, during freezing, remain in great part in the unfrozen water. Suspended impurities are imprisoned in the ice and liberated when this is melted.

Melted snow contains about the same proportion of fixed solid matter as rain-water, but a less proportion of ammoniacal salts and of gases.

Spring-water is rain-water which, having percolated through a portion of the earth's crust (in which it may also have been subjected to pressure), has become charged with solid and gaseous matter; varying in kind and quantity according to the nature of the strata through which it has percolated, the duration of contact, and the pressure to which it was subject during such contact.

Spring-waters from igneous rocks and from the older sedimentary formations are fresh and sweet, and any spring-water may be considered such whose temperature is less than 20° (68° F.), and which does not contain more than 40 parts in 100,000 of solid matter; provided that a large proportion of the solid matter does not consist of salts having a medicinal action, and that sulfurous gases and sulfids are absent.

Artesian wells are artificial springs, produced by boring in a low-lying district, until a pervious layer, between two impervious strata, is reached; the outcrop of the system being in an adjacent elevated region.

River-water is a mixture of rain-water, spring-water, and the drainage water of the district through which the river flows, to which snow-water, ice-water, or sea-water is sometimes added. The water of a river flowing rapidly through a granitic region is, unless polluted by man, bright, fresh, and highly aërated. That of a stream flowing sluggishly through rich alluvial land is unaërated, and rich in dissolved and suspended solids.

The amount of dissolved solids in river-water increases with the distance from its source.

The chief sources of pollution of river-water are by the discharge into them of the sewage of towns and cities, or of the waste products of factories.

Lake-water is an accumulation of river- and rain-water. As the waters of lakes are kept in constant agitation both by the wind and by the current, they become to a certain extent purified from organic contamination.

Well-water may be very good or very bad. If the well be simply a reservoir dug over a spring, and removed from sources of contamination, it has all the characters of fresh spring-water. If, on the other hand, it be simply a hole dug in the earth, the water which it contains is the surface water which has percolated through the thin layer of earth corresponding to the depth of the well, and is consequently warm, unaërated and charged with organic impurity. Such water is sometimes called "ground water."

Wells dug near dwellings are very liable to become charged with the worst of contaminations, animal excreta, by their filtration through the soil, either by reason of the fracture of the house-drain or otherwise.

Impurities in Potable Waters.—A water to be fit for drinking purposes should be cool, limpid, and odorless. It should have an agreeable taste, neither flat, salty, nor sweetish, and it should dissolve soap readily, without formation of any flocculent precipitate.

Although it is safe to condemn a water which does not possess the above characters, it is by no means safe to regard all waters which do possess them as beyond suspicion. To determine whether a water is potable it must be more carefully examined as to the following constituents:

Total Solids.—The amount of solid material dissolved in potable waters varies from 5 to 40 in 100,000; and a water containing more than the latter quantity is to be condemned on that account alone.

To determine the quantity of total solids 500 c.c. of the filtered water are evaporated to dryness in a previously weighed platinum dish, over the water-bath. The dish with the contained dry residue is cooled in a desiccator and again weighed. The increase in weight, multiplied by 200, gives the total solids in parts per 100,000.

Hardness.—The greater part of the solid matter dissolved in natural fresh waters consists of the salts of calcium, accompanied by less quantities of the salts of magnesium. The calcium salt is usually the bicarbonate or the sulfate; sometimes the chlorid, phosphate, or nitrate.

A water containing an excess of calcareous salt is said to be **hard**, and one not so charged is said to be **soft**. If the hardness be due to the presence of the carbonate it is **temporary**, if due to the sulfate it is **permanent**. Calcium carbonate is almost insoluble in pure water, but in the presence of free carbonic acid the more soluble bicarbonate is dissolved. But, on the water being boiled, it is decomposed, with precipitation of the carbonate, if the quantity exceed 50 in 100,000. As calcium sulfate is held in solution by virtue of its own, albeit sparing, solubility, it is not deposited when the water is boiled.

An accurate determination of the quantity of calcium and magnesium salts in water is rarely required. It is, however, frequently desirable to determine their quantity approximately, the result being the **degree of hardness**.

For this purpose a solution of soap of known strength is required. This is made by dissolving 10 grams of air-dried, white Castile soap, cut into thin shavings, in a litre of dilute alcohol (sp. gr. 0.949). To determine whether this solution contains the proper amount of soap, 10 c.c. of a solution, made by dissolving 1.11 grams of pure, recently fused calcium chlorid in a litre of water, are diluted with 60 c.c. of water and the soap solution added until a persistent lather is produced on agitation. If 11 c.c. of soap solution have been used it has the proper strength; if a greater or less quantity have been added it must be concentrated or diluted in proportion to the excess or deficiency. The soap solution must not be filtered, but, if turbid, must be shaken before using.

To determine the hardness, 70 c.c. of the water to be tested are placed in a glass-stoppered bottle of 250 c.c. capacity, and the soap solution gradually added from a burette. After each addition of soap solution the bottle is shaken, and allowed to lie upon its side five minutes. This is continued until at the end of five minutes a lather remains upon the surface of the liquid in the bottle. At this time the hardness is indicated by the number of c.c. of soap solution added, minus one. If more than 16 c.c. of soap solution are added the liquid in the bottle must be diluted with 70 c.c. of distilled water.

A good drinking-water should not have a hardness of more than fifteen.

Chlorids.—The presence of the chlorids of the alkaline metals, in quantities not sufficient to be detectable by the taste, is of no importance *per se;* but in connection with the presence of organic impurity, a determination of the amount of chlorin affords a ready method of indicating the probable source of the organic contamination. As vegetable organic matter brings with it but small quantities of chlorids, while animal contaminations are rich in those compounds, the presence of a large amount of chlorin serves to indicate that organic impurity is of animal origin. Indeed, when time presses, as during an epidemic, it is best to rely upon determinations of chlorin, and condemn all waters containing more than 1.5 in 100,000 of that element.

For the determination of chlorin two solutions are required: a solution of silver nitrate containing 4.79 grams per litre; a strong solution of potassium chromate. One hundred c.c. of the water are placed in a beaker with enough of the chromate solution to communicate a distinct yellow color. If the reaction be acid it is rendered neutral or *faintly* alkaline by the addition of sodium carbonate solution. The silver solution is now allowed to flow in from a burette, drop by drop, during constant agitation, until a *faint* reddish tinge persists. At this time the burette reading is taken; each c.c. of silver solution added represents 0.01 of chlorin per litre.

Organic Matter.—The most serious of the probable contaminations of drinking-water is that by organic matters containing nitrogen. When these are present in even moderate quantity, and when, at the same time, the proportion of chlorin is greater than usual, the water has been contaminated by animal excreta and contains, under suitable conditions, the causes of disease, be they germs or poisons.

Of the methods suggested for the determination of the amount of organic matter in natural waters there is, unfortunately, none which is easy of application and at the same time reliable. That which yields the best results is Wanklyn's process:

The following solutions are required: *a.* Made by dissolving 200 grams of potassium hydroxid and 8 grams of potassium permanganate in a litre of water. The solution is boiled down to about 725 c.c., cooled, and brought to its original bulk by the addition of boiled distilled water. *b. Nessler's reagent.* 35 grams of potassium iodid and 13 grams of mercuric chlorid are dissolved in 800 c.c. of water by the aid of heat and agitation. A cold, saturated solution of mercuric chlorid is then added, drop by drop, until the red precipitate which is formed is no longer redissolved on agitation: 160 grams of potassium hydroxid are then dissolved in the liquid, to and the bulk of the whole made up to a litre with water. The solution is allowed to stand, decanted, and preserved in completely filled, well-stoppered bottles. *c. Standard solutions of ammonia.* The stronger of these is made by dissolving 3.15 grams of ammonium chlorid in a litre of water. The weaker, by mixing one volume of the stronger with 99 volumes of water. The latter contains 0.00001 gram of ammonia in each c.c., and is the one used in the determinations, the stronger solution serving only for its convenient preparation. *d. A saturated solution of sodium carbonate.* *e. Distilled water.* The middle third of the distillate, 100 c.c. of which must not be perceptibly colored in ten minutes by the addition of 2 c.c. of Nessler's reagent.

The testing of a water is conducted as follows: Half a litre of the water to be tested (before taking the sample the demijohn or other vessel containing the water must be thoroughly shaken) is introduced, by a funnel, into a tubulated retort capable of holding one litre. If the water be acid, 10 c.c. of the solution of sodium carbonate *d* are added. Having connected the retort with a Liebig's condenser, the joint being made tight by a packing of moistened filter-paper, the water is made to boil as soon as possible by applying the flame of a Bunsen burner brought close to the bottom of the naked retort. The first 50 c.c. of distillate are collected in a cylindrical vessel of clear glass, about an inch in diameter. The following 150 c.c. are collected and thrown away, after which the fire is withdrawn. While these are passing over, the first 50 c.c. are Nesslerized (*vide infra*), and the result, plus one-third as much again, is the amount of free ammonia contained in the half-litre of water.

When 200 c.c. have distilled over, all the free ammonia has been removed, and it now remains to decompose the organic material, and determine the amount of ammonia formed. To effect this, 50 c.c. of the permanganate solution *a* are added through the funnel to the contents of the retort, which is shaken, stoppered, and again heated. The distillate is now collected in separate portions of 50 c.c. each, in glass cylinders, until 3 such portions have been collected. These are then separately Nesslerized as follows: 2 c.c. of the Nessler reagent are added to the sample of 50 c.c. of distillate; if ammonia be present, a yellow or brown color will be produced, dark in proportion to the quantity of ammonia present. Into another cylinder a given quantity of the standard solution of ammonia *c* is allowed to flow from a burette; enough water is added to make the bulk up to 50 c.c., and then 2 c.c. of Nessler reagent. This cylinder, and that containing the 50 c.c. of Nesslerized distillate, are then placed side by side on a sheet of white paper and their color examined. If the shade of color in the two cylinders be *exactly* the same, the 50 c.c. of distillate contain the same amount of ammonia as the quantity of standard solution of ammonia used. If the colors be different in intensity, another comparison-cylinder must be arranged, using more or less of the standard solution, as the first comparison-cylinder was lighter or darker than the distillate. When the proper similarity of shades has been attained, the number of cubic centimetres of the standard solution used is determined by the reading on the burette. This process, which, with a little practice, is neither difficult nor tedious, is to be repeated with the first 50 c.c. of distillate and with the three portions of 50 c.c. each, distilled after the addition of the permanganate solution. If, for example, it required 1 c.c. of standard solution in Nesslerizing the first 50 c.c., and for the others 3.5 c.c., 1.5 c.c., and 0.2 c.c., the following is the result and the usual method of recording it:

Free ammonia	.01	
Correction	.003	
	.013	
Free ammonia per litre	.026	milligr.
Albuminoid ammonia	.035	
	.015	
	.002	
	.052	
Albuminoid ammonia per litre	.104	milligr.

If a water yield no albuminoid ammonia it is organically pure, even if it contains much free ammonia and chlorids. If it contain from .02 to .05 milligrams per litre, it is still quite pure. When the albuminoid ammonia reaches 0.1 milligr. per litre the water is to be looked upon with suspicion; and it is to be condemned when the proportion reaches 0.15. When free ammonia is also present in considerable quantity, a water yielding 0.05 of albuminoid ammonia is to be looked upon with suspicion.

Nitrates and Nitrites—Are present in rain-water in quantities less than 2 parts in 100,000, calculated as N_2O_5. When the amount exceeds this, these salts are considered as indicating previous contamination by organic matter which has been oxidized and whose nitrogen has been to some extent converted into nitrites and nitrates.

To determine the amount of nitrous acid the following solutions are used: 1.) Dilute sulfuric acid 1 : 3; 2.) A solution containing 5 grams of metaphenylendiamin and sufficient sulfuric acid to form an acid reaction in 1 litre of H_2O; 3.) A solution made by dissolving 0.406 gram pure, dry silver nitrite in hot water, adding pure sodium chlorid so long as a precipitate is formed, diluting with H_2O to 1 litre, after cooling and without filtration. 100 c.c. of the clear liquid are then diluted to 1 litre. 1 c.c. of this solution contains 0.01 mgr. N_2O_3.

To make the determination 100 c.c. of the water are placed in a glass cylinder and 1 c.c. each of solutions 1 and 2 added. Three other cylinders are at the same time prepared, by diluting from 0.3 to 2.5 c.c. of solution 3 to 100 c.c. with pure H_2O, and adding to each 1 c.c. each of solutions 1 and 2. The shade of color of the water-cylinder is then compared with that of the others, as described above in Nesslerizing. The amount of N_2O_3 in the water is equal to that in the comparison-cylinder having the same shade.

Poisonous Metals.—Those most liable to occur in drinking-waters are iron, copper, and lead, and of these the last is the most important.

The power possessed by a water of dissolving lead varies materially with the nature of the substances which it holds in solution. Lead is not dissolved by water as lead, but only after conversion into an oxid; therefore any condition favoring the oxidation of the metal favors its solution. The presence of nitrates is favorable to the solution of lead, an influence which is, however, much diminished by the simultaneous presence of other salts. A water highly charged with oxygen dissolves lead readily, especially if the metallic surface be so exposed to the action of the water as to be alternately acted upon by it and by the air. On the other hand, waters containing carbonates or free carbonic acid may be left in contact with lead with comparative impunity, owing to the formation of a protective coating of the insoluble carbonate of lead on the surface of the metal. This does not apply, however, to water charged with a large excess of carbon dioxid under pressure. Of all natural waters, that most liable to contamination with lead is rain-water. It contains ammonium nitrate with very small quantities of other salts; and it is highly aërated, but contains no carbonates, and comparatively small quantities of carbon dioxid. Obviously, therefore, rain-water should neither be collected from a leaden roof, nor stored in leaden tanks, nor drank after having been long in contact with lead pipes. As a rule, the purer the water the more liable it is to dissolve lead when brought in contact with that metal, especially if the contact occur when the water is at a high temperature, or when it lasts for a long period.

To determine the power of water for dissolving lead, take two tumblers of the water to be tested; in one place a piece of lead, whose surface has been scraped bright, and allow them to stand twenty-four hours. At the end of that time, remove the lead and pass hydrogen sulfid through the water in both tumblers. If the one which contained the metal become perceptibly darker than the other, the water has a power of dissolving lead, such as to render its contact with surfaces of that metal dangerous if prolonged beyond a short time.

To test for the presence of poisonous metals, solution of ammonium sulfhydrate is added to the water, contained in a porcelain capsule. If a dark color be produced, which is not discharged on addition of hydrochloric acid, the water is contaminated with lead or copper.

For quantitative determinations, solutions containing known quantities of the poisonous metals are used: for iron 4.96 grams of ferrous sulfate in a litre of water; for copper 3.93 grams of cupric sulfate to the litre; and for lead 1.66 gram of lead acetate to the litre. One c.c. of each solution contains 0.001 gram of the metal. To use the solutions 100 c.c. of the water to be tested and 100 c.c. of pure water are placed in two porcelain capsules, to each of which some ammonium sulfhydrate is then added. The appropriate standard solution is then allowed to flow into the capsule containing the pure water, until the shade of color produced is the same as that of the liquid in the other capsule. The burette reading at this time gives the number of centigrams of the metal in a litre of water.

Suspended Solids.—Most natural waters deposit, on standing, more or less solid, insoluble material. These substances have been either suspended mechanically in the water, which deposits them when it remains at rest, or they have been in solution, and are deposited by becoming insoluble as the water is deprived of carbon dioxid by exposure to air and by relief from pressure.

The suspended particles should be collected by subsidence in a conical glass, and should be examined microscopically for low forms of animal and vegetable life. The quantity of suspended solids is determined by passing a litre of the turbid water through a dried and weighed filter, which, with the collected deposit, is again dried and weighed. The difference between the two weights is the weight of suspended matter in a litre of the water.

Bacteriological Examination of Water.—In recent years much attention has been given to the examination of natural waters by bacteriological methods, plate cultures on gelatin, cultures in blood serum and on potatoes, and experiments on animals. Although in some instances pathogenic bacteria have been found in water, and although in the future valuable results will probably be attained by these methods, the chief reliance in determining the quality of a drinking-water is still to be placed upon the older chemical processes.

Purification of Water.—The artificial means of rendering a more or less contaminated water fit for use are of five kinds: 1. Distillation; 2. Subsidence; 3. Filtration; 4. Precipitation; 5. Boiling.

The method of **distillation** is used in the laboratory when a very pure water is desired, and also at sea. Distilled water is, however, too pure for continued use, being hard of digestion, and flat to the taste from the absence of gases and of solid matter in solution. When circumstances oblige the use of such water, it should be agitated with air, and should be charged with inorganic matter to the extent of about 0.03 gram each of calcic bicarbonate and sodium chlorid to the litre.

Purification by **subsidence** is adopted only as an adjunct to precipitation and filtration, and for the separation of the heavier particles of suspended matter.

The ideal process of **filtration** consists in the separation of all particles of suspended matter, without any alteration of such substances as are held in solution. In the filtration of potable waters on a large scale, however, the more minute particles of suspended matters are only partially separated, while, on the other hand, an important change in the dissolved materials takes place, at least in certain kinds of filters, in the oxidation of organic matters, whether in solution or in suspension. In the filtration of large quantities of water it is passed through sand or charcoal, or through both substances arranged in alternate layers. Filtration through charcoal is much more effective than that through sand, owing to the much greater activity of the oxidation of nitrogenized organic matter in the former case.

Precipitation processes are only adapted to hard waters, and are designed to separate the excess of calcium salt, and at the same time a considerable quantity of organic matter, which is mechanically carried down with the precipitate. The method usually followed consists in the addition of lime (in the form of lime-water), in just sufficient quantity to neutralize the excess of carbon dioxid present in the water. The added lime, together with the calcium salt naturally present in the water, is then precipitated, except that small portion of calcium carbonate which the water, freed from carbon dioxid, is capable of dissolving. To determine when sufficient lime-water has been added, take a sample from time to time during the addition, and test it with solution of silver nitrate until a brown precipitate is formed. At this point cease the addition of lime-water and mix the limed water with further portions of the hard water, until a sample, treated with silver-nitrate solution, gives a yellowish in place of a brown color. Alum is also used as a precipitant, particularly in combination with filtration.

The purification of water by **boiling** can only be carried on upon a small scale. It is, however, of great value for the softening of temporarily hard waters, and for the destruction of organized impurities, for which latter purpose it should never be neglected during outbreaks of cholera and typhoid.

Natural Purification of Water.—The water of brooks, rivers, and lakes which have been contaminated by sewage and other organic impurity becomes gradually purified by natural processes. Suspended particles are deposited upon the bottom and sides of the stream, more or less rapidly, according to their gravity and the rapidity of the current. The bicarbonates of calcium, magnesium, and iron gradually lose carbon dioxid, and are precipitated as carbonates, which mechanically carry down dissolved as well as suspended impurities. The fermentations, oxidations, and reductions to which organic matters are subject bring about their gradual mineralization and the conversion of ammonia into nitrates. The processes of nutrition of aquatic plant life absorb dissolved organic impurity, as well as the products of decomposition of nitrogenized substances. This natural purification proceeds the more rapidly the more contact with air is favored.

Mineral Waters.—Under this head are classed all waters which are of therapeutic or industrial value, by reason of the quantity or nature of the dissolved solids which they contain; or which have a temperature greater than 20° (68° F.).

The composition of mineral waters varies greatly, according to the nature of the strata or veins through which the water passes, and to the conditions of pressure and previous composition under which it is in contact with these deposits.

The substances almost universally present in mineral waters are: oxygen, nitrogen, carbon dioxid; sodium carbonate, bicarbonate, sulfate and chlorid; and calcium bicarbonate. Of substances occasionally present the most important are: sulfhydric acid; sulfids of sodium, iron, and magnesium; bromids and iodids of sodium and magnesium; calcium and magnesium chlorids; carbonate, bicarbonate, sulfate, peroxid, and crenate of iron; silicates of sodium, calcium, magnesium, and iron; aluminium salts; salts of lithium, cesium, and rubidium; free sulfuric, silicic, arsenic, and boric acids; and ammoniacal salts.

Although a sharply defined classification of mineral waters is not possible, one which is useful, if not accurate, may be made, based upon the predominance of some constituent, or constituents, which impart to the water a well-defined therapeutic value. A classification which has been generally adopted includes five classes:

I. *Acidulous waters;* whose value depends upon dissolved carbonic acid. They contain but small quantities of solids, principally the bicarbonates of sodium and calcium and sodium chlorid.

II. *Alkaline waters;* which contain notable quantities of the carbonates or bicarbonates of sodium, potassium, lithium, and calcium, sufficient to communicate to them an alkaline reaction, and frequently a soapy taste; either naturally, or after expulsion of carbon dioxid by boiling.

III. *Chalybeate waters;* which contain salts of iron in greater proportion than 4 parts in 100,000. They contain ferrous bicarbonate, sulfate, crenate, and apocrenate, calcium carbonate, sulfates of potassium, sodium, calcium, magnesium, and aluminium, notable quantities of sodium chlorid, and frequently small amounts of arsenic. They have the taste of iron and are usually clear as they emerge from the earth. Those containing ferrous bicarbonate deposit a sediment on standing, by loss of carbon dioxid, and formation of ferrous carbonate.

IV. *Saline waters;* which contain neutral salts in considerable quantity. The nature of the salts which they contain is so diverse that the group may well be subdivided:

α. *Chlorin waters;* which contain large quantities of sodium chlorid, accompanied by less amounts of the chlorids of potassium, calcium, and magnesium. Some are so rich in sodium chlorid that they are not of service as therapeutic agents, but are evaporated to yield a more or less pure salt. Any natural water containing more than 300 parts in 100,000 of sodium chlorid belongs to this class, provided it do not contain substances more active in their medicinal action in such proportion as to warrant its classification elsewhere. Waters containing more than 1,500 parts in 100,000 are too concentrated for internal administration.

β. *Sulfate waters* are actively purgative from the presence of considerable proportions of the sulfates of sodium, calcium, and magnesium. Some contain large quantities of sodium sulfate, with mere traces of the calcium and magnesium salts, while in others the proportion of the sulfates of magnesium and calcium is as high as 3,000 parts in 100,000 to 2,000 parts in 100,000 of sodium sulfate. They vary much in concentration; from 500 to nearly 6,000 parts of total solids in 100,000. They have a salty, bitter taste, and vary much in temperature.

γ. *Bromin and iodin waters* are such as contain the bromids or iodids of potassium, sodium, or magnesium in sufficient quantity to communicate to them the medicinal properties of those salts.

V. *Sulfurous waters;* which hold hydrogen sulfid or metallic sulfids in solution. They have a disagreeable odor and are usually warm. They contain 20 to 400 parts in 100,000 of total solids.

Physiological.—Water is taken into the body both as a liquid and as a constituent of every article of food; the amount ingested by a healthy adult being 2.25 to 2.75 litres (2¼ to 3 quarts) per diem. The greater the elimination and the drier the nature of the food the greater is the amount of H_2O taken in the liquid form.

Water is a constituent of every tissue and fluid of the body, varying from 0.2 per cent. in the enamel of the teeth to 99.5 per cent. in the perspiration and saliva. It constitutes about 60 per cent. of the weight of the body.

The consistency of the various parts does not depend entirely upon the relative proportion of solids and H_2O, but is influenced by the nature of the solids. The blood, although liquid in the ordinary sense of the term, contains a less proportional amount of H_2O than does the tissue of the kidneys, and about the same proportion as the tissue of the heart. Although the bile and mucus are not as fluid as the blood, they contain a larger proportion of H_2O to solids than does that liquid.

Water is discharged by the kidneys, intestine, skin, and pulmonary surfaces. The quantity discharged is greater than that ingested; the excess being formed in the body by the oxidation of the H of its organic constituents.

Hydrogen Dioxid.

Hydrogen peroxid—Oxygenated water.

H_2O_2—*Molecular weight* = 34—*Sp. gr.* = 1.455—*Discovered by Thénard in* 1818.

Exists naturally in very minute quantity in rain-water, in air, and in the saliva.

This substance may be obtained in a state of purity by accurately following the process of Thénard. It may also be obtained, mixed with a large quantity of H_2O, by the action of carbon dioxid on barium perhydroxid: $BaO_2H_2 + CO_2 = BaCO_3 + H_2O_2$ or of dilute sulfuric acid on barium peroxid: $BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$. It is also formed in small quantity during the slow oxidation of many elements and compounds, such as P, Pb, Zn, Cd, Al, alcohol, ether, and the essences.

It is prepared industrially of 10–12 volume strength by gradually adding barium peroxid to dilute hydrofluoric acid solution, the mixture being maintained at a low temperature and constantly agitated.

The pure substance is a colorless, syrupy liquid, which, when poured into H_2O, sinks under it before mixing. It has a disagreeable, metallic taste, somewhat resembling that of tartar emetic. When taken into the mouth it produces a tingling sensation, increases the flow of saliva, and bleaches the tissues with which it comes in contact. It is still liquid at −30° (−22° F.). It is very unstable, and, even in darkness and at ordinary temperature, is gradually decomposed. At 20° (68° F.) the decomposition takes place more quickly, and at 100° (212° F.) rapidly and with effervescence. The dilute substance, however, is comparatively stable, and may be boiled and even distilled without suffering decomposition. Yet it is liable to explosive decomposition when exposed to summer temperature in closed vessels.

Hydrogen peroxid acts both as a reducing and an oxidizing agent. Arsenic, sulfids, and sulfur dioxid are oxidized by it at the expense of half its oxygen. When it is brought in contact with silver oxid both substances are violently decomposed, water and elementary silver remaining. By certain substances, such as gold, platinum, and charcoal in a state of fine division, fibrin, or manganese dioxid, it is decomposed with evolution of oxygen; the decomposing agent remaining unchanged.

The pure substance, when decomposed, yields 475 times its volume of oxygen; the dilute 15 to 20 volumes.

In dilute solution it is used as a bleaching agent and in the renovation of old oil-paintings. It is an energetic disinfectant and antiseptic, and is extensively used in surgery.

Analytical Characters.—1. To a solution of starch a few drops of cadmium iodid solution are added, then a small quantity of the fluid to be tested, and, finally, a drop of a solution of ferrous sulfate. A blue color is produced in the presence of hydrogen peroxid, even if the solution contain only 0.05 milligram per litre.

2. Add freshly prepared tincture of guaiacum and a few drops of a cold infusion of malt. A blue color—1 in 2,000,000.

3. Add to the liquid a few drops of potassium dichromate and a little dilute sulfuric acid, and agitate with ether. The ether assumes a brilliant blue-violet color.

4. Add to 6 c.c. of the liquid sulfuric acid, iodid of zinc, starch-paste, two drops of a two per cent. solution of cupric sulfate, and a little one-half per cent. solution of ferrous sulfate, in the order named. A blue color.

5. Add a trace of acetic acid, some α naphthylamin and solid sodium chlorid. After a short time a blue or blue-violet color and, after some hours, a flocculent ppt. of the same color.

Atmospheric Hydrogen Dioxid.—It has been claimed that atmospheric air, rain-water, snow, and hoar-frost constantly contain small quantities of hydrogen peroxid; the amount in rain-water varying from 0.0008 to 0.05 part in 100,000. The most recent experiments bearing upon the supposed presence of ozone and hydrogen peroxid in atmospheric air seem, however, to justify the belief that those substances, if present in air at all, are not met with in the amounts and with the constancy that have been claimed. According to this later view, the appearances from which the presence of ozone and hydrogen peroxid has been inferred are not caused by those substances, but by nitrous acid and the oxids of nitrogen.

CLASS II.—ACIDULOUS ELEMENTS.

Elements all of whose Hydrates are Acids, and which do not form Salts with the Oxacids.

I. CHLORIN GROUP.

FLUORIN. CHLORIN. BROMIN. IODIN.

The elements of this group are univalent. With hydrogen they form acid compounds, composed of one volume of the element in the gaseous state with one volume of hydrogen. Their hydrates are monobasic acids when they exist (fluorin forms no hydrate). The first two are gases, the third liquid, the fourth solid at ordinary temperatures. They are known as the **halogens.** The relations of their compounds to each other are shown in the following table :

HF	——	——	——	——	——	——	——
HCl	Cl_2O	Cl_2O_3	Cl_2O_4	HClO	$HClO_2$	$HClO_3$	$HClO_4$
HBr	——	——	——	HBrO	——	$HBrO_3$	$HBrO_4$
HI	——	——	I_2O_4	HIO	HIO_2	HIO_3	HIO_4
Hydro-ic acid.	Monoxid.	Trioxid.	Tetroxid.	Hypo-ous acid.	-ous acid.	-ic acid.	Per-ic acid.

FLUORIN.

Symbol = **F**—*Atomic weight* = 19—*Sp. gr.* 1.265 A (*calculated* = 1.316)—*Discovered by Sir H. Davy in* 1812.

Fluorin has been isolated by the electrolysis of HF at −23° (−9°.4 F.).

It is a gas, colorless in thin layers, greenish-yellow in layers 50 cent. thick.

It decomposes H_2O, with formation of HF and ozone. In it Si, Bo, As, Sb, S, and I fire spontaneously. With H it detonates violently, even in the dark. It attacks organic substances violently. The apparatus in which it is liberated must be made of platinum and fluor-spar. It forms compounds with all other elements except oxygen.

Hydrogen Fluorid—*Hydrofluoric acid* = **HF**—*Molecular weight* = 20. Hydrofluoric acid is obtained by the action of an excess of sulfuric acid upon fluor-spar or upon barium fluorid, with the aid of gentle heat : $CaF_2 + H_2SO_4 = CaSO_4 + 2\,HF$. If a solution be desired, the operation is conducted in a platinum or lead retort, whose beak is connected with a U-shaped receiver of the same metal, which is cooled and contains a small quantity of water.

The aqueous acid is a colorless liquid, highly acid and corrosive, and having a penetrating odor. Great care must be exercised that neither the solution nor the gas come in contact with the skin, as they produce painful ulcers which heal with difficulty, and also constitutional symptoms which may last for days. The inhalation of air containing very small quantities of HF has caused permanent loss of voice and, in two cases, death. When the acid has accidentally come in contact with the skin the part should be washed with dilute solution of potash, and the vesicle which forms should be opened.

Both the gaseous acid and its solution remove the silica from glass, a property utilized in etching upon that substance, the parts upon which no action is desired being protected by a coating of wax.

The presence of fluorin in a compound is detected by reducing the substance to powder, moistening it with sulfuric acid in a platinum crucible, over which is placed a slip of glass prepared as above; at the end of half an hour the wax is removed from the glass, which will be found to be etched if the substance examined contained a fluorid.

CHLORIN.

Symbol = **Cl**—*Atomic weight*=35.5—*Molecular weight* = 71—*Sp. gr.* = 2.4502 *A—One litre weighs* 3.17 *grams*—100 *cubic inches weigh* 76.3 *grains—Name derived from* χλωρός = *yellowish-green—Discovered by Scheele in* 1774.

Occurrence.—Only in combination, most abundantly in sodium chlorid.

Preparation.—(1.) By heating together manganese dioxid and hydrochloric acid (Scheele). The reaction takes place in two stages. Manganic chlorid is first formed according to the equation: $MnO_2 + 4HCl = MnCl_4 + 2H_2O$; and is subsequently decomposed into manganous chlorid and chlorin: $MnCl_4 = MnCl_2 + Cl_2$.

This and similar operations are usually conducted in an apparatus such as that shown in Fig. 23. The earthenware vessel A (which on a small scale may be replaced by a glass flask) is two-thirds filled with lumps of manganese dioxid of the size of hazelnuts, and adjusted in the water-bath; hydrochloric acid is poured in through the safety-tube and the bath heated. The disengaged gas is caused to bubble through the small quantity of water in B, is then dried by passage over the fragments of calcium chlorid in C, and is finally collected by displacement of air in the vessel D.

When the vessel A has become half filled with liquid it is best to decant the solution of manganous chlorid, wash the remaining oxid with water and begin anew. A kilo. of oxid yields 257.5 litres of Cl.

(2.) By the action of manganese dioxid upon hydrochloric acid in the presence of sulfuric acid, manganous sulfate being also formed: $MnO_2 + 2HCl + H_2SO_4 = MnSO_4 + 2H_2O + Cl_2$. The same quantity of chlorin is obtained as in (1), with the use of half the amount of hydrochloric acid.

(3.) By heating a mixture of one part each of manganese dioxid and sodium chlorid, with three parts of sulfuric acid. Hydrochloric acid and sodium sulfate are first formed: $H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl$; and the acid is immediately decomposed by either of the reactions indicated in (1) and (2), according as sulfuric acid is or is not present in excess.

(4.) By the action of potassium dichromate upon hydrochloric acid; potassium and chromic chlorids being also formed: $K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + 3Cl_2$. Two parts of powdered dichromate are heated with 17 parts of acid of sp. gr. 1.16; 100 grams of the salt yielding 22.5 litres of Cl.

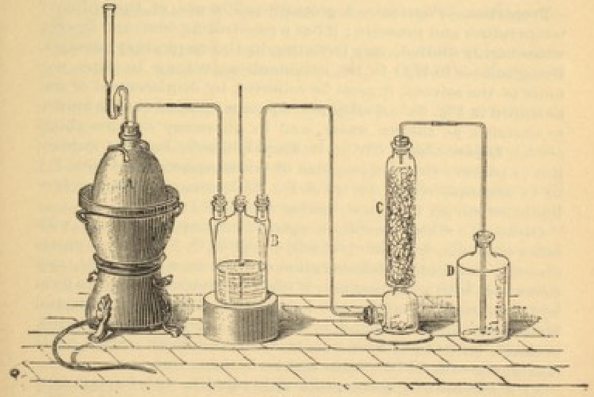


FIG. 23.

(5.) A convenient method of obtaining chlorin on a laboratory scale is by the use of "chlorin cubes." These are made by pressing together 1 part of plaster of Paris and 4 parts of chlorid of lime (q. v.), cutting into small cubes and drying. The cubes are used in one of the forms of constant apparatus (Figs. 19, 20, 21), with dilute hydrochloric acid, Cl being evolved at the ordinary temperature.

When a slow evolution of Cl, extending over a considerable period of time, is desired, as for ordinary disinfection, moistened chlorid of lime is exposed to the air, the calcium hypochlorite being decomposed by the atmospheric carbon dioxid. If a more rapid evolution of gas be desired, the chlorid of lime is moistened with dilute hydrochloric acid in place of with water.

(6.) By the action of potassium chlorate upon hydrochloric acid Cl is liberated, slowly at the ordinary temperature, more rapidly at the temperature of the water-bath:

$$\underset{\substack{\text{Potassium}\\\text{chlorate.}}}{2KClO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{4HCl} = \underset{\text{Chlorin.}}{Cl_2} + \underset{\substack{\text{Chlorin}\\\text{tetroxid.}}}{Cl_2O_4} + \underset{\substack{\text{Potassium}\\\text{chlorid.}}}{2KCl} + \underset{\text{Water.}}{2H_2O}.$$

Properties.—*Physical.*—A greenish-yellow gas, at the ordinary temperature and pressure; it has a penetrating odor, and is, even when highly diluted, very irritating to the respiratory passages. Being soluble in H_2O to the extent of one volume to three volumes of the solvent, it must be collected by displacement of air, as shown in Fig. 23. A saturated aqueous solution of Cl is known to chemists as **chlorin water,** and in pharmacy as **aqua chlori** (*U. S.*), **Liquor chlori** (*Br.*). It should bleach, but not redden, litmus paper. Under a pressure of 6 atmospheres at 0° (32° F.), or 8½ atmospheres at 12° (53°.6 F.), Cl becomes an oily, yellow liquid, of sp. gr. 1.33; and boiling at −33.6° (−28°.5 F.).

Chemical.—Chlorin exhibits a great tendency to combine with other elements, with all of which, except F, O, N, and C, it unites directly, frequently with evolution of light as well as heat, and sometimes with an explosion. With H it combines slowly, to form hydrochloric acid, under the influence of diffuse daylight, and violently in direct sunlight, or in highly actinic artificial lights. A candle burns in Cl with a faint flame and thick smoke, its H combining with the Cl, while carbon becomes free.

At a red heat Cl decomposes H_2O rapidly, with formation of hydrochloric, chloric, and probably hypochlorous acids. The same change takes place slowly under the influence of sunlight, hence chlorin water should be kept in the dark or in bottles of yellow glass.

In the presence of H_2O, chlorin is an active bleaching and disinfecting agent. It acts as an indirect oxidant, decomposing H_2O, the nascent O from which then attacks the coloring or odorous principle.

Chlorin is readily fixed by many organic substances, either by addition or substitution. In the first instance, as when Cl and olefiant gas unite to form ethylene chlorid, the organic substance simply takes up one or more atoms of chlorin: $C_2H_4 + Cl_2 = C_2H_4Cl_2$. In the second instance, as when Cl acts upon marsh gas to produce methyl chlorid: $CH_4 + Cl_2 = CH_3Cl + HCl$, each substituted atom of Cl displaces an atom of H, which combines with another Cl atom to form hydrochloric acid.

Hydrate of chlorin, Cl $5H_2O$, is a yellowish-green, crystalline substance, formed when Cl is passed through chlorin water, cooled to 0° (32° F.). It is decomposed at 10° (50° F.).

Hydrogen Chlorid—Hydrochloric Acid—Muriatic Acid—Acidum Hydrochloricum (U. S.; Br.)—HCl—*Molecular weight* = 36.5—*Sp. gr.* 1.259 *A*—*A litre weighs* 1.6293 *gram.*

Occurrence.—In volcanic gases and in the gastric juice of the mammalia.

Preparation.—(1.) By the direct union of its constituent elements.

(2.) By the action of sulfuric acid upon a chlorid, a sulfate being at the same time formed: $H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl$.

This is the reaction by which the HCl used in the arts is produced.

(3.) Hydrochloric acid is also formed in a great number of reactions, as when Cl is substituted in an organic compound.

Properties.—*Physical.*—A colorless gas, acid in reaction and taste, having a sharp, penetrating odor, and producing great irritation when inhaled. It becomes liquid under a pressure of 40 atmospheres at 4° (29° F.). It is very soluble in H_2O, one volume of which dissolves 480 volumes of the gas at 0° (32° F.).

Chemical.—Hydrochloric acid is neither combustible nor a supporter of combustion, although certain elements, such as K and Na, burn in it. It forms white clouds on contact with moist air.

Solution of Hydrochloric Acid.—It is in the form of aqueous solution that this acid is usually employed in the arts and in pharmacy. It is, when pure, a colorless liquid (yellow when impure), acid in taste and reaction, whose sp. gr. and boiling-point vary with the degree of concentration. When heated, it evolves HCl, if it contain more than 20 per cent. of that gas, and H_2O if it contain less. A solution containing 20 per cent. boils at 111° (232° F.), is of sp. gr. 1.099, has the composition $HCl + 8H_2O$, and distils unchanged.

Commercial muriatic acid is a yellow liquid; sp. gr. about 1.16; contains 32 per cent. HCl; and contains ferric chlorid, sodium chlorid, and arsenical compounds.

Acidum hydrochloricum is a colorless liquid, containing small quantities of impurities. It contains 31.9 per cent. HCl and its sp. gr. is 1.16 (U. S.; Br.). The dilute acid is the above diluted with water. Sp. gr. 1.049 = 10 per cent. HCl (U. S.); sp. gr. 1.052 = 10.5 per cent. HCl (Br.).

C. P. (*chemically pure*) *acid* is usually the same as the strong pharmaceutical acid and far from pure (see below).

Hydrochloric acid is classed, along with nitric and sulfuric acids, as one of the three **strong mineral acids.** It is decomposed by many elements, with formation of a chlorid and liberation of hydrogen: $2HCl + Zn = ZnCl_2 + H_2$. With oxids and hydroxids of the metals it enters into double decomposition, forming H_2O and a chlorid: $CaO + 2HCl = CaCl_2 + H_2O$ or $CaH_2O_2 + 2HCl = CaCl_2 + 2H_2O$.

Oxidizing agents decompose HCl with liberation of Cl. A mixture of hydrochloric and nitric acids in the proportion of three molecules of the former to one of the latter, is the **acidum nitrohydrochloricum** (*U. S.; Br.*), or **aqua regia.** The latter name alludes to its power of dissolving gold, by combination of the nascent Cl, which it liberates, with that metal, to form the soluble auric chlorid.

Impurities.—A chemically pure solution of this acid is exceedingly rare. The impurities usually present are: *Sulfurous acid*—hydrogen sulfid is given off when the acid is poured upon zinc; *Sulfuric acid*—a white precipitate is formed with barium chlorid; *Chlorin* colors the acid yellow; *Lead* gives a black color when the acid is treated with hydrogen sulfid; *Iron*—the acid gives a red color with ammonium sulfocyanate; *Arsenic*—the method of testing by hydrogen sulfid is not sufficient. If the acid is to be used for toxicological analysis, a litre, diluted with half as much H_2O, and to which a small quantity of potassium chlorate has been added, is evaporated over the water-bath to 400 c.c.; 25 c.c. of sulfuric acid are then added, and the evaporation continued until the liquid measures about 100 c.c. This is introduced into a Marsh apparatus and must produce *no* mirror during an hour.

Chlorids.—A few of the chlorids are liquid, $SnCl_4$, $SbCl_5$; the remainder are solid, crystalline and more or less volatile. The metallic chlorids are soluble in water, except AgCl, Hg_2Cl_2, which are insoluble, and $PbCl_2$, which is sparingly soluble. The chlorids of the non-metals are decomposed by H_2O.

The chlorids are formed: 1.) By the direct union of the elements: $P + Cl_5 = PCl_5$; 2.) By the action of chlorin upon a heated mixture of oxid and carbon: $Al_2O_3 + 3C + 3Cl_2 = Al_2Cl_6 + 3CO$; 3.) By solution of the metal, oxid, hydroxid, or carbonate in HCl: $Zn + 2HCl = ZnCl_2 + H_2$; 4.) By double decomposition between a solution of a chlorid and that of another salt whose metal forms an insoluble chlorid: $AgNO_3 + NaCl = AgCl + NaNO_3$.

Analytical Characters.—1.) With $AgNO_3$ a white, flocculent ppt., insoluble in HNO_3, soluble in NH_4HO. 2.) With $Hg_2(NO_3)_2$, a white ppt., which turns black with NH_4HO.

Toxicology.—Poisons and corrosives.—A poison is any substance which, being in solution in the blood, produces death or serious bodily harm.

A corrosive is a substance capable of producing death by its chemical action upon a tissue with which it comes in direct contact.

The corrosives act much more energetically when concentrated than when dilute; and when the dilution is great they have no deleterious action. The degree of concentration in which the true poisons are taken is of little influence upon their action if the dose taken remain the same.

Under the above definitions the strong mineral acids act as corrosives rather than as poisons. They produce their injurious results by destroying the tissues with which they come in contact, and will cause death as surely by destroying a large surface of skin, as when they are taken into the stomach.

The symptoms of corrosion by the mineral acids begin immediately, during the act of swallowing. The chemical action of the acid upon every part with which it comes in contact causes acute burning pain, extending from the mouth to the stomach and intestine, referred chiefly to the epigastrium. Violent and distressing vomiting of dark, tarry, or "coffee-ground," highly acid material is a prominent symptom. Eschars, at first white or gray, later brown or black, are formed where the acid has come in contact with the skin or mucous membrane. Respiration is labored and painful, partly by pressure of the abdominal muscles, but also, in the case of hydrochloric acid, from entrance of the irritating, acid gas into the respiratory passages. Death may occur within 24 hours, from collapse; more suddenly from perforation of large blood-vessels, or from peritonitis; or after several weeks, secondarily, from starvation, due to closure of the pylorus by inflammatory thickening, and destruction of the gastric glands.

The object of the treatment in corrosion by the mineral acids is to neutralize the acid and convert it into a harmless salt. For this purpose the best agent is magnesia (magnesia usta), suspended in a small quantity of water, or if this be not at hand, a strong solution of soap. Chalk and the carbonates and bicarbonates of sodium and potassium should not be given, as they generate large volumes of gas. The scrapings of a plastered wall, or oil, are entirely useless. The stomach-pump, or any attempt at the introduction of a tube into the œsophagus, is not to be thought of.

Compounds of Chlorin and Oxygen.—Three compounds of chlorin and oxygen have been isolated, two being anhydrids. They are all very unstable, and prone to sudden and violent decomposition.

Chlorin Monoxid.—Cl_2O—87—*Hypochlorous anhydrid* or *oxid*, is formed by the action, below 20° (68° F.), of dry Cl upon precipitated mercuric oxid : $HgO + 2Cl_2 = HgCl_2 + Cl_2O$.

On contact with H_2O it forms **hypochlorous acid**, $HClO$, which, owing to its instability, is not used industrially, although the hypochlorites of Ca, K, and Na are.

Chlorin Trioxid—*Chlorous anhydrid* or *oxid*, **Cl_2O_3**—119—is a yellowish-green gas formed by the action of dilute nitric acid upon potassium chlorate in the presence of arsenic trioxid. At 50° (122° F.) it explodes. It is a strong bleaching agent ; is very irritating when inhaled and readily soluble in H_2O, the solution probably containing **chlorous acid**, $HClO_2$.

Chlorin Tetroxid—*Chlorin peroxid*, **Cl_2O_4**—135—is a violently explosive body, produced by the action of sulfuric acid upon potassium chlorate. Below – 20° (– 4° F.) it is an orange-colored liquid; above that temperature a yellow gas. It explodes violently when heated to a temperature below 100° (212° F.). There is no corresponding hydrate known, and if it be brought in contact with an alkaline hydroxid, a mixture of chlorate and chlorite is formed.

Besides the above, two oxacids of Cl are known, the anhydrids corresponding to which have not been isolated.

Chloric Acid—$HClO_3$—84.5—obtained, in aqueous solution, as a strongly acid, yellowish, syrupy liquid, by decomposing its barium salt by the proper quantity of sulfuric acid.

Perchloric Acid—$HClO_4$—100.5—is the most stable of the series. It is obtained by boiling potassium chlorate with hydrofluosilicic acid, decanting the cold fluid, evaporating until white fumes appear, decanting from time to time, and finally distilling. It is a colorless, oily liquid ; sp. gr. 1.782 ; which explodes on contact with organic substances or charcoal.

BROMIN.

Bromum, U.S., Br.—*Symbol* = **Br**—*Atomic weight* = 80—*Molecular weight* = 160—*Sp. gr. of liquid* = 3.1872 at 0° ; *of vapor* = 5.52 *A—Freezing-point* = – 24°.5 (–12°.1 *F.*)—*Boiling-point* = 63° (145°.4 *F.*)—*Name derived from* βρῶμος = *a stench—Discovered by Balard in* 1826.

Occurrence.—Only in combination, most abundantly with Na and Mg in sea-water and the waters of mineral springs.

Preparation.—It is obtained from the mother liquors, left by the evaporation of sea-water, and of that of certain mineral springs, and from sea-weed. These are mixed with sulfuric acid and manganese dioxid and heated, when the bromids are decomposed by the Cl produced, and Br distils.

Properties.—*Physical.*—A dark reddish-brown liquid, volatile at all temperatures above − 24°.5 (−12°.1 F.); giving off brown-red vapors which produce great irritation when inhaled. Soluble in water to the extent of 3.2 parts per 100 at 15° (59° F.); more soluble in alcohol, carbon disulfid, chloroform, and ether.

Chemical.—The chemical characters of Br are similar to those of Cl, but less active. With H_2O it forms a crystalline hydrate at 0° (32° F.): $Br\ 5H_2O$. Its aqueous solution is decomposed by exposure to light, with formation of hydrobromic acid.

It is highly poisonous.

Hydrogen Bromid—Hydrobromic acid—Acidum hydrobromicum dil. (U. S.) = HBr—*Molecular weight* = 81—*Sp. gr.* = 2.71 *A—A litre weighs* 3.63 *grams—Liquefies at* − 69° (−92°.2 *F.*)—*Solidifies at* − 73° (− 99°.4 *F.*).

Preparation.—This substance cannot be obtained from a bromid as HCl is obtained from a chlorid. It is produced, along with phosphorous acid, by the action of H_2O upon phosphorus tribromid: $PBr_3 + 3H_2O = H_3PO_3 + 3HBr$; or by the action of Br upon paraffin.

Properties.—A colorless gas; produces white fumes with moist air; acid in taste and reaction, and readily soluble in H_2O, with which it forms a hydrate, $HBr\ 2H_2O$. Its chemical properties are similar to those of HCl.

Bromids closely resemble the chlorids and are formed under similar conditions. They are decomposed by chlorin, with formation of a chlorid and liberation of Br: $2KBr + Cl_2 = 2KCl + Br_2$. The metallic bromids are soluble in H_2O, except AgBr and Hg_2Br_2, which are insoluble, and $PbBr_2$, which is sparingly soluble. The bromids of Mg, Al, Ca are decomposed into oxid and HBr on evaporation of their aqueous solutions.

Analytical Characters.—(1.) With $AgNO_3$, a yellowish-white ppt., insoluble in HNO_3, sparingly soluble in NH_4HO. (2.) With chlorin water a yellow solution which communicates the same color to chloroform and to starch-paste. (3.) With palladic nitrate a black ppt. in the absence of chlorids.

Oxacids of Bromin.—No oxids of bromin are known, although three oxacids exist, either in the free state or as salts:

Hypobromous Acid—HBrO—97—is obtained, in aqueous solution, by the action of Br upon mercuric oxid, silver oxid, or silver nitrate. When Br is added to concentrated solution of potassium hydroxid no hypobromite is formed, but a mixture of bromate and bromid, having no decolorizing action. With sodium hydroxid, however, sodium hypobromite is formed in solution; and such a solution, freshly prepared, is used in Knop's process for determining urea (q. v.).

Bromic Acid—**$HBrO_3$**—129—has only been obtained in aqueous solution, or in combination. It is formed by decomposing barium bromate with an equivalent quantity of sulfuric acid: $Ba(BrO_3)_2+H_2SO_4=2HBrO_3+BaSO_4$. In combination it is produced, along with the bromid, by the action of Br on caustic potassa: $3Br_2 + 6KHO = KBrO_3 + 5KBr + 3H_2O$.

Perbromic Acid—**$HBrO_4$**—145—is obtained on a comparatively stable, oily liquid, by the decomposition of perchloric acid by Br, and concentrating over the water-bath.

It is noticeable in this connection that, while HCl and the chlorids are more stable than the corresponding Br compounds, the oxygen compounds of Br are more permanent than those of Cl.

IODIN.

Iodum (U. S.; Br.)—*Symbol* = **I**—*Atomic weight* = 127—*Molecular weight* = 254—*Sp. gr. of solid* = 4.948; *of vapor* = 8.716 *A*—*Fuses at* 113°.6 (236°.5 *F.*)—*Boils at* 175° (347° *F.*)—*Name derived from* ἰώδης = *violet*—*Discovered by Courtois in* 1811.

Occurrence.—In combination with Na, K, Ca, and Mg, in sea-water, the waters of mineral springs, marine plants and animals. Cod-liver oil contains about 37 parts in 100,000.

Preparation.—It is obtained from the ashes of sea-weed, called *kelp* or *varech*. These are extracted with H_2O, and the solution evaporated to small bulk. The mother liquor, separated from the other salts which crystallize out, contains the iodids, which are decomposed by Cl, aided by heat, and the liberated iodin condensed.

Properties.—*Physical.*—Blue-gray, crystalline scales, having a metallic lustre. Volatile at all temperatures, the vapor having a violet color, and a peculiar odor. It is sparingly soluble in H_2O, which, however, dissolves larger quantities on standing over an excess of iodin, by reason of the formation of hydriodic acid. The presence of certain salts, notably potassium iodid, increases the solvent power of H_2O for iodin. The **Liq. Iodi Comp.** (*U. S.*), **Liq. Iodi**, *Br.* is solution of potassium iodid containing free iodin. Very soluble in alcohol; **Tinct. iodi** (*U. S.; Br.*); in ether, chloroform, benzol, and carbon disulfid. With the three last-named solvents it forms violet solutions, with the others brown solutions.

Chemical.—In its chemical characters I resembles Cl and Br, but is less active. It decomposes H_2O slowly, and is a weak bleaching and oxidizing agent. It decomposes hydrogen sulfid with formation of hydriodic acid, and liberation of sulfur. It does not combine directly with oxygen, but does with ozone. Potassium hydroxid solution dissolves it, with formation of potassium iodid, and some hypoiodite. Nitric acid oxidizes it to iodic acid. With ammonium hydroxid solution it forms the explosive nitrogen iodid.

Impurities.—*Non-volatile substances* remain when the I is heated. *Water* separates as a distinct layer when I is dissolved in carbon disulfid. *Cyanogen iodid* appears in white, acicular crystals among the crystals of sublimed I, when half an ounce of the substance is heated over the water-bath for twenty minutes, in a porcelain capsule, covered with a flat-bottomed flask filled with cold water. The last named is the most serious impurity as it is actively poisonous.

Toxicology.—Taken internally, iodin acts both as a local irritant and as a true poison. It is discharged as an alkaline iodid by the urine and perspiration, and when taken in large quantity it appears in the fæces.

The poison should be removed as rapidly as possible by the use of the stomach-pump and of emetics. Farinaceous substances may also be given.

Hydrogen Iodid—Hydriodic acid—HI—*Molecular weight*= 128—*Sp. gr.* 4.443 A.

Preparation.—By the decomposition of phosphorus triiodid by water: $PI_3 + 3H_2O = H_3PO_3 + 3HI$. Or, in solution by passing hydrogen sulfid through water holding iodin in suspension: $H_2S + I_2 = 2HI + S$.

Properties.—A colorless gas, forming white fumes on contact with air, and of strongly acid reaction. Under the influence of cold and pressure it forms a yellow liquid, which solidifies at —55°(—67° F.). Water dissolves it to the extent of 425 volumes for each volume of the solvent at 10° (50° F.).

It is partly decomposed into its elements by heat. Mixed with O it is decomposed, even in the dark, with formation of H_2O and liberation of I. Under the influence of sunlight the gas is slowly decomposed, although its solutions are not so affected, if they be free from air. Chlorin and bromin decompose it, with liberation of iodin. With many metals it forms iodids. It yields up its H readily and is used in organic chemistry as a source of that element in the nascent state.

Iodids—are formed under the same conditions as the chlorids and bromids, which they resemble in their properties. The metallic iodids are soluble in water except AgI, Hg_2I_2, which are insoluble, and PbI_2, which is very slightly soluble. The iodids of the earth metals are decomposed into oxid and HI on evaporation of their aqueous solutions. Chlorin decomposes the iodids as it does the bromids.

Analytical Characters.—(1.) With $AgNO_3$, a yellow ppt., insoluble in HNO_3, and in NH_4HO. (2.) With fuming HNO_3 or with chlorin water, a yellow liquid, which colors starch-paste black or purple, and chloroform violet. (3.) With palladic nitrate, a black ppt., insoluble in cold HNO_3 and in solutions of alkaline chlorids, but forming a dark brown solution with alkaline iodids.

Chlorids of Iodin.—Chlorin and iodin combine with each other in two proportions: **Iodin monochlorid,** or **protochlorid—ICl** is a red-brown, oily, pungent liquid, formed by the action of dry Cl upon I, and distilling at 100° (212° F.). **Iodin trichlorid** or **perchlorid—ICl_3** is a yellow, crystalline solid, having an astringent, acid taste, and a penetrating odor; very volatile; its vapor irritating; easily soluble in water. It is formed by saturating H_2O holding I in suspension with Cl, and adding concentrated sulfuric acid. ICl_3 has been used as an antiseptic.

Oxacids of Iodin.—The best known of these are the highest two of the series—iodic and periodic acids.

Iodic Acid—HIO_3—176—is formed as an iodate, whenever I is dissolved in a solution of an alkaline hydroxid: $I_6 + 6KHO = KIO_3 + 5KI + 3H_2O$. As the free acid, by the action of strong oxidizing agents, such as nitric acid, or chloric acid, upon I; or by passing Cl for some time through H_2O holding I in suspension.

Iodic acid appears in white crystals, decomposable at 170° (338° F.), and quite soluble in H_2O, the solution having an acid reaction, and a bitter, astringent taste.

It is an energetic oxidizing agent, yielding up its O readily, with separation of elementary I or of HI. It is used as a test for the presence of morphin (*q. v.*).

Periodic Acid—HIO_4—192—is formed by the action of Cl upon an alkaline solution of sodium iodate. The sodium salt thus obtained is dissolved in nitric acid, treated with silver nitrate, and the resulting silver periodate decomposed with H_2O. From the solution the acid is obtained in colorless crystals, fusible at 130° (266° F.), very soluble in water, and readily decomposable by heat.

II. SULFUR GROUP.

SULFUR—SELENIUM—TELLURIUM.

The elements of this group are bivalent. With hydrogen they form compounds composed of one volume of the element, in the form of vapor, with two volumes of hydrogen—the combination being attended with a condensation in volume of one-third.

Their hydrates are dibasic acids. They are all solid at ordinary temperatures. The relation of their compounds to each other is shown in the following table:

H_2S	SO_2	SO_3	H_2SO_2	H_2SO_3	H_2SO_4
H_2Se	SeO_2	SeO_3	———	H_2SeO_3	H_2SeO_4
H_2Te	TeO_2	TeO_3	———	H_2TeO_3	H_2TeO_4
Hydro-ic acid.	Dioxid.	Trioxid.	Hypo-ous acid.	-ous acid.	-ic acid.

SULFUR.

Symbol = **S**—*Atomic weight* = 32—*Molecular weight* = 64—*Sp. gr. of vapor* = 2.22 A—*Fuses at* 114° (237.2° F.)—*Boils at* 447.3° (837° F.).

Occurrence.—Free in crystalline powder, large crystals, or amorphous, in volcanic regions. In combination in sulfids and sulfates, and in albuminoid substances.

Preparation.—By purification of the native sulfur, or decomposition of *pyrites*, natural sulfids of iron.

Crude sulfur is the product of a first distillation. A second distillation, in more perfectly constructed apparatus, yields *refined sulfur*. During the first part of the distillation, while the air of the condensing chamber is still cool, the vapor of S is suddenly condensed into a fine, crystalline powder, which is **flowers of sulfur, sulfur sublimatum** (*U. S.*). Later, when the temperature of the condensing chamber is above 114°, the liquid S collects at the bottom, whence it is drawn off and cast into sticks of **roll sulfur.**

Properties.—*Physical.*—Sulfur is usually yellow in color. At low temperatures, and in minute subdivision, as in the precipitated **milk of sulfur, sulfur præcipitatum** (*U. S.*), it is almost or quite colorless. Its taste and odor are faint but characteristic. At 114° (237°.2 F.) it fuses to a thin yellow liquid, which at 150°–160° (302°–320° F.) becomes thick and brown; at 330°–340° (626°–642°.2 F.) it again becomes thin and light in color; finally it boils, giving off brownish-yellow vapor at a temperature variously stated between 440° (824° F.) and 448° (838°.4 F.). If heated to about 400° (752° F.) and suddenly cooled, it is converted into **plastic sulfur,** which may be moulded into any desired form. It is insoluble in water, sparingly soluble in anilin, phenol, benzene, benzin, and chloroform; readily soluble in protochlorid of sulfur and carbon disulfid. It dissolves in hot alcohol, and crystallizes from the solution, on cooling, in white prismatic crystals. It is dimorphous. When fused sulfur crystallizes it does so in oblique rhombic prisms. Its solution in carbon disulfid deposits it on evaporation in rhombic octahedra. The prismatic variety is of sp. gr. 1.95 and fuses at 120° (248° F.); the sp. gr. of the octahedral is 2.05, and its fusing point 114°.5 (238° F.). The prismatic crystals, by exposure to air, become opaque, by reason of a gradual conversion into octahedra.

Chemical.—Sulfur unites readily with other elements, especially at high temperatures. Heated in air or O, it burns with a blue flame to sulfur dioxid, SO_2. In H it burns with formation of hydrogen sulfid, H_2S. The compounds of S are similar in constitution, and to some extent in chemical properties, to those of O. In many organic substances S may replace O, as in sulfocyanic acid, CNSH, corresponding to cyanic acid, CNOH.

Sulfur is used principally in the manufacture of gunpowder; also to some extent in making sulfuric acid, sulfur dioxid, and matches, and for the prevention of fungoid and parasitic growths.

Hydrogen Monosulfid—Sulfhydric acid—*Hydrosulfuric acid*—**Sulfuretted hydrogen—H_2S**—*Molecular weight* = 34—*Sp. gr.* = 1.19 A.

Occurrence.—In volcanic gases; as a product of the decomposition of organic substances containing S; in solution, in the waters of some mineral springs; and, occasionally, in small quantity, in the gases of the intestine.

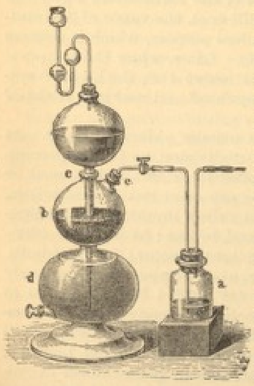


FIG. 24.

Preparation.—(1.) By direct union of the elements; either by burning S in H, or by passing H through molten S.

(2.) By the action of nascent H upon sulfuric acid, if the mixture become heated. (See Marsh test for arsenic.)

(3.) By the action of HCl upon antimony trisulfid: $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$.

(4.) By the action of dilute sulfuric acid upon ferrous sulfid: $FeS + H_2SO_4 = FeSO_4 + H_2S$. This is the method generally used. The gas should be purified by passage over dry calcium chlorid, then through a tube, 20 cent. long, loosely filled with solid iodin and, finally, through a solution of potassium sulfid.

(5.) By the action of HCl upon calcium sulfid: $CaS + 2HCl = CaCl_2 + H_2S$.

The gas is usually obtained in the laboratory by reaction (4), either in an apparatus such as that shown in Fig. 20 (p. 43) or in one of the forms of apparatus shown in Figs. 24, 25. The sulfid is put into the bulb *b*, Fig. 24, through the opening *e*, or into the bottle *b*, Fig. 25. The dilute acid, with which the uppermost and lowest bulbs, Fig. 24, are filled, comes in contact with the sulfid

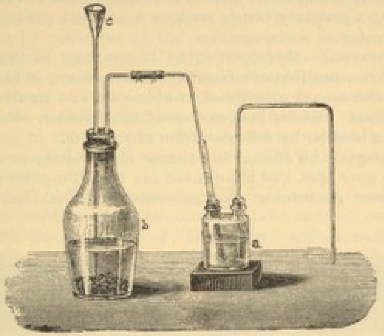


FIG. 25.

when the stopcock is opened, or in the apparatus, Fig. 25, is poured through the funnel tube *c*. *a* is a wash-bottle partly filled with water.

As ferrous sulfid is liable to contain arsenic, and as hydrogen sulfid generated from it may be contaminated with hydrogen arsenid, the gas, when required for toxicological analysis should always be obtained by reaction (5) in the apparatus, Fig. 24, or should be purified as above directed.

Properties.—*Physical.*—A colorless gas, having the odor of rotten eggs and a disgusting taste; soluble in H_2O to the extent of 3.23 parts to 1 at 15° (59° F.); soluble in alcohol. Under 17 atmospheres pressure, or at −74° (−101°.2 F.) at the ordinary pressure, it liquefies; at −85.5° (−122° F.) it forms white crystals.

Chemical.—Burns in air with formation of sulfur dioxid and water: $2H_2S + 3O_2 = 2SO_2 + 2H_2O$. If the supply of oxygen be deficient, H_2O is formed, and sulfur liberated: $2H_2S + O_2 = 2H_2O + S_2$. Mixtures of H_2S and air or O explode on contact with flame. Solutions of the gas when exposed to air become oxidized with deposition of S. Such solutions should be made with boiled H_2O, and kept in bottles which are completely filled, and well corked. Oxidizing agents, Cl, Br, and I remove its H with deposition of S. Hydrogen sulfid and sulfur dioxid mutually decompose each other into water, pentathionic acid and sulfur: $4SO_2 + 3H_2S = 2H_2O + H_2S_5O_6 + S_2$.

When the gas is passed through a solution of an alkaline hydroxid its S displaces the O of the hydroxid to form a sulfhydrate: $H_2S + KHO = H_2O + KHS$. With solutions of metallic salts H_2S usually relinquishes its S to the metal: $CuSO_4 + H_2S = CuS + H_2SO_4$, a property which renders it of great value in analytical chemistry.

Physiological.—Hydrogen sulfid is produced in the intestine by the decomposition of albuminous substances or of taurochloric acid; it also occurs sometimes in abscesses, and in the urine in tuberculosis, variola, and cancer of the bladder. It may also reach the bladder by diffusion from the rectum.

Toxicology.—An animal dies almost immediately in an atmosphere of pure H_2S, and the diluted gas is still rapidly fatal. An atmosphere containing one per cent. may be fatal to man, although individuals habituated to its presence can exist in an atmosphere containing three per cent. Even when highly diluted it produces a condition of low fever, and care is to be taken that the air of laboratories in which it is used shall not become contaminated with it. Its toxic powers are due primarily, if not entirely, to its power of reducing and combining with the blood-coloring matter.

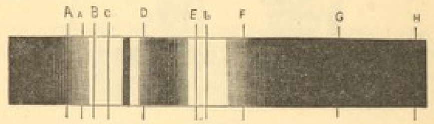


Fig. 26.

The form in which hydrogen sulfid generally produces deleterious effects is as a constituent of the gases emanating from sewers, privies, burial vaults, etc. These give rise to either slow poisoning, as when sewer gases are admitted to sleeping and other apartments by defective plumbing, or to sudden poisoning, as when a person enters a vault or other locality containing the noxious atmosphere.

The treatment should consist in promoting the inhalation of pure air, artificial respiration, cold affusions, and the administration of stimulants.

After death the blood is found to be dark in color, and gives the spectrum shown in Fig. 26, due to sulfhæmoglobin.

Sulfids and Hydrosulfids.—These compounds bear the same relation to sulfur that the oxids and hydroxids do to oxygen. The two sulfids of arsenic, AS_2S_3 and AS_2S_5, correspond to the two oxids, AS_2O_3 and AS_2S_5, and the hydrosulfid of potassium, KHS, corresponds to the hydroxid, KHO.

Many metallic sulfids occur in nature and are important ores of the metals, as the sulfids of zinc, mercury, cobalt, nickel, and iron. They are formed artificially, either by direct union of the elements at elevated temperatures, as in the case of iron: $Fe + S = FeS$; or by reduction of the corresponding sulfate, as in the case of calcium: $CaSO_4 + 2C = CaS + 2CO_2$.

The sulfids are insoluble in H_2O, except those of the alkali metals. Many of the sulfids are soluble in alkaline liquids, and behave as **sulfanhydrids,** forming sulfo- or thio-salts, corresponding to the oxysalts. Thus potassium arsenate, K_3AsO_4 and thioarsenate, K_3AsS_4; antimonate, K_3SbO_4, and thioantimonate, K_3SbS_4.

The metallic sulfids are decomposed when heated in air, usually with the formation of sulfur dioxid and the metallic oxid; sometimes with the formation of the sulfate; and sometimes with the liberation of the metal, and the formation of sulfur dioxid. The strong mineral acids decompose the sulfids with formation of hydrogen monosulfid.

Analytical Characters.—*Hydrogen Sulfid.*—(1.) Blackens paper moistened with lead acetate solution. (2.) Has an odor of rotten eggs.

Sulfids.—(1.) Heated in the oxidizing flame of the blowpipe, give a blue flame and odor of SO_2. (2.) With a mineral acid give off H_2S (except sulfids of Hg, Au, and Pt).

Sulfur Dioxid—*Sulfurous oxid, or anhydrid*—**Acidum sulfurosum (U. S.; Br.)**—$\mathbf{SO_2}$—*Molecular weight* = 64—*Sp. gr. of gas* = 2.213; *of liquid* = 1.45—*Boils at* −10° (14° F.); *solidifies at* −75° (−103° *F.*).

Occurrence.—In volcanic gases and in solution in some mineral waters.

Preparation.—(1.) By burning S in air or O.

(2.) By roasting iron pyrites in a current of air.

(3.) During the combustion of coal or coal-gas containing S or its compounds.

(4.) By heating sulfuric acid with copper: $2H_2SO_4 + Cu = CuSO_4 + 2H_2O + SO_2$.

(5.) By heating sulfuric acid with charcoal: $2H_2SO_4 + C = 2SO_2 + CO_2 + 2H_2O$.

(6.) By decomposing calcium sulfite, made into cubes with plaster of Paris, by HCl, at the ordinary temperature.

When the gas is to be used as a disinfectant it is usually obtained by reaction (1); in sulfuric acid factories (2) is used; (3) indicates the method in which atmospheric SO_2 is chiefly produced; in the laboratory (4) and (6) are used; (5) is the process directed by the U. S. and Br. Pharmacopœias.

Properties.—*Physical.*—A colorless, suffocating gas, having a disagreeable and persistent taste. Very soluble in H_2O, which at 15° (59° F.) dissolves about 40 times its volume (see below); also soluble in alcohol. At −10° (14° F.) it forms a colorless, mobile, transparent liquid, by whose rapid evaporation a cold of −65° (−85° F.) is obtained.

Chemical.—Sulfur dioxid is neither combustible nor a supporter of combustion. Heated with H it is decomposed: $SO_2 + 2H_2 = S + 2H_2O$. With nascent hydrogen, H_2S is formed: $SO_2 + 3H_2 = H_2S + 2H_2O$.

Water not only dissolves the gas, but combines with it to form the true sulfurous acid, H_2SO_3. With solutions of metallic hydrates it forms metallic sulfites: $SO_2 + KHO = KHSO_3$; or $SO_2 + 2KHO = K_2SO_3 + H_2O$. A hydrate having the composition $H_2SO_3, 8H_2O$ has been obtained as a crystalline solid, fusible at +4° (39°.2 F.).

Sulfur dioxid and sulfurous acid solution are powerful reducing agents, being themselves oxidized to sulfuric acid: $SO_2 + H_2O + O = H_2SO_4$; or $H_2SO_3 + O = H_2SO_4$. It reduces nitric acid with formation of sulfuric acid and nitrogen tetroxid: $SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2$. It decolorizes organic pigments, without, however, destroying the pigment, whose color may be restored by an alkali or a stronger acid. It destroys H_2S, acting in this instance, not as a reducing, but as an oxidizing agent: $4SO_2 + 3H_2S = 2H_2O + H_2S_4O_6 + S_3$. With Cl it combines directly under the influence of sunlight to form **sulfuryl** chlorid $(SO_2)''Cl_2$.

Analytical Characters.—(1.) Odor of burning sulfur.

(2.) Paper moistened with starch-paste and iodic acid solution turns blue in air containing 1 in 3,000 of SO_2.

Sulfur Trioxid—*Sulfuric oxid or anhydrid*—SO_3—*Molecular weight* = 80—*Sp. gr.* 1.95.

Preparation.—(1.) By union of SO_2 and O at 250°–300° (482°–572° F.) or in presence of spongy platinum.

(2.) By heating sulfuric acid in presence of phosphoric anhydrid: $H_2SO_4 + P_2O_5 = SO_3 + 2HPO_3$.

(3.) By heating dry sodium pyrosulfate: $Na_2S_2O_7 = Na_2SO_4 + SO_3$.

(4.) By heating pyrosulfuric acid below 100° (212° F.), in a retort fitted with a receiver, cooled by ice and salt: $H_2S_2O_7 = H_2SO_4 + SO_3$.

Properties.—White, silky, odorless crystals which give off white fumes in damp air. It unites with H_2O with a hissing sound, and elevation of temperature, to form sulfuric acid. When dry it does not redden litmus.

Sulfur trioxid exists in two isomeric (see isomerism) modifications, being one of the few instances of isomerism among mineral substances. The α modification, liquid at summer temperature, solidifies in colorless prisms at 16° (60°.8 F.) and boils at 46° (114°.8 F.). The β isomere is a white, crystalline solid which gradually fuses and passes into the α form at about 50° (122° F.).

Oxacids of Sulfur.

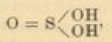
H_2SO_2 Hyposulfurous acid.
H_2SO_3 Sulfurous acid.
H_2SO_4 Sulfuric acid.

$H_2S_2O_3$ Thiosulfuric acid.

$H_2S_2O_7$ Pyrosulfuric acid.
$H_2S_2O_6$ Dithionic acid.
$H_2S_3O_6$ Trithionic acid.
$H_2S_4O_6$ Tetrathionic acid.
$H_2S_5O_6$ Pentathionic acid.

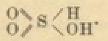
Hyposulfurous Acid—**H_2SO_2**—66.—*Hydrosulfurous acid*—Is an unstable body only known in solution, obtained by the action of zinc upon solution of sulfurous acid. It is a powerful bleaching and deoxidizing agent.

Sulfurous Acid—**H_2SO_3**—82.—Although sulfurous acid has not been isolated, it, in all probability, exists in the acid solution, formed when sulfur dioxid is dissolved in water: $SO_2 + H_2O = SO_3H_2$. Its salts, the sulfites, are well defined. From the existence of certain organic derivatives (see sulfonic acids) it would seem that two isomeric modifications of the acid may exist. They are distinguished as the *symmetrical*, in which the S atom is quadrivalent,



$$O = S\begin{matrix}/OH \\ \backslash OH\end{matrix},$$

and the *unsymmetrical*, in which the S atom is hexavalent,



$$\begin{matrix}O\backslash \\ O/\end{matrix} S \begin{matrix}/H \\ \backslash OH\end{matrix}.$$

Sulfites.—The sulfites are decomposed by the stronger acids, with evolution of sulfur dioxid. Nitric acid oxidizes them to sulfates. The sulfites of the alkali metals are soluble, and are active reducing agents.

The **analytical characters** of the sulfites are: (1.) With HCl they give off SO_2. (2.) With zinc and HCl they give off H_2S. (3.) With $AgNO_3$ they form a white ppt., soluble in excess of sulfite, and depositing metallic Ag when the mixture is boiled. (4.) With $Ba(NO_3)_2$ they form a white ppt., soluble in HCl. If chlorin water be added to the solution so formed a white ppt., insoluble in acids, is produced.

Sulfuric Acid—Oil of Vitriol—Acidum sulfuricum (U. S.; Br.) —H_2SO_4—98.

Preparation.—(1.) **By the union of sulfur trioxid and water: $SO_3 + H_2O = H_2SO_4$.**

(2.) By the oxidation of SO_2 or of S in the presence of water: $2SO_2 + 2H_2O + O_2 = 2H_2SO_4$; or $S_2 + 2H_2O + 3O_2 = 2H_2SO_4$.

The manufacture of H_2SO_4 may be said to be the basis of all chemical industry, as there are but few processes in chemical technology into some part of which it does not enter. The method followed at present, the result of gradual improvement, may be divided into two stages: 1st, the formation of a dilute acid; 2d, the concentration of this product.

The first part is carried on in immense chambers of timber, lined with lead, and furnishes an acid having a sp. gr. of 1.55, **and containing 65 per cent. of true sulfuric acid, H_2SO_4.** Into these chambers SO_2, obtained by burning sulfur, or by roasting pyrites, is driven, along with a large excess of air. In the chambers it comes in contact with nitric acid, at the expense of which it is oxidized to H_2SO_4, while nitrogen tetroxid (red fumes) is formed: $SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2$. Were this the only reaction, the disposal of the red fumes would present a serious difficulty and the amount of nitric acid consumed would be very great. A second reaction occurs between the red fumes and H_2O, which is injected in the form of steam, by which nitric acid and nitrogen dioxid are produced: $3NO_2 + H_2O = 2HNO_3 + NO$. The nitrogen dioxid in turn combines with O to produce the tetroxid, which then regenerates a further quantity of nitric acid, and so on. This series of reactions is made to go on continuously, the nitric acid being constantly regenerated, and acting merely as a carrier of O from the air to the SO_2, in such manner that the sum of the reactions may be represented by the equation: $2SO_2 + 2H_2O + O_2 = 2H_2SO_4$.

The acid is allowed to collect in the chambers until it has the sp. gr. 1.55, when it is drawn off. This *chamber acid*, although used in a few industrial processes, is not yet strong enough for most purposes. It is concentrated, first by evaporation in shallow leaden pans, until its sp. gr. reaches 1.746. At this point it begins to act upon the lead, and is transferred to platinum stills, where the concentration is completed.

Varieties.—Sulfuric acid is met with in several conditions of concentration and purity:

(1.) The *commercial oil of vitriol*, largely used in manufacturing processes, is a more or less deeply colored, oily liquid, varying in sp. gr. from 1.833 to 1.842, and in concentration from 93 per cent. to 99¼ per cent. of true H_2SO_4.

(2.) *C. P. acid* = **Acidum sulfuricum** (*U. S.; Br.*), of sp. gr. 1.84, colorless and comparatively pure (see below).

(3.) *Glacial sulfuric acid* is a hydrate of the composition H_2SO_4,H_2O, sometimes called *bihydrated sulfuric acid*, which crystallizes in rhombic prisms, fusible at +8°.5 (47°.3 F.) when an acid of sp. gr. 1.788 is cooled to that temperature.

(4.) *Ac. sulf. dil.* (*U. S.; Br.*) **is a dilute acid of sp. gr. 1.069** and containing between 9 and 10 per cent. H_2SO_4 (U. S.), or of sp. gr. 1.094, containing between 12 and 13 per cent. H_2SO_4 (Br.).

Properties.—*Physical.*—A colorless, heavy, oily liquid; sp. gr. 1.842 at 12° (53°.6 F.); crystallizes at 10°.5 (50°.9 F.); boils at 338° (640°.4 F.). It is odorless, intensely acid in taste and reaction, and highly corrosive. It is non-volatile at ordinary temperatures. Mixtures of the acid with H_2O have a lower boiling-point, and lower sp. gr. as the proportion of H_2O increases.

Chemical.—At a red heat vapor of H_2SO_4 is partly dissociated into SO_3 and H_2O; or, in the presence of platinum, into SO_2, H_2O and O. When heated with S, C, P, Hg, Cu, or Ag, it is reduced, with formation of SO_2.

Sulfuric acid has a great tendency to absorb H_2O, the union being attended with elevation of temperature, increase of bulk, and diminution of sp. gr. of the acid, and contraction of volume of the mixture. Three parts, by weight, of acid of sp. gr. 1.842, when mixed with one part of H_2O produce an elevation of temperature to 130° (266° F.), and the resulting mixture occupies a volume 1-6 less than the sum of the volumes of the constituents. Strong H_2SO_4 is a good desiccator of air or gases. It should not be left exposed in uncovered vessels lest, by increase of volume, it overflow. When it is to be diluted with H_2O, the acid should be added to the H_2O in a vessel of thin glass, to avoid the projection of particles or the rupture of the vessel. It is by virtue of its affinity for H_2O that H_2SO_4 chars or dehydrates organic substances. Sulfuric acid is a powerful dibasic acid.

Impurities.—The commercial acid is so impure that it is only fit for manufacturing and the coarsest chemical uses. The so-called C. P. acid may further contain: *Lead;* becomes cloudy when mixed with ten times its volume of H_2O, if the quantity of Pb be sufficient. The dilute acid gives a black color with H_2S. *Salts;* leave a fixed residue when the acid is evaporated. *Sulfur dioxid;* gives off H_2S when the acid, diluted with an equal volume of H_2O, comes in contact with Zn. *Carbon;* communicates a brown color to the acid. *Arsenic;* is very frequently present. When the acid is to be used for toxicological analysis, the test by H_2S is not sufficient. The acid, diluted with an equal volume of H_2O, is to be introduced into a Marsh apparatus, in which no visible stain should be produced during an hour. *Oxids of nitrogen* are almost invariably present; they communicate a pink or red color to pure brucin.

Sulfates.—Sulfuric acid being dibasic, there exist two sulfates of the univalent metals: $HKSO_4$ and K_2SO_4, and but one sulfate of each bivalent metal: $CaSO_4$. The sulfates of Ba, Ca, Sr, and Pb are insoluble, or very sparingly soluble, in H_2O. Other sulfates are soluble in H_2O, but all are insoluble in alcohol.

Analytical Characters.—(1.) Barium chlorid (or nitrate); a white ppt., insoluble in acids. The ppt., dried and heated with charcoal, forms BaS, which, with HCl, gives off H_2S. (2.) Plumbic acetate forms a white ppt., insoluble in dilute acids. (3.) Calcium chlorid forms a white ppt., either immediately or on dilution with two volumes of alcohol; insoluble in dilute HCl or HNO_3.

Toxicology.—Sulfuric acid is an active corrosive, and may be, if taken in sufficient quantity in a highly diluted state, a true poison. The concentrated acid causes death, either within a few hours, by corrosion and perforation of the walls of the stomach and œsophagus, or, after many weeks, by starvation, due to destruction of the gastric mucous membrane and closure of the pyloric orifice of the stomach.

The treatment is the same as that for corrosion by HCl. (See p. 85.)

Thiosulfuric Acid.—*Hyposulfurous acid*—$\mathbf{H_2S_2O_3}$—114—may be considered as sulfuric acid, H_2SO_4, in which one atom of oxygen has been replaced by one of sulfur. The acid itself has not been isolated, being decomposed, on liberation from the thiosulfates, into sulfur, water and sulfur dioxid; $H_2S_2O_3 = S + SO_2 + H_2O$.

Pyrosulfuric Acid—*Fuming sulfuric acid—Nordhausen oil of vitriol—Disulfuric hydrate*—$\mathbf{H_2S_2O_7}$—*Molecular weight* = 178—*Sp. gr.* = 1.9—*Boils at* 52°.2 (126° *F.*).

Preparation.—By distilling dry ferrous sulfate; and purification of the product by repeated crystallizations and fusions, until a substance fusing at 35° (95° F.) is obtained.

Properties.—The commercial Nordhausen acid, which is a mixture of $H_2S_2O_7$ with excess of SO_3, or of H_2SO_4, is a brown, oily liquid, which boils below 100° (212° F.) giving off SO_3; and is solid or liquid according to the temperature. It is used chiefly as a solvent for indigo, and in the anilin industry.

SELENIUM AND TELLURIUM.

Se—79.5. Te—128.

These are rare elements which form compounds similar to those of sulfur. Elementary selenium is used in some forms of electrical apparatus.

III. NITROGEN GROUP.

NITROGEN—PHOSPHORUS—ARSENIC—ANTIMONY.

The elements of this group are trivalent or quinquivalent, occasionally univalent. With hydrogen they form non-acid compounds, composed of one volume of the element in the gaseous state with three volumes of hydrogen, the union being attended with a condensation of volume of one-half. Their hydrates are acids containing one, two, three, or four atoms of replaceable hydrogen.

Bismuth, frequently classed in this group, is excluded, owing to the existence of the nitrate $Bi(NO_3)_3$. The relations existing between the compounds of the elements of this group are shown in the following table:

NH_3,	N_2O,	NO,	N_2O_3,	NO_2,	N_2O_5,	—
PH_3,	—	—	P_2O_3,	—	P_2O_5,	H_3PO_2,
AsH_3,	—	—	As_2O_3,	—	As_2O_5,	—
SbH_3,	—	—	Sb_2O_3,	—	Sb_2O_5,	—
Hyd-rid.	Mon-oxid.	Di-oxid.	Tri-oxid.	Tetr-oxid.	Pent-oxid.	Hypo-ous acid.

—	—	—	HNO_3
H_3PO_3,	H_3PO_4,	$H_4P_2O_7$,	HPO_3
H_3AsO_3,	H_3AsO_4,	$H_4As_2O_7$,	$HAsO_3$
—	H_3SbO_4,	$H_4Sb_2O_7$,	$HSbO_3$
-ous acid.	-ic acid.	Pyro-ic acid.	Meta-ic acid.

NITROGEN.

*Azote—Symbol=***N***—Atomic weight=*14*—Molecular weight=*28 *—Sp. gr.=*0.9701*—One litre weighs* 1.254 *grams—Name from νίτρον=nitre, γένεσις=source; or from ἀ, privative ζωή=life—Discovered by Mayow in* 1669.

Occurrence.—Free in atmospheric air and in volcanic gases. In combination in the nitrates, in ammoniacal compounds and in a great number of animal and vegetable substances.

Preparation.—(1.) By removal of O from atmospheric air; by burning P in air, or by passing air slowly over red-hot copper. It is contaminated with CO_2, H_2O, etc.

(2.) By passing Cl through excess of ammonium hydroxid solution. If ammonia be not maintained in excess, the Cl reacts with the ammonium chlorid formed, to produce the explosive nitrogen chlorid.

(3.) By heating ammonium nitrite, $(NH_4) NO_2$: or a mixture of ammonium chlorid and potassium nitrite.

Properties.—A colorless, odorless, tasteless, non-combustible gas; not a supporter of combustion; very sparingly soluble in water.

It is very slow to enter into combination, and most of its compounds are very prone to decomposition, which may occur explosively or slowly. Nitrogen combines directly with O under the influence of electric discharges; and with H under like conditions, and, indirectly, during the decomposition of nitrogenized organic substances. It combines directly with magnesium, boron, vanadium and titanium.

Nitrogen is not poisonous, but is incapable of supporting respiration.

Atmospheric Air.—The alchemists considered air as an element, until Mayow, in 1669, demonstrated its complex nature. It was not, however, until 1770 that Priestley repeated the work of Mayow; and that the compound nature of air, and the characters of its constituents were made generally known by the labors (1770–1781) of Priestley, Rutherford, Lavoisier, and Cavendish. The older chemists used the terms *gas* and *air* as synonymous.

Composition.—Air is not a chemical compound, but a mechanical mixture of O and N, with smaller quantities of other gases. Leaving out of consideration about 0.4 to 0.5 per cent. of other gases, air consists of 20.93 O and 79.07 N, by volume; or 23 O and 77 N, by weight; proportions which vary but very slightly at different times and places; the extremes of the proportion of O found having been 20.908 and 20.999.

That air is not a compound is shown by the fact that the proportion of its constituents does not represent a relation between their atomic weights, or between any multiples thereof; as well as by the solubility of air in water. Were it a compound it would have a definite degree of solubility of its own, and the dissolved gas would have the same composition as when free. But each of its constituents dissolves in H_2O according to its own solubility, and air dissolved in H_2O at 14°.1 (57.4 F.) consists of N and O, not in the proportion given above, but in the proportion 66.76 to 33.24.

Besides these two main constituents, air contains about 4–5 thousandths of its bulk of other substances: **vapor of water**, carbon dioxid, ammoniacal compounds, hydrocarbons, ozone, oxids of nitrogen, and solid particles held in suspension.

Vapor of Water.—Atmospheric moisture is either visible, as in fogs and clouds, when it is in the form of a finely divided liquid; or invisible, as vapor of water. The amount of H_2O which a given volume of air can hold, without precipitation, varies according to the temperature and the pressure. It happens rarely that air is as highly charged with moisture as it is capable of being for the existing temperature. The difference between the amount of water which the air is capable of holding at the existing temperature, and that which it actually does hold is its **fraction of saturation,** or **hygrometric state,** or **relative humidity.** Ordinarily air contains from 66 to 70 per cent. of its possible amount of moisture. If the quantity be less than this, the air is too dry, and causes a parched sensation, and the sense of "stuffiness" so common in furnace-heated houses. If it be greater, evaporation from the skin is impeded, and the air is oppressive if warm.

The actual amount of moisture in air is determined by passing a known volume through tubes filled with calcium chlorid; whose increase in weight represents the amount of H_2O in the volume of air used. The fraction of saturation is determined by instruments called **hygrometers, hygroscopes** or **psychrometers.**

Carbon dioxid.—The quantity of carbon dioxid in free air varies from 3 to 6 parts in 10,000 by volume. (See Carbon dioxid.)

Ammoniacal compounds.—Carbonate, nitrate, and nitrite of ammonium occur in small quantity (0.1 to 6.0 parts per million of NH_3) in air, as products of the decomposition of nitrogenized organic substances. They are absorbed and assimilated by plants.

Nitric and nitrous acids, usually in combination with ammonium, are produced either by the oxidation of combustible substances containing N, or by direct union of N and H_2O during discharges of atmospheric electricity. Rain-water, falling during thunder-showers, has been found to contain as much as 3.71 per million of HNO_3. (See Hydrogen peroxid, p. 77.)

Sulfuric and sulfurous acids occur, in combination with NH_4, in the air over cities, and manufacturing districts, where they are produced by the oxidation of S, existing in coal and coal-gas.

Hydrocarbons have been detected in the air of cities, and of swampy places, in small quantities.

Solid particles of the most diverse nature are always present in air and become visible in a beam of sunlight. Sodium chlorid is almost always present, always in the neighborhood of salt water. Air contains myriads of germs of vegetable organisms, mould, etc., which are propagated by the transportation of these germs by air-currents. It seems probable, also, that the germs or poisons by which certain diseases are propagated float in the air.

The continued inhalation of air containing large quantities of solid particles in suspension may cause severe pulmonary disorder, by mere mechanical irritation, and apart from any poisonous quality in the substance; such is the case with the air of carpeted ball-rooms, and of the workshops of certain trades, furniture-polishers, metal-filers, etc.

Compounds of Nitrogen and Hydrogen.—Three are known: **Ammonia, NH_3; Hydrazin, N_2H_4,** and **Hydrazoic acid, N_3H;** as well as salts corresponding to two hydroxids.

Ammonia. *Hydrogen nitrid—Volatile alkali*—**NH_3**—*Molecular weight*=17—*Sp. gr.*=0.589 *A*—*Liquefies at* −40° (−40° *F.*)—*Boils at* −33°.7 (−28°.7 *F.*)—*Solidifies at* −75° (−103° *F.*)—*A litre weighs* 0.7655 *gram.*

Preparation.—(1.) By union of nascent H with N.

(2.) By decomposition of organic matter containing N, either spontaneously or by destructive distillation.

(4.) By heating solution of ammonium hydroxid: $NH_4HO = NH_3 + H_2O$.

Properties.—*Physical.*—A colorless gas, having a pungent odor, and an acrid taste. It is very soluble in H_2O, 1 volume of which at 0° (32° F.) dissolves 1050 vols. NH_3, and at 15° (59° F.), 727 vols. NH_3. Alcohol and ether also dissolve it readily. Liquid ammonia is a colorless, mobile fluid, used in ice machines for producing artificial cold, the liquid absorbing a great amount of heat in volatilizing.

Chemical.—At a red heat ammonia is decomposed into a mixture of N and H, occupying double the volume of the original gas. It is similarly decomposed by the prolonged passage through it of discharges of electricity. It is not readily combustible, yet it burns in an atmosphere of O with a yellowish flame. Mixtures of NH_3 with O, nitrogen monoxid, or nitrogen dioxid, explode on contact with flame.

The solution of ammonia in H_2O constitutes a strongly alkaline liquid, known as **aqua ammoniæ**, which is possessed of strongly basic properties. It is neutralized by acids with the formation of crystalline salts, which are also formed, without liberation of hydrogen, by direct union of gaseous NH_3, with acid vapors. The ammoniacal salts and the alkaline base in aqua ammoniæ are compounds of a radical, **ammonium, NH_4**, which forms compounds corresponding to those of potassium or sodium. The compound formed by the union of ammonia and water is **ammonium hydroxid, NH_4HO**: $NH_3 + H_2O = NH_4HO$; and that formed by the union of hydrochloric acid and ammonia is **ammonium chlorid, NH_4Cl**: $NH_3 + HCl = NH_4Cl$.

Hydrazin—Diamid—$H_2N.NH_2$—is known in the form of its hydroxid, corresponding to ammonium hydroxid,in the form of its salts and in numerous organic derivatives. The sulfate is produced by the action of H_2SO_4 upon triazoacetic acid, and the hydroxid by decomposition of the sulfate by caustic soda. The hydroxid is an oily liquid, intensely corrosive, capable of attacking glass. It combines with acids to form well-defined salts, and precipitates many metals from solutions of their salts.

Hydrazoic acid—Azoimid—N_3H—is a substance recently obtained from benzoyl-diazoimid, which, although containing the same elements as ammonia, is distinctly acid in character. It is a colorless liquid, boiling at 37°, having a very pungent and unpleasant odor. It is extremely unstable and explodes with great violence. It reacts with metals, oxids, and hydroxids, as does hydrochloric acid, to form nitrids, which like the free acid are very explosive.

Hydroxylamin—NH_2HO—33.—The amins and amids (q.v.) are compounds derived from ammonia by the substitution of radicals for a part or all of its hydrogen. This substance, which is intermediate in composition between ammonia and ammonium hydroxid, may be considered as ammonia, one of whose hydrogen atoms has been replaced by the radical hydroxyl, HO. It is obtained in aqueous solution by the union of nascent hydrogen with nitrogen dioxid: $NO + H_2 = NH_2HO$; or by the action of nascent hydrogen upon nitric acid: $HNO_3 + 3H_2 = 2H_2O + NH_2HO$. Hydroxylamin is only known in solution and in combination. Its aqueous solution, which probably contains the corresponding hydrate, NH_3O, HO, is strongly alkaline and behaves with regard to acids as does ammonium hydroxid solution, forming salts corresponding to those of ammonium. Thus hydroxylammonium chlorid, NH_4OCl, crystallizes in prisms or tables, fusible at 100° (212° F.), and decomposed into HCl, H_2O and NH_4Cl at a slightly higher temperature.

Hydroxylammonium chlorid has been used in the treatment of cutaneous disorders. It is an actively toxic agent, converting oxyhæmoglobin into methæmoglobin.

Oxids of Nitrogen.—Five are known, forming a regular series: N_2O, NO, N_2O_3, NO_2, N_2O_5. Of these two, the trioxid, N_2O_3, and pentoxid, N_2O_5, are anhydrids.

Nitrogen Monoxid. *Nitrous oxid—Laughing gas—Nitrogen protoxid*—N_2O—*Molecular weight=44—Sp. gr.=1.527A—Fuses at* −100° (−148° *F.)—Boils at* −87° (−124° *F.)—Discovered in* 1776 *by Priestley.*

Preparation.—By heating ammonium nitrate: $(NH_4)NO_3 = N_2O + 2H_2O$. To obtain a pure product there should be no ammonium chlorid present (as an impurity of the nitrate), and the heat should be applied gradually, and not allowed to exceed 250° (482° F.), and the gas formed should be passed through wash-bottles containing sodium hydroxid and ferrous sulfate.

Properties.—*Physical.*—A colorless, odorless gas, having a sweetish taste; soluble in H_2O; more so in alcohol. Under a pressure of 30 atmospheres, at 0° (32° F.), it forms a colorless, mobile liquid which, when dissolved in carbon disulfid and evaporated *in vacuo*, produces a cold of −140° (−220° F.).

Chemical.—It is decomposed by a red heat and by the continuous passage of electric sparks. It is not combustible, but is, after oxygen, the best supporter of combustion known.

Physiological.—Although, owing to the readiness with which N_2O is decomposed into its constituent elements, and the nature and relative proportions of these elements, it is capable of maintaining respiration longer than any gas except oxygen or air; an animal will live for a short time only in an atmosphere of pure nitrous oxid. When inhaled, diluted with air, it produces the effects first observed by Davy in 1799: first an exhilaration of spirits, frequently accompanied by laughter, and a tendency to muscular activity, the patient sometimes becoming aggressive; afterward there is complete anæsthesia, and loss of consciousness. It has been much used, by dentists especially, as an anæsthetic in operations of short duration, and in one or two instances anæsthesia has been maintained by its use for nearly an hour.

A solution in water under pressure, containing five volumes of the gas, is sometimes used for internal administration.

Nitrogen Dioxid. *Nitric oxid*—**NO**—*Molecular weight*=30—*Sp. gr.*=1.039*A—Discovered by Hales in* 1772.

Preparation.—By the action of copper on moderately diluted nitric acid in the cold: $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$; the gas being collected after displacement of air from the apparatus.

Properties.—A colorless gas, whose odor and taste are unknown; very sparingly soluble in H_2O; more soluble in alcohol.

It combines with O, when mixed with that gas or with air, to form the reddish-brown nitrogen tetroxid. It is absorbed by solution of ferrous sulfate, to which it communicates a dark brown or black color. It is neither combustible nor a good supporter of combustion, although ignited C and P continue to burn in it, and the alkaline metals, when heated in it, combine with its O with incandescence.

Nitrogen Trioxid. *Nitrous anhydrid*—**N_2O_3**—76—Is prepared by the direct union of nitrogen dioxid and oxygen at low temperatures, or by decomposing liquefied nitrogen tetroxid with a small quantity of H_2O at a low temperature: $4NO_2 + H_2O = 2HNO_3 + N_2O_3$. It is a dark indigo-blue liquid, which, boiling at about 0° (32° F.), is partly decomposed. It solidifies at − 82° (− 115°.6 F.).

Nitrogen Tetroxid. *Nitrogen peroxid—Hyponitric acid—Nitrous fumes*—**NO_2**—*Molecular weight*=46—*Sp. gr.*=1.58*A* (*at* 154° *C.*)—*Boils at* 22° (71°.6 *F.*)—*Solidifies at* 9° (15°.8 *F.*).

Preparation.—(1.) By mixing one volume O with two volumes NO; both dry and ice-cold.

(2.) By heating perfectly dry lead nitrate, O being also produced: $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$.

(3.) By dropping strong nitric acid upon a red-hot platinum surface.

Properties.—When pure and dry, it is an orange-yellow liquid at the ordinary temperature; the color being darker the higher the temperature. The red fumes, which are produced when nitric acid is decomposed by starch or by a metal, consist of NO_2, mixed with N_2O_3. It dissolves in nitric acid, forming a dark yellow liquid, which is blue or green if N_2O_3 be also present. With SO_2 it combines to form a solid, crystalline compound, which is sometimes produced in the manufacture of H_2SO_4. This substance, which forms the **lead chamber crystals**, is a substituted sulfurous acid, **nitrosulfonic acid, NO_2SO_2OH** (see sulfonic acids). A small quantity of H_2O decomposes NO_2 into HNO_3 and N_2O_3, which latter colors it green or blue. A larger quantity of H_2O decomposes it into HNO_3 and NO. By bases it is transformed into a mixture of nitrite and nitrate: $2NO_2 + 2KHO = KNO_2 + KNO_3 + H_2O$.

It is an energetic oxydant, for which it is largely used. With certain organic substances it does not behave as an oxydant, but becomes substituted as an univalent radical; thus with benzene it forms nitro-benzene: $C_6H_5(NO_2)$.

Toxicology.—The brown fumes given off during many processes, in which nitric acid is decomposed, are dangerous to life. All such operations, when carried on on a small scale, as in the laboratory, should be conducted under a hood or some other arrangement, by which the fumes are carried into the open air. When in industrial processes, the volume of gas formed becomes such as to be a nuisance when discharged into the air, it should be utilized in the manufacture of H_2SO_4 or absorbed by H_2O or an alkaline solution.

An atmosphere contaminated with brown fumes is more dangerous than one containing Cl, as the presence of the latter is more immediately annoying. At first there is only coughing, and it is only two to four hours later that a difficulty in breathing is felt, death occurring in ten to fifteen hours. At the autopsy the lungs are found to be extensively disorganized and filled with black fluid.

Even air containing small quantities of brown fumes, if breathed for a long time, produces chronic disease of the respiratory organs. To prevent such accidents, thorough ventilation in locations where brown fumes are liable to be formed is imperative. In cases of spilling nitric acid, safety is to be sought in retreat from the apartment until the fumes have been replaced by pure air from without.

Nitrogen Pentoxid. *Nitric anhydrid* — $\mathbf{N_2O_5}$ — *Molecular weight*=108—*Fuses at* 30° (86° *F.*)—*Boils at* 47° (116°.6 *F.*).

Preparation.—(1.) By decomposing dry silver nitrate with dry Cl in an apparatus entirely of glass: $4AgNO_3+2Cl_2=4AgCl+2N_2O_5+O_2$.

(2.) By removing water from fuming nitric acid with phosphorus pentoxid: $6HNO_3+P_2O_5=2H_3PO_4+3N_2O_5$.

Properties.—Prismatic crystals at temperatures above 30° (86° F.). It is very unstable, being decomposed by a heat of 50° (122° F.); on contact with H_2O, with which it forms nitric acid; and even spontaneously. Most substances which combine readily with O, remove that element from N_2O_5.

Nitrogen Acids.—Three are known, either free or in combination, corresponding to the three oxids containing uneven numbers of O atoms:

$$\begin{aligned} N_2O &+ H_2O = H_2N_2O_2\text{—Hyponitrous acid.} \\ N_2O_3 &+ H_2O = 2HNO_2\text{—Nitrous acid.} \\ N_2O_5 &+ H_2O = 2HNO_3\text{—Nitric acid.} \end{aligned}$$

Hyponitrous acid—$\mathbf{H_2N_2O_2}$—31—Known only in combination. Silver hyponitrite is formed by reduction of sodium nitrate by nascent H and decomposition with silver nitrate.

Nitrous acid—$\mathbf{HNO_2}$—47—has not been isolated, although its salts, the nitrites, are well-defined compounds: $M^{\prime}NO_2$ or $M^{\prime\prime}(NO_2)_2$.

The *nitrites* occur in nature, in small quantity, in natural waters, where they result from the decomposition of nitrogenous organic substances; also in saliva. They are produced by heating the corresponding nitrate, either alone or in the presence of a readily oxidizable metal, such as lead. Solutions of the nitrites are readily decomposed by the mineral acids, with evolution of brown fumes. They take up oxygen readily and are hence used as reducing agents. Solutions of potassium permanganate are instantly decolorized by nitrites. A mixture of thin starch paste and zinc iodid solution is colored blue by nitrites, which decompose the iodid, liberating the iodin. A solution of metaphenylendiamin, in the presence of free acid, is colored brown by very minute traces of a nitrite, the color being due to the formation of triamido-azobenzene (Bismark brown).

Nitric Acid. **Aquafortis**—*Hydrogen nitrate*—**Acidum nitricum—U.S.; Br.—HNO_3**—63.

Preparation.—(1.) By the direct union of its constituent elements under the influence of electric discharges.

(2.) By the decomposition of an alkaline nitrate by strong H_2SO_4. With moderate heat a portion of the acid is liberated: $2NaNO_3+H_2SO_4=NaHSO_4+NaNO_3+HNO_3$, and at a higher temperature the remainder is given off: $NaNO_3+NaHSO_4=Na_2SO_4+HNO_3$. This is the reaction used in the manufacture of HNO_3.

Varieties.—**Commercial**—a yellowish liquid, impure, and of two degrees of concentration: **single aquafortis**; sp. gr. about 1.25 = 39% HNO_3; and **double aquafortis**; sp. gr. about 1.4=64% HNO_3. **Fuming**—a reddish-yellow liquid, more or less free from impurities; charged with oxids of nitrogen. Sp. gr. about 1.5. Used as an oxidizing agent. **C. P.**—a colorless liquid, sp. gr. 1.522, which should respond favorably to the tests given below. **Acidum nitricum, U. S.; Br.**—a colorless acid, of sp. gr. 1.42=70% HNO_3. **Acidum nitricum dilutum, U. S.; Br.**—the last mentioned, diluted with H_2O to sp. gr. 1.059=10% HNO_3 (*U. S.*), or to sp. gr. 1.101 =17.44% HNO_3 (*Br.*).

Properties.—*Physical.*—The pure acid is a colorless liquid: sp. gr. 1.522; boils at 86° (186°.8 F.); solidifies at −40° (−40° F.); gives off white fumes in damp air; and has a strong acid taste and reaction. The sp. gr. and boiling-point of dilute acids vary with the concentration. If a strong acid be distilled, the boiling-point gradually rises from 86° (186°.8 F.) until it reaches 123° (253°.4 F.), when it remains constant, the sp. gr. of distilled and distillate being 1.42=70% HNO_3. If a weak acid be taken originally the boiling-point rises until it becomes stationary at the same point.

Chemical.—When exposed to air and light, or when strongly heated, HNO_3 is decomposed into NO_2; H_2O and O. Nitric acid is a valuable oxydant; it converts I, P, S, C, B, and Si or their lower oxids into their highest oxids; it oxidizes and destroys most organic substances, although with some it forms products of substitution. Most of the metals dissolve in HNO_3 as nitrates, a portion of the acid being at the same time decomposed into NO and H_2O: $4HNO_3+3Ag=3AgNO_3+NO+2H_2O$. The chemical activity of HNO_3 is much reduced, or even almost arrested, when the intervention of nitrous acid is prevented by the presence of carbamid. The so-called "noble metals," gold and platinum, are not dissolved by either HNO_3 or HCl, but dissolve as chlorids in a mixture of the two acids, called **aqua regia.** In this mixture the two acids mutally decompose each other according to the equations: $HNO_3+3HCl=2H_2O+NOCl+Cl_2$ and $2HNO_3+6HCl=4H_2O+2NOCl_2+Cl_2$ with formation of **nitrosyl chlorid,** NOCl and **bichlorid,** $NOCl_2$, and nascent Cl; the last named combining with the metal. Iron dissolves easily in dilute HNO_3, but if dipped into the concentrated acid, it is rendered **passive,** and does not dissolve when subsequently brought in contact with the dilute acid. This passive condition is destroyed by a temperature of 40° (104° F.) or by contact with Pt, Ag or Cu. When HNO_3 is decomposed by zinc or iron, or in the porous cup of a Grove battery, N_2O_3 and NO_2 are formed, and dissolve in the acid, which is colored dark yellow, blue or green. An acid so charged is known as **nitroso-nitric acid.** Nitric acid is monobasic.

Impurities.—*Oxids of Nitrogen* render the acid yellow, and decolorize potassium permanganate when added to the dilute acid. *Sulfuric acid* produces cloudiness when $BaCl_2$ is added to the acid, diluted with two volumes of H_2O. *Chlorin, iodin* cause a white ppt. with $AgNO_3$. *Iron* gives a red color when the diluted acid is treated with ammonium sulfocyanate. *Salts* leave a fixed residue when the acid is evaporated to dryness on platinum.

Nitrates.—The nitrates of K and Na occur in nature. Nitrates are formed by the action of HNO_3 on the metals, or on their oxids or carbonates. They have the composition $M'NO_3$, $M''(NO_3)_2$ or $M'''(NO_3)_3$, except certain basic salts, such as the sesquibasic lead nitrate, $Pb(NO_3)_2, 2PbO$. With the exception of a few basic salts, the nitrates are all soluble in water. When heated, they fuse and act as powerful oxidants. They are decomposed by H_2SO_4 with liberation of HNO_3.

Analytical Characters.—(1.) Add an equal volume of concentrated H_2SO_4, cool, and float on the surface of the mixture a solution of $FeSO_4$. The lower layer becomes gradually colored brown, black or purple, beginning at the top.

(2.) Boil in a test-tube a small quantity of HCl, containing enough sulfindigotic acid to communicate a blue color, add the suspected solution and boil again; the color is discharged.

(3.) If acid, neutralize with KHO, evaporate to dryness, add to the residue a few drops of H_2SO_4 and a crystal of brucin (or some sulfanilic acid); a red color is produced.

(4.) Add H_2SO_4 and Cu to the suspected liquid and boil, brown fumes appear (best visible by looking into the mouth of the test-tube).

(5.) A solution of diphenylamin in concentrated H_2SO_4 (.01 grm. in 100 c.c.) is colored blue by nitric acid A similar color is produced by other reducing agents.

(6.) To 0.5 c.c. nitrate solution add 1 drop aqueous solution of resorcin (10%), and 1 drop HCl (15%), and float on the surface of 2 c.c. concentrated H_2SO_4; a purple-red band.

Toxicology.—Although most of the nitrates are poisonous when taken internally in sufficiently large doses, their action seems to be due rather to the metal than to the acid radical. Nitric acid itself is one of the most powerful of corrosives.

Any animal tissue with which the concentrated acid comes in contact is immediately disintegrated. A yellow stain, afterward turning to dirty brownish, or, if the action be prolonged, an eschar, is formed. When taken internally, its action is the same as upon the skin, but, owing to the more immediately important function of the parts, is followed by more serious results (unless a large cutaneous surface be destroyed).

The symptoms following its ingestion are the same as those produced by the other mineral acids, except that all parts with which the acid has come in contact, including vomited shreds of mucous membrane, are colored yellow. The treatment is the same as that indicated when H_2SO_4 or HCl have been taken; *i.e.* neutralization of the corrosive by magnesia or soap.

Compounds of Nitrogen with the Halogens.—Nitrogen chlorid—NCl_3—120.5—is formed by the action of excess of Cl upon NH_3 or an ammoniacal compound. It is an oily, light yellow liquid; sp. gr. 1.653; has been distilled at 71° (159°.8 F.). When heated to 96° (204°.8 F.), when subjected to concussion, or when brought in contact with phosphorus, alkalies or greasy matters it is decomposed, with a violent explosion, into one volume N and three volumes Cl.

Nitrogen bromid—NBr_3—254—has been obtained, as a reddish-brown, syrupy liquid, very volatile, and resembling the chlorid in its properties, by the action of potassium bromid upon nitrogen chlorid.

Nitrogen iodid—NI_3—395—When iodin is brought in contact with ammonium hydroxid solution, a dark brown or black powder, highly explosive when dried, is formed. This substance varies in composition according to the conditions under which the action occurs; sometimes the iodid alone is formed; under other circumstances it is mixed with compounds containing N, I and H.

PHOSPHORUS.

Symbol=**P**—*Atomic weight*=31—*Molecular weight*=124—*Sp. gr. of vapor*=4.2904 *A*—*Name from* φῶς=*light*, φέρω=*I bear*—*Discovered by Brandt in* 1669—**Phosphorus (U. S.; Br.).**

Occurrence.—Only in combination; in the mineral and vegetable worlds as phosphates of Ca, Mg, Al, Pb, K, Na. In the animal kingdom as phosphates of Ca, Mg, K and Na, and in organic combination.

Preparation.—From bone-ash, in which it occurs as tricalcic phosphate. Three parts of bone-ash are digested with 2 parts of strong H_2SO_4, diluted with 20 volumes H_2O, when insoluble calcic sulfate and the soluble monocalcic phosphate, or "superphosphate," are formed: $Ca_3(PO_4)_2+2H_2SO_4=H_4Ca(PO_4)_2+2CaSO_4$. The solution of superphosphate is filtered off and evaporated, the residue is mixed with about one-fourth its weight of powdered charcoal and sand, and the mixture heated, first to redness, finally to a white heat, in earthenware retorts, whose beaks dip under water in suitable receivers. During the first part of the heating the monocalcic phosphate is converted into metaphosphate: $CaH_4(PO_4)_2=Ca(PO_3)_2+2H_2O$; which is in turn reduced by the charcoal, with formation of carbon monoxid and liberation of phosphorus, while the calcium is combined as silicate: $2Ca(PO_3)_2+2SiO_2+5C_2=2CaSiO_3+10CO+P_4$.

Another process consists in dissolving bone-ash or mineral phosphate in HNO_3. K_2SO_4 is then added to the solution, and the greater part of the Ca removed by filtration as $CaSO_4$. Mercurous phosphate is then formed by addition of mercurous nitrate to the solution. The dried Hg salt is finally mixed with carbon, and decomposed by heat, when Hg and P distil over.

The crude product is purified by fusion, first under a solution of bleaching powder, next under ammoniacal H_2O, and finally under water containing a small quantity of H_2SO_4 and potassium dichromate. It is then strained through leather and cast into sticks under warm H_2O.

Properties.—*Physical.*—Phosphorus is capable of existing in four allotropic forms:

(1.) *Ordinary, or yellow variety*, in which it usually occurs in commerce. This is a yellowish, translucid solid of the consistency of wax. Below 0° (32° F.) it is brittle; it fuses at 44°.3 (111°.7 F.); and boils at 290° (554° F.) in an atmosphere not capable of acting upon it chemically. Its vapor is colorless; sp. gr.=4.5A—65 H at 1040° (1940° F.). It volatilizes below its boiling-point, and H_2O boiled upon it gives off steam charged with its vapor. Exposed to air, it gives off white fumes, and produces ozone. It is luminous in the dark. It is insoluble in H_2O; sparingly soluble in alcohol and ether; soluble in carbon disulfid, and in the fixed and volatile oils. It crystallizes on evaporation of its solutions in octahedræ or dodecahedræ. Sp. gr. 1.83 at 10° (50° F.).

(2.) *White phosphorus* is formed as a white, opaque pellicle upon the surface of the ordinary variety, when this is exposed to light under aërated H_2O. Sp. gr. 1.515 at 15° (59° F.). When fused it reproduces ordinary phosphorus without loss of weight.

(3.) *Black variety* is formed when ordinary phosphorus is heated to 70° (158° F.) and suddenly cooled.

(4.) *Red variety* is produced from the ordinary by maintaining it at from 240° (464° F.) to 280° (536° F.) for two or three days, in an atmosphere of carbon dioxid; and, after cooling, washing out the unaltered yellow phosphorus with carbon disulfid. It is also formed upon the surface of the yellow variety, when it is exposed to direct sunlight.

It is a reddish, odorless, tasteless solid, which does not fume in air, nor dissolve in the solvents of the yellow variety. Sp. gr. 2.1. Heated to 500° (932° F.) with lead, in the absence of air, it dissolves in the molten metal, from which it separates on cooling in violet-black, rhombohedral crystals, of sp. gr. 2.34. If prepared at 250° (482° F.) it fuses below that temperature, and at 260° (500° F.) is transformed into the yellow variety, which distils. The crystalline product does not fuse. It is not luminous at ordinary temperatures.

Chemical.—The most prominent property of P is the readiness with which it combines with O. The yellow variety ignites and burns with a bright flame if heated in air to 60° (140° F.), or if exposed in a finely divided state to air at the ordinary temperature; with formation of P_2O_3; P_2O_5; H_3PO_3, or H_3PO_4, according as O is present in excess or not, and according as the air is dry or moist. The temperature of ignition of yellow P is so low that it must be preserved under boiled water. By directing a current of O upon it, P may be burned under H_2O, heated above 45° (113° F.). The red variety combines with O much less readily, and may be kept in contact with air without danger.

The luminous appearance of yellow P is said to be due to the formation of ozone. It does not occur in pure O at the ordinary temperature, nor in air under pressure, nor in the absence of moisture, nor in the presence of minute quantities of carbon disulfid, oil of turpentine, alcohol, ether, naphtha, and many gases.

Yellow phosphorus burns in Cl with formation of PCl_3 or PCl_5, according as P or Cl is present in excess. Both yellow and red varieties combine directly with Cl, Br, and I.

Phosphorus is not acted on by HCl or cold H_2SO_4. Hot H_2SO_4 oxidizes it with formation of phosphorous acid and sulfur dioxid: $P_4+6H_2SO_4=4H_3PO_3+6SO_2$. Nitric acid oxidizes it violently to phosphoric acid and nitrogen di- and tetr-oxids: $12HNO_3+P_4=4H_3PO_4+8NO_2+4NO$.

Phosphorus is a reducing agent. When immersed in cupric sulfate solution, it becomes covered with a coating of metallic copper. In silver nitrate solution it produces a black deposit of silver phosphid.

Toxicology.—The red variety differs from the other allotropic forms of phosphorus in not being poisonous, probably owing to its insolubility, and in being little liable to cause injury by burning.

The burns produced by yellow phosphorus are more serious than a like destruction of cutaneous surface by other substances. A burning fragment of P adheres tenaciously to the skin, into which it burrows. One of the products of the combustion is metaphosphoric acid (q. v.) which, being absorbed, gives rise to true poisoning. Burns by P should be washed immediately with dilute javelle water, liq. sodæ chlorinatæ, or solution of chlorid of lime. Yellow P should never be allowed to come in contact with the skin, except it be under cold water.

Yellow P is one of the most insidious of poisons. It is taken or administered usually as "ratsbane" or match-heads. The former is frequently starch paste, charged with phosphorus; the latter, in the ordinary sulfur match, a mixture of potassium chlorate, very fine sand, phosphorus, and a coloring matter. The symptoms in acute phosphorus-poisoning appear with greater or less rapidity, according to the dose, and the presence or absence in the stomach of substances which favor its absorption. Their appearance may be delayed for days, but as a rule they appear within a few hours. A disagreeable garlicky taste in the mouth, and heat in the stomach are first observed, the latter gradually developing into a burning pain, accompanied by vomiting of dark-colored matter, which, when shaken in the dark, is phosphorescent; low temperature and dilatation of the pupils. In some cases, death follows at this point suddenly, without the appearance of any further marked symptoms. Usually, however, the patient rallies, seems to be doing well, until, suddenly, jaundice makes its appearance, accompanied by retention of urine, and frequently delirium, followed by coma and death.

There is no known chemical antidote to phosphorus. The treatment is, therefore, limited to the removal of the unabsorbed portions of the poison by the action of an emetic, zinc or copper sulfate, or apomorphin, as expeditiously as possible, and the administration of French oil of turpentine—the older the oil the better—as a physiological antidote. The use of fixed oils or fats is to be avoided, as they favor the absorption of the poison, by their solvent action. The prognosis is very unfavorable.

As commercial phosphorus is usually contaminated with arsenic, the effects of the latter substance may also appear in poisoning by the former.

Analysis.—When, after a death supposed to be caused by phosphorus, chemical evidence of the existence of the poison in the body, etc., is desired, the investigation must be made as soon after death as possible, for the reason that the element is rapidly oxidized, and the detection of the higher stages of oxidation of phosphorus is of no value as evidence of the administration of the element, because they are normal constituents of the body and of the food.

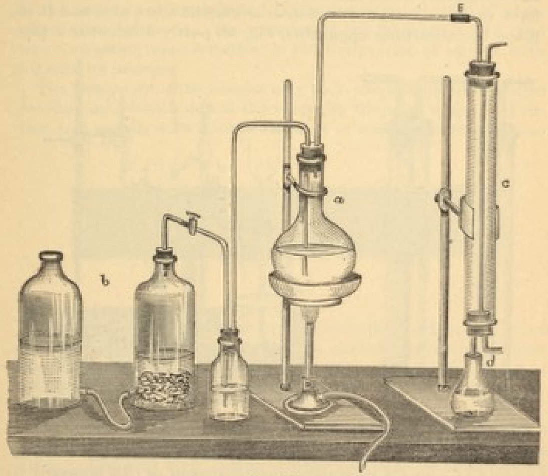


Fig. 28.

The detection of elementary phosphorus in a systematic toxicological analysis is connected with that of prussic acid, alcohol, ether, chloroform, and other volatile poisons. The substances under examination are diluted with H_2O, acidulated with H_2SO_4, and heated over a sand-bath in the flask *a* (Fig. 28). This flask is connected with a CO_2 generator, *b*, whose stopcock is closed, and with a Liebig's condenser, *c*, which is in darkness (the operation is best conducted in a dark room), and so placed as to deliver the distillate into the flask *d*. The odor of the distillate is noted. In the presence of P it is usually alliaceous. The condenser is also observed. If, at the point of greatest condensation, a faint, luminous ring be observed (in the absence of *all* reflections), it is proof positive of the presence of unoxidized phosphorus. The absence, however, of that poison is not to be inferred from the absence of the luminous ring (see above). If this fail to appear, when one-third the fluid contents of the flask *a* have distilled over, the condenser is disconnected at *e*, and in its place the absorbing apparatus, Fig. 29, partly filled with a neutral solution of silver nitrate, is adjusted by a rubber tube attached at *g*, and a slow and constant stream of CO_2 is caused to traverse the apparatus from *b*, Fig. 28. If, during continuation of the distillation, no black deposit is formed in the silver solution, the absence of P may be inferred. If a black deposit be formed, it must be further examined to determine if it be silver phosphid. For this purpose the apparatus shown in Fig. 30 is used. In the bottle *a* hydrogen is generated from *pure* Zn and H_2SO_4, the gas passing through the drying-tube *b*, filled with fragments of $CaCl_2$, and out through the platinum tip at *c*; *d* and *e* are pinch-cocks. When the apparatus is filled with H, *d* is closed until the funnel-tube *f* is three-quarters filled with the liquid from *a*; then *e* is closed and *d* opened, and the black silver deposit, which has been collected on a filter and washed, is

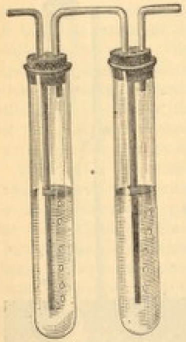


FIG. 29.

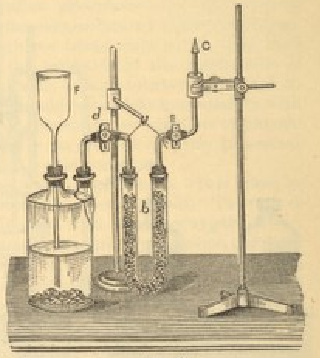


FIG. 30.

thrown into *f*; *e* is then slightly opened and the escaping gas ignited at *c*, the size of the flame being regulated by *e*. If the deposit contain P, the flame will have a green color; and, when examined with the spectroscope, will give the spectrum of bright bands shown in Fig. 31.

Chronic phosphorus poisoning, or *Lucifer disease*, occurs among operatives engaged in the dipping, drying, and packing of phosphorus matches. Those engaged in the manufacture of phosphorus itself are not so affected. Sickly women and children are most subject to it. The cause of the disease has been ascribed to the presence of arsenic, and to the formation of oxids of phosphorus, and of ozone. The progress of the disorder is slow, and its culminating manifestation is the destruction of one or both maxillæ by necrosis.

The frequency of the disease may be in some degree diminished by thorough ventilation of the shops, by frequent washing of the face and mouth with a weak solution of sodium carbonate, and by exposing oil of turpentine in saucers in the workshops. None of these methods, however, effect a perfect prevention, which can only be attained by the substitution of the red variety of phosphorus for the yellow in this industry.

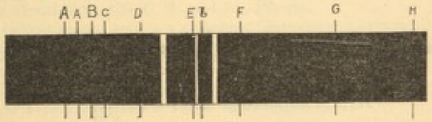


Fig. 31.

Hydrogen Phosphids.—Gaseous hydrogen phosphid—Phosphin —*Phosphonia*, *Phosphamin*, **PH_3**—34—A colorless gas, having a strong alliaceous odor, which is obtained pure by decomposing phosphonium iodid, PH_4I, with H_2O. Mixed with H and vapor of P_2H_4, it is produced, as a spontaneously inflammable gas, by the action of hot, concentrated solution of potassium hydroxid on P, or by decomposition of calcium phosphid by H_2O. It is highly poisonous. After death, the blood is found to be of a dark violet color, and to have, in a great measure, lost its power of absorbing oxygen.

Liquid hydrogen phosphid—P_2H_4—66—is the substance whose vapor communicates to PH_3 its property of igniting on contact with air. It is separated by passing the spontaneously inflammable PH_3 through a bulb tube, surrounded by a freezing mixture.

It is a colorless, heavy liquid, which is decomposed by exposure to sunlight, or to a temperature of 30° (86° F.).

Solid hydrogen phosphid—P_4H_2—126—is a yellow solid, formed when P_2H_4 is decomposed by sunlight. It is not phosphorescent and only ignites at 160° (320° F.).

Oxids of Phosphorus.—Two are known: P_2O_3 and P_2O_5.

Phosphorus trioxid—*Phosphorous anhydrid, Phosphorous oxid*—**P_2O_3**—110—is formed when P is burned in a very limited supply of perfectly dry air, or O. It is a white, flocculent solid, which, on exposure to air, ignites by the heat developed by its union with H_2O to form phosphorous acid.

Phosphorus pentoxid—*Phosphoric anhydrid, Phosphoric oxid*—**P_2O_5**—142—is formed when P is burned in an excess of dry O. It is a white, flocculent solid, which has almost as great a tendency to combine with H_2O as has P_2O_3. It absorbs moisture rapidly, deliquescing to a highly acid liquid, containing, not phosphoric, but metaphosphoric acid. It is used as a drying agent.

Phosphorous acids.—Five oxyacids of phosphorus are known:

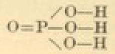
Hypophosphorous acid:

$$O{=}P\begin{cases}O{-}H\\H\\H\end{cases}$$

Phosphorous acid:

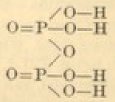
$$O{=}P\begin{cases}O{-}H\\O{-}H\\H\end{cases}$$

Phosphoric acid:



$$O{=}P\begin{cases}O{-}H\\O{-}H\\O{-}H\end{cases}$$

Pyrophosphoric acid:



$$\begin{array}{l}O{=}P\begin{cases}O{-}H\\O{-}H\end{cases}\\ \quad\;\;\rangle O\\ O{=}P\begin{cases}O{-}H\\O{-}H\end{cases}\end{array}$$

Metaphosphoric acid:

$$O{=}P\begin{cases}O{-}H\\=O\end{cases}$$

Only those H atoms which are connected with the P atoms through O atoms are basic. Hence H_3PO_2 is monobasic; H_3PO_3 is dibasic; H_3PO_4 is tribasic; $H_4P_2O_7$ is tetrabasic, and HPO_3 is monobasic.

Hypophosphorous acid—H_3PO_2—66—is a crystalline solid, or, more usually, a strongly acid, colorless syrup. It is oxidized by air to a mixture of H_3PO_3 and H_3PO_4.

The **hypophosphites** as well as the free acid, are powerful reducing agents.

Phosphorous acid—H_3PO_3—82—is formed by decomposition of phosphorous trichlorid by water: $PCl_3+3H_2O=H_3PO_3+3HCl$. It is a highly acid syrup, is decomposed by heat, and is a strong reducing agent.

Phosphoric acid—*Orthophosphoric acid—Common, or tribasic, phosphoric acid*—**Acidum phosphoricum, U. S.; Br.—H_3PO_4**—98—does not occur free in nature, but is widely disseminated in combination, in the phosphates, in the three kingdoms of nature.

It is prepared: (1) By converting bone phosphate, $Ca_3(PO_4)_2$, into the corresponding lead or barium salt, $Pb_3(PO_4)_2$ or $Ba_3(PO_4)_2$, and decomposing the former by H_2S, or the latter by H_2SO_4. (2) By oxidizing P by dilute HNO_3, aided by heat. The operation should be conducted with caution, and heat gradually applied by the sand-bath. It is best to use red phosphorus. This is the process directed by the U. S. and Br. Pharm.

The concentrated acid is a colorless, transparent, syrupy liquid; still containing H_2O, which it gives off on exposure over H_2SO_4, leaving the pure acid, in transparent, deliquescent, prismatic crystals. It is decomposed by heat to form, first, pyrophosphoric acid, then metaphosphoric acid. It is tribasic.

If made from arsenical phosphorus, and commercial phosphorus is usually arsenical, it is contaminated with arsenic acid, whose presence may be recognized by Marsh's test (q. v.). The acid should not respond to the indigo and ferrous sulfate tests for HNO_3.

Phosphates.—Phosphoric acid being tribasic the phosphates have the composition $M'H_2PO_4$; M'_2HPO_4; M'_3PO_4; $M''(H_2PO_4)_2$; $M''_2(HPO_4)_2$; $M''_3(PO_4)_2$; $M''M'PO_4$; and $M'''PO_4$. The monometallic salts are all soluble and are strongly acid. Of the dimetallic salts, those of the alkali metals only are soluble and their solutions are faintly alkaline; the others are unstable, and exhibit a marked tendency to transformation into monometallic or trimetallic salts. The normal phosphates of the alkali metals are the only soluble trimetallic phosphates. Their solutions are strongly akaline, and they are decomposed even by weak acids:

$$\underset{\text{Trisodic phosphate.}}{Na_3PO_4} + \underset{\text{Carbonic acid.}}{CO_3H_2} = \underset{\text{Disodic phosphate.}}{HNa_2PO_4} + \underset{\text{Monosodic carbonate.}}{HNaCO_3}$$

All the monometallic phosphates, except those of the alkali metals, are decomposed by ammonium hydroxid, with precipitation of the corresponding trimetallic salt.

Analytical Characters.—(1) With ammoniacal solution of silver nitrate, a yellow precipitate. (2) With solution of ammonium molybdate in HNO_3, a yellow precipitate. (3) With magnesia mixture,* a white, crystalline precipitate, soluble in acids, insoluble in ammonium hydroxid.

Pyrophosphoric acid—$H_4P_2O_7$—178.—When phosphoric acid (or hydro-disodic phosphate) is maintained at 213° (415°.4 F.), two of its molecules unite, with the loss of the elements of a molecule of water: $2H_3PO_4=H_4P_2O_7+H_2O$, to form pyrophosphoric acid.

Metaphosphoric acid—*Glacial phosphoric acid*—**HPO_3**—80—is formed by heating H_3PO_4 or $H_4P_2O_7$ to near redness: $H_3PO_4=HPO_3+H_2O$; or $H_4P_2O_7=2HPO_3+H_2O$. It is usually obtained from bone phosphate; this is first converted into ammonium phosphate, which is then subjected to a red heat.

It is a white, glassy, transparent solid, odorless, and acid in taste and reaction. Slowly deliquescent in air, it is very soluble in H_2O, although the solution takes place slowly, and is accompanied by a peculiar crackling sound. In constitution and basicity it resembles HNO_3.

The metaphosphates are capable of existing in five polymeric modifications (see polymerism): Mono- di- tri- tetra- and hexmetaphosphates: $M'PO_3$; $M'_2(PO_3)_2$ and $M''(PO_3)_2$; $M'_3(PO_3)_3$; $M'_4(PO_3)_4$ and $M''_2(PO_3)_4$; and $M'_6(PO_3)_6$.

Action of the Phosphates on the Economy.—The salts of phosphoric acid are important constituents of animal tissues, and give rise, when taken internally, in reasonable doses, to no untoward symptoms. The acid itself may act deleteriously, by virtue of its acid reaction. Meta- and pyro-phosphoric acids, even when taken in the form of neutral salts, have a distinct action (the pyro being the more active) upon the motor ganglia of the heart, producing diminution of the blood-pressure, and, in comparatively small doses, death from cessation of the heart's action.

Compounds of Phosphorus with the Halogens.—Phosphorus trichlorid—PCl_3—137.5—is obtained by heating P in a limited supply of Cl. It is a colorless liquid; sp. gr. 1.61; has an irritating odor; fumes in air; boils at 76° (169° F.). Water decomposes it with formation of H_3PO_3 and HCl.

Phosphorus pentachlorid—PCl_5—208.5—is formed when P is burnt in excess of Cl. It is a light yellow, crystalline solid: gives off irritating fumes; and is decomposed by H_2O.

Phosphorus oxychlorid — $POCl_3$ — 153.5 — is formed by the ac-

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* Made by dissolving 11 pts. crystallized magnesium chlorid and 28 pts. ammonium chlorid in 130 pts. water, adding 70 pts. dilute ammonium hydroxid and filtering after two days.

tion of a limited quantity of H_2O on the pentachlorid: $PCl_5 + H_2O = POCl_3 + 2HCl$. It is a colorless liquid; sp. gr. 1.7; boils at 110° (230° F.); and solidifies at −10° (+14° F.).

With **bromin** P forms compounds similar in composition and properties to the chlorin compounds. With **iodin** it forms two compounds, **P_2I_4** and **PI_3**. With **fluorin** it forms two compounds, **PF_3** and **PF_5**, the former liquid, the second gaseous.

ARSENIC.

Symbol=**As**—*Atomic weight=75—Molecular weight=300—Sp. gr. of solid=5.75; of vapor=10.6A at 860° (1580° F.)—Name from ἀρσενικόν=orpiment.*

Occurrence.—Free in small quantity; in combination as arsenids of Fe, Co, and Ni, but most abundantly in the sulfids, orpiment and realgar, and in arsenical iron pyrites or mispickel.

Preparation.—(1.) By heating mispickel in clay cylinders, which communicate with sheet iron condensing tubes.

(2.) By heating a mixture of arsenic trioxid and charcoal; and purifying the product by resublimation.

Properties.—*Physical.*—A brittle, crystalline, steel gray solid, having a metallic lustre, or a dull, black, amorphous powder. At the ordinary pressure, and without contact of air, it volatilizes without fusion at 180° (356° F.); under strong pressure it fuses at a dull red heat. Its vapor is yellowish, and has the odor of garlic. It is insoluble in H_2O and in other liquids unless chemically altered.

Chemical.—Heated in air it is converted into the trioxid and ignites somewhat below a red heat. In O it burns with a brilliant, bluish-white light. In dry air it is not altered, but in the presence of moisture its surface becomes tarnished by oxidation. In H_2O it is slowly oxidized, a portion of the oxid dissolving in the water. It combines readily with Cl, Br, I, and S, and with most of the metals. With H it only combines when that element is in the nascent state. Warm, concentrated H_2SO_4 is decomposed by As, with formation of SO_2, As_2O_3, and H_2O. Nitric acid is readily decomposed, giving up its O to the formation of arsenic acid. With hot HCl, arsenic trichlorid is formed. When fused with potassium hydroxid, arsenic is oxidized, H is given off, and a mixture of potassium arsenite and arsenid remains, which by greater heat is converted into arsenic, which volatilizes, and potassium arsenate, which remains.

Elementary arsenic enters into the composition of fly poison and of shot, and is used in the manufacture of certain pigments and fire-works.

Compounds of Arsenic and Hydrogen.—Two are known: the solid As_2H (?), and the gaseous, AsH_3.

Hydrogen arsenid—**Arsin**—*Arseniuretted or arsenetted hydrogen*=*Arsenia*—*Arsenamin*—**AsH_3**—*Molecular weight*=78—*Sp. gr.* =2.695 *A*—*Liquefies at* −40° (−40° *F.*).

Formation.—(1.) By the action of H_2O upon an alloy, obtained by fusing together native sulfid of antimony, 2 pts.; cream of tartar, 2 pts.; and arsenic trioxid, 1 pt.

(2.) By the action of dilute HCl or H_2SO_4 upon the arsenids of Zn and Sn.

(3.) Whenever a reducible compound of arsenic is in presence of nascent hydrogen. (See Marsh test.)

(4.) By the action of H_2O upon the arsenids of the alkali metals.

(5.) By the combined action of air, moisture and organic matter upon arsenical pigments.

(6.) By the action of hot solution of potassium hydroxid upon reducible compounds of As in the presence of zinc.

Properties.—*Physical.*—A colorless gas; having a strong alliaceous odor; soluble in 5 vols. of H_2O, free from air.

Chemical.—It is neutral in reaction. In contact with air and moisture its H is slowly removed by oxidation, and elementary As deposited. It is also decomposed into its elements by the passage through it of luminous electric discharges; and when subjected to a red heat. It is acted on by dry O at ordinary temperatures with the formation of a black deposit which is at first solid hydrogen arsenid, later elementary As. A mixture of AsH_3 and O, containing 3 vols. O and 2 vols. AsH_3, explodes when heated, forming As_2O_3 and H_2O. If the proportion of O be less, elementary As is deposited.

The gas burns with a greenish flame, from which a white cloud of arsenic trioxid arises. A cold surface, held above the flame, becomes coated with a white, crystalline deposit of the oxid. If the flame be cooled, by the introduction of a cold surface into it, the H alone is oxidized, and elementary As is deposited. Chlorin decomposes the gas explosively, with formation of HCl and arsenic trioxid. Bromin and iodin behave similarly, but with less violence.

All oxidizing agents decompose it readily; H_2O and arsenic trioxid being formed by the less active oxidants, and H_2O and arsenic acid by the more active. Solid potassium hydroxid decomposes the gas partially, and becomes coated with a dark deposit, which seems to be elementary arsenic. Solution of the alkaline hydroxids absorb and decompose it; H is given off and an alkaline arsenite remains in the solution. Many metals, when heated in H_3As, decompose it with formation of a metallic arsenid and liberation of hydrogen. Solution of silver nitrate is reduced by it; elementary silver is deposited, and the solution contains silver arsenite.

Although H_2S and H_3As decompose each other to a great extent, with formation of arsenic trisulfid, in the presence of air, the two gases do not act upon each other at the ordinary temperature, even in the direct sunlight, either dry or in the presence of H_2O, when air is absent. Hence in making H_2S for use in toxicological analysis, materials free from As must be used; or the H_2S must be purified as described on p. 92.

Compounds of Arsenic and Oxygen.—Two are known: As_2O_3 and As_2O_5.

Probably the gray substance formed by the action of moist air on elementary arsenic is a lower oxid.

Arsenic trioxid—*Arsenious anhydrid—Arsenious oxid—White arsenic—Arsenic—Arsenious acid*—**Acidum arseniosum, U. S.; Br.—As_2O_3**—198.

Preparation.—(1.) By roasting the native sulfids of arsenic in a current of air.

(2.) By burning arsenic in air or oxygen.

Properties.—*Physical.*—It occurs in two distinct forms: *crystallized* or "*powdered*," and *vitreous* or *porcelainous*. When freshly fused, it appears in colorless or faintly yellow, translucent, vitreous masses, having no visible crystalline structure. Shortly, however, these masses become opaque upon the surface, and present the appearance of porcelain. This change, which is due to the substance assuming the crystalline form, slowly progresses toward the centre of the mass, which, however, remains vitreous for a long time. The change is attended by the slow liberation of heat, and, if it be made to take place more rapidly, a faint light is visible in obscurity. When arsenic trioxid is sublimed, if the vapors be condensed upon a cool surface, it is deposited in the form of brilliant octahedral crystals, which are larger and more perfect the nearer the temperature of the condensing surface is to 180° (356° F.). The crystalline variety may be converted into the vitreous, by keeping it for some time at a temperature near its point of volatilization.

The taste of arsenic trioxid in solution is at first faintly sweet, afterward very slightly metallic. The solid is almost tasteless. It is odorless. In aqueous solution (see below) it has a faintly acid reaction. The sp. gr. of the vitreous variety is 3.785; that of the crystalline, 3.689.

Its solubility in water varies with the temperature, the method of making the solution, the presence of foreign substances and the nature of the oxid:

	Transparent Form.	Opaque Form.	Fresh Crystalline Oxid.
1,000 parts of cold distilled water, after standing 24 hours, dissolved........	1.74 parts.	1.16 parts.	2.0 parts.
1,000 parts of boiling water poured on the oxid, and allowed to stand for 24 hours, dissolved........	10.12 parts.	5.4 parts.	15.0 parts.
1,000 parts of water boiled for one hour, the quantity being kept uniform by the addition of boiling water from time to time, and filtered immediately, dissolved.......	64.5 parts.	76.5 parts.	87.0 parts.

The vitreous variety is more soluble than the crystalline, but, by prolonged boiling, the crystalline is converted into the vitreous, or, at all events, the solubility of the two forms becomes the same. The solution of the crystallized oxid in cold H_2O is always very slow (the vitreous oxid dissolves more rapidly), and continues for a long time. If white arsenic be thrown upon cold H_2O, only a portion of it sinks, the remainder floating upon the surface, notwithstanding its high specific gravity. This is due to a repulsion of the H_2O from the surfaces of the crystals, which also accounts, to some extent at least, for its slow solution. Even after several days, cold H_2O does not dissolve all the oxid with which it is in contact. If one part of oxid be digested with 80 parts of H_2O, at ordinary temperatures for several days, the resulting solution contains $\frac{1}{96}$; with 160 parts H_2O, $\frac{1}{180}$; with 240 parts, $\frac{1}{250}$; with 1,000 parts H_2O, $\frac{1}{1200}$; and even when 16,000 or 100,000 parts of H_2O are used, a portion of the oxid remains undissolved. Arsenious oxid, which had remained in contact with cold H_2O in closed vessels for eighteen years, dissolved to the extent of 1 part in 54 of H_2O, or 18.5 parts in 1,000, which may be given as the maximum solubility of the crystallized oxid in cold water. The power of H_2O of holding the acid in solution, once it is dissolved, is not the same as its power of dissolving it. If a concentrated solution be made, by boiling H_2O upon the oxid, and filtering hot, the filtrate may be evaporated to one-half its original bulk, without depositing any of the acid, of which this concentrated fluid now contains as much as one part in six of

H_2O, or 166.6 parts per 1,000. If a hot solution of the acid be allowed to cool, the solution will contain 62.5 parts per 1,000 at 16° (60°.8 F.), and 50 parts per 1,000 at 7° (44°.6 F.).

The solubility of the oxid in alcohol varies with the strength of the spirit, and the nature of the oxid, the vitreous variety being more soluble in strong than in weak alcohol, while the contrary is the case with the crystalline, as is shown in the following table:

1,000 parts dissolve		Alcohol at 56%.	Alcohol at 79%.	Alcohol at 86%.	Absolute alcohol.
Crystallized oxid	At 15° (59° F.)......	16.80	14.30	7.15	0.25
	At the boiling-point	48.95	45.51	31.97	34.02
Vitreous oxid at 15° (59° F.)..........		5.04	5.40	.....	10.60

The presence of the mineral acids and alkalies, ammonia and ammoniacal salts, alkaline carbonates, tartaric acid, and the tartrates, increases the solubility of arsenic trioxid in water. It is less soluble in fluids containing fats, or extractive or other organic matters (the various liquid articles of food), than it is in pure water.

In chemico-legal cases, in which the question of the solubility of arsenic is likely to arise, it must not be forgotten that the quantity of As_2O_3 which a person may unconsciously take in a given quantity of fluid is not limited, under certain circumstances, to that which the fluid is capable of *dissolving*. A much greater quantity than this may be taken, while in suspension in the liquid, especially if it be mucilaginous.

CHEMICAL.—Its solutions are acid in reaction, and probably contain the true arsenious acid, H_3AsO_3. They are neutralized by bases, with formation of **arsenites**. Solutions of sodium or potassium hydroxid dissolve it, with formation of the corresponding arsenite. It is readily reduced, with separation of As, when heated with hydrogen, carbon, or potassium cyanid, and at lower temperatures by more active reducing agents. Oxidizing agents, such as HNO_3, the hydrates of chlorin, chromic acid, convert it into arsenic pentoxid or arsenic acid. Its solution, acidulated with HCl and boiled in presence of copper, deposits on the metal a gray film, composed of an alloy of Cu and As.

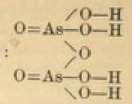
Arsenic pentoxid—*Arsenic anhydrid*—*Arsenic oxid*—$\mathbf{As_2O_5}$—230—is obtained by heating arsenic acid to redness. It is a white, amorphous solid, which, when exposed to the air, slowly absorbs moisture. It is fusible at a dull red heat, and at a slightly higher temperature decomposes to As_2O_3 and O. It dissolves slowly in H_2O, forming arsenic acid, H_3AsO_4.

Arsenic Acids.—The oxyacids of arsenic form a series, corresponding to that of the oxyacids of phosphorus, except that the hypoarsenious acid is unknown

Arsenious acid:

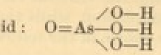
$$O{=}As\begin{cases}-O-H\\-O-H\\-H\end{cases}$$

Pyroarsenic acid:



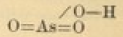
$$\begin{matrix}O{=}As\begin{cases}-O-H\\-O-H\end{cases}\\ \quad\rangle O\\ O{=}As\begin{cases}-O-H\\-O-H\end{cases}\end{matrix}$$

Arsenic acid:



$$O{=}As\begin{cases}-O-H\\-O-H\\-O-H\end{cases}$$

Metarsenic acid:



$$O{=}As\begin{cases}-O-H\\{=}O\end{cases}$$

Arsenious Acid—$\mathbf{H_3AsO_3}$—126—exists in aqueous solutions of the trioxid, although it has not been separated. Corresponding to it are important salts, called **arsenites**, which have the general formulæ HM'_2AsO_3, $HM''AsO_3$, $H_4M''(AsO_3)_2$.

Arsenic Acid—*Orthoarsenic acid*—$\mathbf{H_3AsO_4}$—142—is obtained by oxidizing As_2O_3 with HNO_3 in the presence of H_2O: $As_2O_3+2H_2O+2HNO_3=2H_3AsO_4+N_2O_3$. A similar oxidation is also effected by Cl, aqua regia, and other oxidants.

A syrupy, colorless, strongly acid solution is thus obtained, which, at 15° (59° F.) becomes semi-solid, from the formation of transparent crystals, containing 1 Aq. These crystals, which are very soluble and deliquescent, lose their Aq. at 100° (212° F.), and form a white, pasty mass composed of minute white, anhydrous needles. At higher temperatures it is converted into $H_4As_2O_7$, $HAsO_3$, and As_2O_5. In presence of nascent H it is decomposed into H_2O and AsH_3. It is reducible to H_3AsO_3 by SO_2.

The action of H_2S upon acid solutions of arsenic acid, or of the arsenates, varies with the rapidity of the action, and the temperature at which it occurs. With a slow current of H_2S, at a low temperature, no precipitate is formed, and the solution remains colorless, under these conditions **sulfoxyarsenic acid, $\mathbf{H_3AsO_3S}$** is formed: $H_3AsO_4 + H_2S = H_3AsSO_3 + H_2O$. By a further action of H_2S, arsenic pentasulfid is formed: $2H_3AsO_3S + 3H_2S = As_2S_5 + 6H_2O$. If the current of H_2S be very slow, the sulfoxyarsenic acid produced is decomposed according to the equation: $2H_3AsO_3S = As_2O_3+3H_2O+S_2$ and the precipitate then produced consists of a mixture of As_2S_3, As_2S_5 and S.

Like phosphoric acid, arsenic acid is tribasic; and the arsenates resemble the phosphates in composition, and in many of their chemical and physical properties.

Pyroarsenic acid—$\mathbf{H_4As_2O_7}$—266.—Arsenic acid, when heated to 160° (320° F.), is converted into compact masses of pyroarsenic acid: $2H_3AsO_4=H_4As_2O_7+H_2O$. It is very prone to revert to arsenic acid, by taking up water.

Metarsenic acid—$\mathbf{HAsO_3}$—124.—At 200°-206° (392°-403° F.) $H_4As_2O_7$ gradually loses H_2O to form metarsenic acid: $H_4As_2O_7=2HAsO_3+H_2O$. It forms white, pearly crystals, which dissolve readily in H_2O, with regeneration of H_3AsO_4. It is monobasic.

Compounds of Arsenic and Sulfur.—Arsenic disulfid—*Red sulfid of arsenic—Realgar—Red orpiment—Ruby sulfur—Sandarach*—$\mathbf{As_2S_2}$—214—occurs in nature, in translucent, ruby-red crystals. It is also prepared by heating a mixture of As_2O_3 and S. As so obtained it appears in brick-red masses.

It is fusible, insoluble in H_2O, but soluble in solutions of the alkaline sulfids, and in boiling solution of potassium hydroxid.

Arsenic trisulfid—*Orpiment—Auripigmentum—Yellow sulfid of arsenic—King's yellow*—$\mathbf{As_2S_3}$—246—occurs in nature in brilliant golden yellow flakes. Obtained by passing H_2S through an acid solution of As_2O_3; or by heating a mixture of As and S, or of As_2O_3 and S in equivalent proportions.

When formed by precipitation, it is a lemon-yellow powder, or in orange-yellow, crystalline masses, when prepared by sublimation. Almost insoluble in cold H_2O, but sufficiently soluble in hot H_2O to communicate to it a distinct yellow color. By continued boiling with H_2O it is decomposed into H_2S and As_2O_3. Insoluble in dilute HCl; but readily soluble in solutions of the alkaline hydroxids, carbonates, and sulfids. It volatilizes when heated.

Nitric acid oxidizes it, forming H_3AsO_4 and H_2SO_4. A mixture of HCl and potassium chlorate has the same effect. It corresponds in constitution to As_2O_3, and, like it, may be regarded as an anhydrid, for, although sulfarsenious acid, H_3AsS_3, has not been separated, the sulfarsenites, pyro- and meta-sulfarsenites are well-characterized compounds.

Arsenic pentasulfid—$\mathbf{As_2S_5}$—310—is formed by fusing a mixture of As_2S_3 and S in proper proportions, and, by the prolonged action of H_2S, at low temperatures, upon solutions of the arsenates.

It is a yellow, fusible solid, capable of sublimation in absence of air. There exist well-defined sulfarsenates, pyro- and meta-sulfarsenates.

Compounds of Arsenic with the Halogens.—Arsenic trifluorid—$\mathbf{AsF_3}$—132.—A colorless, fuming liquid, boiling at 63° (145° F.), obtained by distilling a mixture of As_2O_3, H_2SO_4 and fluorspar. It attacks glass.

Arsenic trichlorid—$\mathbf{AsCl_3}$—181.5.—Obtained by distilling a mixture of As_2O_3, H_2SO_4 and NaCl, using a well-cooled receiver.

It is a colorless liquid, boils at 134° (273° F.), fumes when exposed to the air, and volatilizes readily at temperatures below its boiling-point. Its formation must be avoided in processes for the chemico-legal detection of arsenic, lest it be volatilized and lost. It is formed by the action of HCl, even when comparatively dilute, upon As_2O_3 at the temperature of the water-bath;

but, if potassium chlorate be added, the trioxid is oxidized to arsenic acid, and the formation of the chlorid thus prevented. Arsenic trioxid, when fused with sodium nitrate, is converted into sodium arsenate, which is not volatile. If, however, small quantities of chlorids be present, $AsCl_3$ is formed. It is highly poisonous.

Arsenic tribromid—$AsBr_3$—315.—Obtained by adding powdered As to Br, and distilling the product at 220° (428° F.). A solid, colorless, crystalline body, fuses at 20°–25° (68°–77° F.), boils at 220° (428° F.), and is decomposed by H_2O.

Arsenic triiodid—Arsenii iodidum, U. S.—AsI_3—456.—Formed by adding As to a solution of I in carbon disulfid; or by fusing together As and I in proper proportions. A brick-red solid, fusible and volatile. Soluble in a large quantity of H_2O. Decomposed by a small quantity of H_2O into HI, As_2O_3, H_2O and a residue of AsI_3.

Action of Arsenical Compounds upon the Animal Economy.

The poisonous nature of many of the arsenical compounds has been known from remote antiquity, and it is probable that more murders have been committed by their use than by that of all other toxic substances combined. Even at the present time—notwithstanding the fact that, suspicion once aroused, the detection of arsenic in the dead body is certain and comparatively easy—criminal arsenical poisoning is still quite common, especially in rural districts.

The poison is usually taken by the mouth, but it has also been introduced by other channels; the skin, either uninjured or abraded; the rectum, vagina and male urethra. The forms in which it has been taken are: (1.) **Elementary arsenic**, which is not poisonous so long as it remains such. In contact with water, or with the saliva, however, it is converted into an oxid, which is then dissolved, and, being capable of absorption, produces the characteristic effects of the arsenical compounds. Certain fly-papers and fly-poisons contain As, a portion of which has been oxidized by the action of air and moisture. (2.) **Hydrogen arsenid**, the most actively poisonous of the inorganic compounds of arsenic, has been the cause of several accidental deaths, among others, that of the chemist Gehlen, who died in consequence of having inhaled the gas while experimenting with it. In other cases death has followed the inhalation of hydrogen, made from zinc and sulfuric acid contaminated with arsenic. (3.) **Arsenic trioxid** is the compound most frequently used by criminals. It has been given by every channel of entrance to the circulation; in some instances concealed with great art, in others merely held in suspension by stirring in a transparent fluid, given to an intoxicated person. If the poison have been in quantity, and undissolved, it may be found in the stomach after death, in the form of eight-sided crystals, more or less worn by the action of the solvents with which it has come in contact.

The lethal dose is variable, death having occurred from two and one-half grains, and recovery having followed the taking of a dose of two ounces. It is more active when taken fasting than when taken on a full stomach, in which latter case all, or nearly all, the poison is frequently expelled by vomiting, before there has been time for the absorption of more than a small quantity. (4.) **Potassium arsenite,** the active substance in "Fowler's solution," although largely used by the laity in malarial districts as an ague-cure, has, so far as the records show, produced but few cases of fatal poisoning. (5.) **Sodium arsenite** is sometimes used to clean metal vessels, a practice whose natural results are exemplified in the death of an individual who drank beer from a pewter mug so cleaned; and in the serious illness of 340 children in an English institution, in which this material had been used for cleaning the water-boiler. (6.) **Arsenic acid** and **arsenates.**—The acid itself has, so far as we know, been directly fatal to no one. The cases of death and illness, however, which have been put to the account of the red anilin dyes, are not due to them directly, but to arsenical residues remaining in them as the result of defective processes of manufacture. (7.) **Sulfids of arsenic.**—Poisoning by these is generally due to the use of orpiment, introduced into articles of food as a coloring matter, by a combination of fraud and stupidity, in mistake for turmeric. (8.) **The arsenical greens.**—Scheele's green, or cupric arsenite, and Schweinfurth green, or cupric aceto-metarsenite (the latter commonly known in the United States as Paris green, a name applied in Europe to one of the anilin pigments). These substances, although rarely administered with murderous intent, have been the cause of death in a great number of cases. Among suicides in the lower orders of the population in large cities, Paris green has been the favorite.

The arsenical pigments may also produce disastrous results by "accident;" by being incorporated in ornamental pieces of confectionery; by being used in the dyeing of textile fabrics, from which they may be easily rubbed off; from their use for the destruction of insects, and by being used in the manufacture of wall-paper. Many instances of chronic or subacute arsenical poisoning have resulted from inhabiting rooms hung with paper whose whites, reds, or greens were produced by arsenical pigments. From such paper the poison is disseminated in the atmosphere of the room in two ways: either as an impalpable powder, mechanically detached from the paper and floating in the air, or by their decomposition, and the consequent diffusion of volatile arsenical compounds in the air.

The **treatment** in acute arsenical poisoning is the same, whatever may be the form in which the poison has been taken, if it have been taken by the mouth. The first indication is the removal of any unabsorbed poison from the alimentary canal. If vomiting have not occurred from the effects of the toxic, it should be induced by the administration of zinc sulfate, or by mechanical means. The stomach-pump should not be used unless the case is seen soon after the taking of the poison. When the stomach has been emptied, the chemical antidote is to be administered, with a view to the transformation, in the stomach, of any remaining arsenical compound into the insoluble, and therefore innocuous, ferrous arsenate. To prepare the antidote, a solution of ferric sulfate, *Liq. ferri tersulphatis* (U. S.)=*Liq. ferri persulphatis* (Br.) is diluted with three volumes of water, and treated with aqua ammoniæ in slight excess. The precipitate formed is collected upon a muslin filter, and washed with water until the washings are nearly tasteless. The contents of the filter—*Ferri oxidum hydratum* (U. S.), *Ferri peroxidum humidum* (Br.) are to be given moist, in repeated doses of one to two teaspoonfuls, until an amount of the hydrate equal to 20 times the weight of white arsenic taken has been administered. Dialyzed iron may be given while the hydrate is in preparation, or when the materials for its preparation are not obtainable.

Precautions to be taken by the Physician in cases of suspected Poisoning.

It will rarely happen that in a case of suspected homicidal poisoning by arsenic, or by other poisons, the physician in charge will be willing or competent to conduct the chemical analysis, upon which, probably, the conviction or acquittal of the accused will mainly depend. Upon his knowledge and care, however, the success or futility of the chemist's labors depends in a great measure.

It is, as a rule, the physician who first suspects foul play; and, while it is undoubtedly his duty to avoid any public manifestation of his suspicion, it is as certainly his duty toward his patient and toward the community, to satisfy himself as to the truth or falsity of his suspicion by the application of a simple test to the excreta of the patient during life, the result of which may enable him to prevent a crime, or, failing that, take the first step toward the punishment of the criminal.

In a case in which, from the symptoms, the physician suspects poisoning by any substance, he should himself test the urine or fæces, or both, and govern his treatment and his actions toward the patient, and those surrounding the patient, by the results of his examination. Should the case terminate fatally, he should at once communicate his suspicions to the prosecuting officer, and require a post-mortem investigation, which should, if at all possible, be conducted in the presence of the chemist who is to conduct the analysis. For, be the physician as skilled as he may, there are odors and appearances, observable in many cases at the opening of the body, full of meaning to the toxicological chemist, which are ephemeral, and whose bearing upon the case is not readily recognized by those not thoroughly experienced.

Cases frequently arise in which it is impossible to bring the chemist upon the ground in time for the autopsy. In such cases the physician should remember that that portion of the poison remaining in the alimentary tract (we are speaking of true poisons) is but the residue of the dose in excess of that which has been necessary to produce death; and, if the processes of elimination have been active, there may remain no trace of the poison in the alimentary canal, while it still may be detectable in deeper-seated organs. The poison may also have been administered by another channel than the mouth, in which event it may not reach the stomach.

For these reasons it is not sufficient to send the stomach alone for analysis. The chemist should also receive the entire intestinal canal, at least one-half the liver, the spleen, one or both kidneys, a piece of muscular tissue from the leg, the brain, and any urine that may remain in the bladder. The intestinal canal should be removed and sent to the chemist *without having been opened*, and with ligatures, enclosing the contents, at the two ends of the stomach, and at the lower end of the intestine. The brain and alimentary canal are to be placed in separate jars, and the other viscera in another jar together; the urine in a vial by itself. All of these vessels are to be new and clean, and are to be closed by new corks, or by glass stoppers, or covers (not zinc screw-caps), which are then coated with paraffin (not sealing-wax), and so fastened with strings and seals, that it is impossible to open the vessels without cutting the strings, or breaking the seals. Any vomited matters are to be preserved. If the physician fail to observe these precautions, he has probably made the breach in the evidence through which the criminal will escape, and has at the outset defeated the aim of the analysis.

Analytical Characters of the Arsenical Compounds.—Arsenious Compounds.—(1.) H_2S, a yellow color in neutral or alkaline liquids; a yellow ppt. in acid liquids. The ppt. dissolves in solutions of the alkaline hydroxids, carbonates, and sulfhydrates; but is scarcely affected by HCl. Hot HNO_3 decomposes it.

(2.) $AgNO_3$, in the presence of a little NH_4HO, gives a yellow ppt. This test is best applied by placing the neutral arsenical solution in a porcelain capsule, adding neutral solution of $AgNO_3$, and blowing upon it over the stopper of the NH_4HO bottle, moistened with that reagent.

(3.) $CuSO_4$ under the same conditions as in (2) gives a yellowish-green ppt.

(4.) A small quantity of solid As_2O_3 is placed in the point *a* of the tube, Fig. 32; above it, at *b*, a splinter of recently ignited charcoal; *b* is first heated to redness, then *a*; the vapor of As_2O_3, passing over the hot charcoal, is reduced, and elementary As is deposited at *c* in a metallic ring. The tube is then cut between *b* and *c*, the larger piece held with *d* uppermost and heated at *c*;

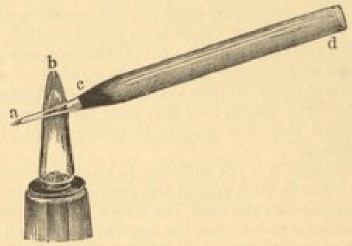


FIG. 32.

the deposit is volatilized, the odor of garlic is observed, and bright, octahedral crystals (Fig. 34), appear in the cool part of the tube.

(5.) **Reinsch test.**—The suspected liquid is acidulated with one-sixth its bulk of HCl. Strips of electrotype copper are immersed in the liquid, which is boiled. In the presence of an arsenious compound, a gray or bluish deposit is formed upon the Cu. A similar deposit is produced by other substances (Bi, Sb, Hg). To complete the test the Cu is removed, washed, and dried between folds of filter-paper, without removing the deposit. The copper, with its adherent film, is rolled into a cylinder, and introduced into a dry piece of Bohemian tubing, about ¼ inch in diameter and six inches long, which is held at the angle shown in Fig. 33 and heated at the point containing the copper. If the deposit consist of arsenic, a white deposit is formed at *a*, which contains brilliant specks, and, when examined with a magnifier, is found to consist of minute octahedral crystals, Fig. 34.

The advantages of this test are: it may be applied in the presence of organic matter, to the urine for instance; it is easily conducted; and its positive results are not misleading, *if the test be carried to completion.* These advantages render it the most suitable method for the physician to use, *during the life of the patient.* It should not be used *after death* by the physician, as by

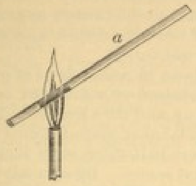


FIG. 33.

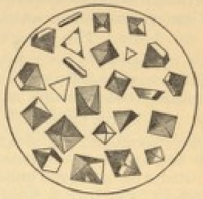


FIG. 34.

it copper is introduced into the substances under examination, which may subsequently interfere seriously with the analysis. The purity of the Cu and HCl must be proved by a blank testing before use. Reinsch's test is not as delicate as Marsh's, and it only reacts slowly and imperfectly when the arsenic is in the higher stage of oxidation, or in presence of oxidizing agents.

(6.) **Marsh's test** is based upon the formation of AsH_3 when a reducible compound of arsenic is in presence of nascent H; and

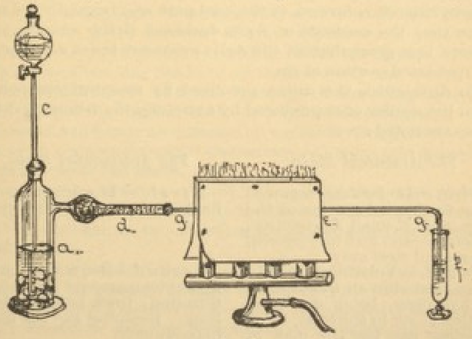


FIG. 35.

the subsequent decomposition of the arsenical gas by heat, with separation of elementary arsenic.

The apparatus used (Fig. 35) consists of a glass generating vessel *a*, of about 150 c.c. capacity (5 fl ℥), into whose upper opening a funnel tube *c* is either ground, or fitted by a section of rubber tube. The lateral outlet is connected with a tube *d*, filled with fragments of calcium chlorid; which in turn connects with the Bohemian glass tube *gg*, which should be about 0.5 cent. in diameter, and about 80 cent. long. This tube is protected by a tube of wire gauze, within which it is adjusted in the furnace as shown in the figure. The other end of *gg* is bent downward, and dips into a solution of silver nitrate in the test-tube *f*.

The vessel *a* is first charged with about 25 grams (6½ ʒ) of pure granulated zinc, which has been in contact with a diluted solution of platinic chlorid for half an hour, and then washed. The apparatus is then connected in such a manner that all joints are gas-tight, and the funnel-tube *c* about half filled with H_2SO_4, diluted with an equal bulk of H_2O, and cooled. By opening the stopcock, the acid is brought in contact with the zinc in small quantities, in such a manner that during the entire testing bubbles of gas pass through *f*, at the rate of 60–80 per minute. After fifteen minutes the burner is lighted, and the heating continued, during evolution of gas from zinc and H_2SO_4, for an hour. At the end of that time, if no stain have formed in *g* beyond *e*, then zinc and acid may be considered pure and the suspected solution, prepared as described on page 137, introduced slowly through the funnel-tube.

If arsenic be present in the substance examined, a hair-brown or gray deposit is formed in the cool part of *g* beyond *e*. At the same time the contents of *f* are darkened if the amount of As present is so great that all the AsH_3 produced is not decomposed in the heated portion of *gg*.

To distinguish the stains produced by arsenical compounds from the similar ones produced by antimony the following differences are noted:

The Arsenical Stain.	*The Antimonial Stain.*
First.—Is farther removed from the heated portion of the tube, and, if small in quantity, is double—the first hair-brown, the second steel-gray.	*First.*—Is quite near the heated portion of the tube.
Second.—Volatilizes readily when heated in an atmosphere of hydrogen, being deposited farther along in the tube. The escaping gas has the odor of garlic.	*Second.*—Requires a much higher temperature for its volatilization; fuses before volatilizing. Escaping gas has no alliaceous odor.
Third.—When cautiously heated in a current of oxygen, brilliant, white, octahedral crystals of arsenic trioxid are deposited farther along in the tube.	*Third.*—No crystals formed by heating in oxygen.

The Arsenical Stain.	*The Antimonial Stain.*
Fourth.—Instantly soluble in solution of sodium hypochlorite.	*Fourth.*—Insoluble in solution of sodium hypochlorite.
Fifth.—Slowly dissolved by solution of ammonium sulfhydrate; more rapidly when warmed.	*Fifth.*—Dissolves quickly in solution of ammonium sulfhydrate.
Sixth.—The solution obtained in 5 leaves, on evaporation over the water-bath, a bright yellow residue.	*Sixth.*—The solution obtained in 5 leaves, on evaporation over the water-bath, an orange-red residue.
Seventh.—The residue obtained in 6 is soluble in aqua ammoniæ, but insoluble in hydrochloric acid.	*Seventh.*—The residue obtained in 6 is insoluble in aqua ammoniæ, but soluble in hydrochloric acid.
Eighth.—Is soluble in warm nitric acid; the solution on evaporation yields a white residue, which turns brick-red when moistened with silver nitrate solution.	*Eighth.*—Is soluble in warm nitric acid; the solution on evaporation yields a white residue, which is not colored when moistened with silver nitrate solution.
Ninth.—Is not dissolved by a solution of stannous chlorid.	*Ninth.*—Dissolves slowly in solution of stannous chlorid.

If, however, the process described on p. 136 have been followed, there can be no antimony in the liquid which would contain arsenic, if present. The silver solution in *f* is tested for arsenious acid, by floating upon its surface a layer of diluted NH_4HO solution, which, in the presence of arsenic, produces a yellow (not brown) band, at the point of junction of the two liquids.

In place of bending the tube *gg'* downward, it may be bent upward and drawn out to a fine opening. If the escaping gas be then ignited, the heating of the tube being discontinued, a white deposit of As_2O_3 may be collected on a glass surface held *above* the flame; or a brown deposit of elementary As upon a cold (porcelain) surface held *in* the flame.

In place of generating nascent hydrogen by the action of Zn on H_2SO_4, it may be produced by the decomposition of acidulated H_2O by the battery, in a Marsh apparatus especially modified for that purpose.

In another modification of the Marsh test the AsH_3 is decomposed, not by passage through a red-hot tube, but by passing through a tube traversed by the spark from an induction coil.

(7.) **Fresenius' and von Babo's test.**—The sulfid, obtained in (1), is dried, and mixed with 12 parts of a *dry* mixture of 3 pts. sodium carbonate and 1 pt. potassium cyanid, and the mixture brought into a tube, drawn out to a fine opening, through which a slow current of CO_2 is allowed to pass. The tube is then heated to redness at the point containing the mixture, when, if arsenic be present, a gray deposit is formed at the constricted portion of the tube; which has the characters of the arsenical stain indicated on pp. 134, 135.

(8.) Place a small crystal of sodium sulfite in a solution of 0.3–0.4 gram of stannous chlorid in pure HCl, sp. gr. 1.13. Float the liquid to be tested on the surface of this mixture. If As be present a yellow band is formed at the junction of the two liquids, and gradually increases upward.

ARSENIC COMPOUNDS—(1.) H_2S does not form a ppt. in neutral or alkaline solutions. In acid solutions a yellow ppt., consisting either of As_2S_3 or As_2S_5, or a mixture of the sulfids with free S, is formed only after prolonged passage of H_2S at the ordinary temperature, more rapidly at about 70° (158° F.).

(2.) $AgNO_3$, under the same conditions as with the arsenious compounds, produces a brick-red ppt. of silver arsenate.

(3.) $CuSO_4$ under like circumstances produces a bluish-green ppt.

Arsenic compounds behave like arsenious compounds with the tests 4, 6 and 7 for the latter.

Method of Analysis for Mineral Poisons.—In cases of suspected poisoning a systematic course of analysis is to be followed by which the presence or absence of *all* the more usual poisons can be determined.

In the search for mineral poisons (see alkaloids), the first step is the destruction of organic matter. To this end the material to be examined, if liquid, is concentrated, and, if solid, is divided into small pieces and suspended in H_2O. About $\frac{1}{10}$ the volume of concentrated HCl, and a small quantity of potassium chlorate are added, and the mixture allowed to stand 24 hours at the ordinary temperature, in a porcelain capsule covered by a glass plate. The contents of the capsule are then heated over the water-bath, while potassium chlorate, in small quantities, and, if necessary, HCl, are added from time to time, and the mixture is occasionally stirred, and lumps of solid matter crushed with a flattened glass rod, until the mass has a uniform light-yellow color. If the liquid smell strongly of Cl, CO_2 is passed through it. When the odor of Cl has disappeared, the liquid is filtered, and the residue washed with hot water. If a deposit form on cooling, the liquid is again filtered. The clear filtrate and washings, if strongly acid, are *partially* neutralized with sodium carbonate, and treated with H_2S; the gas being passed slowly through the liquid for about half an hour at a time, at intervals of 4–6 hours, during 3 days; the vessel being well corked during the intervals. The precipitate formed, which may contain Sn, As, Sb, Hg, Pb, Bi or Cu, is collected on a filter, and washed with H_2O, containing a small quantity of H_2S, until the washings fail to give the *faintest* cloudiness when boiled, acidulated with HNO_3 and treated with silver nitrate.

Solution of ammonium sulfhydrate is added to the precipitate on the filter, which is then washed with water. The solution passing through may contain As, Sb, Sn and Cu; the residue on the filter (A) may contain Hg, Pb, Bi and Cu. The solution is evaporated over the water-bath to dryness, and the residue moistened with fuming HNO_3, dried, moistened with H_2O, and dried several times, and then, after neutralization with caustic soda, fused with a mixture of sodium carbonate and nitrate, until it is colorless, or contains only a black, granular deposit, the heat being slowly increased. The cooled residue of fusion is dissolved in a small quantity of warm H_2O, and CO_2 is passed through the solution, whether it be clear or cloudy. The solution, if not perfectly clear, is filtered. Any deposit retained by the filter (B) may contain Sn, Sb or Cu. The filtrate is strongly acidulated with H_2SO_4, and slowly evaporated and heated, with addition of more H_2SO_4, if necessary, until abundant white fumes are given off. The cooled residue, which may contain As, is dissolved in H_2O, and introduced into the Marsh apparatus when cold.

The residue B, if black, is dissolved in hot HNO_3, and the solution tested for Cu. If it be white, it is ignited, with the filter, in a porcelain crucible; fused with potassium cyanid; and washed with H_2O. The residue is extracted with warm HCl, and the solution tested for Sn. If any residue remain, it is extracted with HCl, to which a few drops of HNO_3 have been added, and the solution tested for Sb.

The residue A, after washing, is boiled with HNO_3, diluted with H_2O and filtered. The filtrate is tested for Cu, Bi and Pb. The residue, if any, is tested for Hg and Pb.

ANTIMONY.

Symbol=**Sb** (*Latin, stibium*)—*Atomic weight*=120—*Molecular weight*=(?)—*Sp. gr.*=6.175—*Fuses at* 450° (842° *F.*).

Occurrence.—Free in small quantity; principally in the trisulfid, Sb_2S_3.

Preparation.—The native sulfid (black, or crude antimony) is roasted, and then reduced, by heating with charcoal. The commercial antimony so obtained may be purified by fusing a mixture of antimony, 16 pts.; native sulfid of antimony, 1 pt.; and dry sodium carbonate, 2 pts. After cooling, the button is powdered, and fused with 1½ pts. sodium carbonate and 1% ferrous sulfid. The antimony is again separated, powdered, and fused with sodium carbonate and a small quantity of sodium nitrate. Each fusion is maintained for an hour.

Properties.—*Physical.*—A bluish-gray, brittle solid, having a metallic lustre; readily crystallizable; tasteless and odorless; volatilizes at a red heat, and may be distilled in an atmosphere of H.

Chemical.—Is not altered by dry or moist air at ordinary temperatures. When sufficiently heated in air, it burns, with formation of Sb_2O_3, as a white, crystalline solid. It also combines directly with Cl, Br, I, S, and many metallic elements. It combines with H under the same circumstances as does As. Cold, dilute H_2SO_4 does not affect it ; the hot, concentrated acid forms with it antimonyl sulfate, $(SbO)_2SO_4$ and SO_2. Hot HCl dissolves it, when finely divided, with evolution of H. It is readily oxidized by HNO_3, with formation of H_3SbO_4 or Sb_2O_4. Aqua regia dissolves it as $SbCl_3$, or $SbCl_5$. Solutions of the alkaline hydroxids do not act on it.

The element itself does not form salts with the oxyacids. There are, however, compounds, formed by the substitution of the group **antimonyl** (SbO), for the basic hydrogen of those acids. (See tartar emetic.)

It enters into the composition of type metal, antifriction metals, and britannia metal.

Hydrogen Antimonid—Stibin—*Antimoniuretted hydrogen—Stibamin—Stibonia*—**SbH_3**—123.—It has not been obtained in a condition of purity, but is produced, mixed with H, when a reducible compound of Sb is in presence of nascent H. It is obtained in larger amount, by decomposing an alloy of 400 parts of a 2% sodium amalgam, and 8 parts of freshly reduced, and dried Sb, by H_2O, in a current of CO_2.

It is a colorless, odorless, combustible gas, subject to the same decompositions as AsH_3; from which it differs in being by no means as poisonous, and in its action upon silver nitrate solution. The arsenical gas acts upon the silver salt according to the equation : $6AgNO_3+2AsH_3+{}^3H_2=Ag_6+2Ag_3HAsO_3+6HNO_3$, and the precipitate formed is elementary silver, while Ag_3HAsO_3 remains in the solution. In the case of SbH_3 the reaction is $3AgNO_3+SbH_3=3HNO_3+SbAg_3$, all of the Sb being precipitated in the black silver antimonid.

Compounds of Antimony and Oxygen.—Three are known, Sb_2O_3, Sb_2O_4 and Sb_2O_5.

Antimony trioxid—*Antimonous anhydrid—Oxid of antimony*—**Antimonii oxidum (U. S.; Br.)**—**Sb_2O_3**—288—occurs in nature; and is prepared artificially by decomposing the oxychlorid ; or by heating Sb in air.

It is an amorphous, insoluble, tasteless, odorless powder; white at ordinary temperatures, but yellow when heated. It fuses readily, and may be distilled in absence of oxygen. Heated in air, it burns like tinder, and is converted into Sb_2O_4.

It is reduced, with separation of Sb, when heated with charcoal, or in H. It is also readily oxidized by HNO_3, or potassium permanganate. It dissolves in HCl as $SbCl_3$; in Nordhausen sulfuric acid, from which solution brilliant crystalline plates of antimonyl pyrosulfate, $(SbO)_2S_2O_7$, separate ; and in solutions of tartaric acid, and of hydropotassic tartrate (see tartar emetic).

Boiling solutions of alkaline hydroxids convert it into antimonic acid.

Antimony pentoxid—*Antimonic anhydrid*—**Sb_2O_5**—320—is obtained by heating metantimonic acid to dull redness. It is an amorphous, tasteless, odorless, pale lemon-yellow colored solid; very sparingly soluble in water and in acids. At a red heat it is decomposed into Sb_2O_4 and O.

Antimony antimoniate—*Intermediate oxid—Diantimonic tetroxid*—**Sb_2O_4**—304—occurs in nature, and is formed when the oxids or hydrates of Sb are strongly heated, or when the lower stages of oxidation or the sulfids are oxidized by HNO_3, or by fusion with sodium nitrate. It is insoluble in H_2O; but is decomposed by HCl, hydropotassic tartrate, and potash.

Antimony Acids.—The normal antimonous acid, H_3SbO_3, corresponding to H_3PO_3, is unknown; but the series of antimonic acids: ortho—H_3SbO_4, pyro—$H_4Sb_2O_7$, and meta—$HSbO_3$, is complete, either in the form of salts, or in that of the free acids. There also exists, in its sodium salt, a derivative of the lacking antimonous acid: **metantimonous acid,** $HSbO_2$.

The compound sometimes used in medicine under the name *washed diaphoretic antimony* is potassium metantimonate, united with an excess of the pentoxid: $2KSbO_3, Sb_2O_5$. The hydropotassic pyroantimonate, $K_2H_2Sb_2O_7.6Aq$ is a valuable reagent for the sodium compounds. It is obtained by calcining a mixture of one part of antimony with four parts of potassium nitrate, and fusing the product with its own weight of potassium carbonate.

Chlorids of Antimony.—Antimony trichlorid—*Protochlorid or butter of antimony*—**$SbCl_3$**—226.5—is obtained by passing dry Cl over an excess of Sb_2S_3; by dissolving Sb_2S_3 in HCl; or by distilling mixtures, either of Sb_2S_3 and mercuric chlorid, or of Sb and mercuric chlorid, or of antimonyl pyrosulfate and sodium chlorid.

At low temperatures it is a solid, crystalline body; at the ordinary temperature a yellow, semi-solid mass, resembling butter; at 73°.2 (164° F.) it fuses to a yellow, oily liquid, which boils at 223° (433°.4 F.). Obtained by solution of Sb_2S_3 in HCl of the usual strength, it forms a dark yellow solution, which, when concentrated to sp. gr. 1.47, constitutes the *Liq. Antimonii chloridi* (*Br.*).

It absorbs moisture from air, and is soluble in a small quantity of H_2O; with a larger quantity it is decomposed, with precipitation of a white powder, **powder of Algaroth,** whose composition is SbOCl if cold H_2O be used, and $Sb_4O_5Cl_2$ if the H_2O be boiling. In H_2O containing 15 per cent. or more HCl, $SbCl_3$ is soluble without decomposition.

Antimony pentachlorid—$SbCl_5$—297.5—is formed by the action of Cl, in excess, upon Sb or $SbCl_3$, and purified by distillation, in a current of Cl.

It is a fuming, colorless liquid, which solidifies at −20° (−4° F.), the solid fusing at −6° (21°.2 F.). It absorbs moisture from air. With a small quantity of H_2O, and by evaporation over H_2SO_4, it forms a hydrate, $SbCl_5,4H_2O$, which appears in transparent, deliquescent crystals. With more H_2O, a crystalline oxychlorid, $SbOCl_3$, is formed; and with a still greater quantity, a white precipitate of orthoantimonic acid, H_3SbO_4.

Sulfids of Antimony.—Antimony trisulfid—*Sesquisulfid of antimony—Black antimony*—**Antimonii sulfidum** (**U. S.**)—**Antimonium nigrum** (**Br.**)—**Sb_2S_3**—336—is the chief ore of antimony; and is formed when H_2S is passed through a solution of tartar emetic.

The native sulfid is a steel-gray, crystalline solid; the artificial product, an orange-red, or brownish-red, amorphous powder. The **crude antimony** of commerce is in conical loaves, prepared by simple fusion of the native sulfid. It is soft, fusible, readily pulverized, and has a bright metallic lustre.

Heated in air, it is decomposed into SO_2 and a brown, vitreous, more or less transparent mass, composed of varying proportions of oxid and oxysulfids, known as **crocus,** or **liver,** or **glass of antimony.** Sb_2S_3 is an anhydrid, corresponding to which are salts known as **sulfantimonites**, having the general formula M'_2HSbS_3. If an excess of Sb_2S_3 be boiled with a solution of potash or soda, a liquid is obtained, which contains an alkaline sulfantimonite, and an excess of Sb_2S_3. If this solution be filtered, and decomposed by an acid while still hot, an orange-colored, amorphous precipitate is produced, which is the **antimonium sulfuratum** (**U. S.**; **Br.**), and consists of a mixture, in varying proportions, of Sb_2S_3 and Sb_2O_3. If, however, the solution be allowed to cool, a brown, voluminous, amorphous precipitate separates, which consists of antimony trisulfid and trioxid, potassium or sodium sulfid, and alkaline sulfantimonite in varying proportions; and is known as **Kermes mineral.** If now the solution from which the Kermes has been separated, be decomposed with H_2SO_4, a reddish-yellow substance separates, which is the **golden sulfuret of antimony**, and consists of a mixture of Sb_2S_3 and Sb_2S_5. The precipitate obtained when H_2S acts upon a solution of an antimonial compound is, according to circumstances, Sb_2S_3 or Sb_2S_5, mixed with free S. By the action of HCl on Sb_2S_3, H_2S is produced.

Antimony pentasulfid—Sb_2S_5—400—is obtained by decomposing an alkaline sulfantimonate by an acid. It is a dark orange-red, amorphous powder, readily soluble in solutions of the alkalies, and alkaline sulfids, with which it forms **sulfantimonates.**

An oxysulfid, $Sb_6S_6O_3$, is obtained by the action of a solution of sodium hyposulfite upon $SbCl_3$ or tartar emetic. It is a fine red powder, used as a pigment, and called **antimony cinnabar** or **antimony vermilion.**

Action of Antimony Compounds on the Economy.—The compounds of antimony are poisonous, and act with greater or less energy as they are more or less soluble. The compound which is most frequently the cause of antimonial poisoning is tartar emetic (q. v.), which has caused death in a dose of half a grain, although recovery has followed the ingestion of half an ounce in several instances. Indeed, the chances of recovery seem to be better with large, than with small doses, probably owing to the more rapid and complete removal of the poison by vomiting with large doses. Antimonials have been sometimes criminally administered in small and repeated doses, the victim dying of exhaustion. In such a case an examination of the urine will reveal the cause of the trouble.

If vomiting have not occurred in cases of acute antimonial poisoning it should be provoked by warm water, or the stomach should be evacuated by the pump. Tannin in some form (decoction of oak bark, cinchona, nutgalls, tea) should then be given, with a view to rendering any remaining poison insoluble.

Medicinal antimonials are very liable to contamination with arsenic.

Analytical characters of Antimonial Compounds.—(1.) With H_2S in acid solution, an orange-red ppt., soluble in NH_4HS and in hot HCl.

(2.) A strip of bright copper, suspended in a boiling solution of an Sb compound, acidulated with HCl, is coated with a blue-gray deposit. This deposit when dried (on the copper), and heated in a tube, open at both ends yields a white, *amorphous* sublimate (see No. 5, p. 132).

(3.) Antimonial compounds yield a deposit by Marsh's test, similar to that obtained with arsenical compounds, but differing in the particulars given above (see No. 6, p. 134).

If, in cases of suspected poisoning, the examination have been conducted as directed on p. 136, any Sb present is separated during the fusion with sodium nitrate and carbonate, and the subsequent solution and filtration, so completely that As and Sb cannot be mistaken for one another.

IV.—BORON GROUP.

BORON.

Symbol=**B**—*Atomic weight*=11—*Molecular weight*=22 (?)=*Isolated by Davy in* 1807.

Boron constitutes a group by itself; it is trivalent in all of its compounds; it forms but one oxid, which is the anhydrid of a tribasic acid; and it forms no compound with H.

It is separable in two allotropic modifications. **Amorphous boron** is prepared by decomposition of the oxid, by heating with metallic potassium or sodium. It is a greenish-brown powder; sparingly soluble in H_2O; infusible, and capable of direct union with Cl, Br, O, S, and N.

Crystallized boron is produced when the oxid, chlorid or fluorid is reduced by Al. It crystallizes in quadratic prisms; more or less transparent, and varying in color from a faint yellow to deep garnet-red; very hard; sp. gr. 2.68. It burns when strongly heated in O, and readily in Cl; it also combines with N, which it is capable of removing from NH_3 at a high temperature.

Boron trioxid—*Boric* or *boracic anhydrid*—$\mathbf{B_2O_3}$—70—is obtained by heating boric acid to redness in a platinum vessel. It is a transparent, glass-like mass, used in blowpipe analysis under the name **vitreous boric acid.**

Boric Acids.—Boric acid—*Boracic acid*—**Acidum boricum (U. S.)**—$\mathbf{H_3BO_3}$—62—occurs in nature; and is prepared by slowly decomposing a boiling, concentrated solution of borax, with an excess of H_2SO_4, and allowing the acid to crystallize.

It forms brilliant crystalline plates, unctuous to the touch; odorless; slightly bitter; soluble in 25 parts H_2O at 10° (50° F.); soluble in alcohol. Its solution reddens litmus, but turns turmeric paper brown. When its aqueous solution is distilled, a portion of the acid passes over.

Boric acid readily forms ethers with the alcohols. When heated with ethylic alcohol, **ethyl borate** is formed, which burns with a green flame. Heated with glycerin a soluble, neutral ether is formed, known as **boroglycerid,** and used as an antiseptic.

If H_3BO_3 be heated for some time at 80° (176° F.), it loses H_2O and is converted into **metaboric acid,** HBO_2. If maintained at 100° (212° F.) for several days, it loses a further quantity of H_2O, and is converted into **tetraboric** or **pyroboric acid,** $H_2B_4O_7$, whose sodium salt is borax.

V.—CARBON GROUP.

CARBON—SILICON.

The elements of this group are bivalent or quadrivalent. The saturated oxid of each is the anhydrid of a dibasic acid. They are both combustible, and each occurs in three allotropic forms.

CARBON.

Symbol=**C**—*Atomic weight*=12—*Molecular weight*=24 (?).

Occurrence.—Free in its three allotropic forms: The **diamond** in octahedral crystals; in alluvial sand, clay, sandstone and conglomerate; **graphite,** in amorphous or imperfectly crystalline forms; **amorphous,** in the different varieties of anthracite and bituminous coal, jet, etc. In combination, it is very widely distributed in the so-called organic substances.

Properties.—Diamond.—The crystals of diamond, which is almost pure carbon, are usually colorless or yellowish, but may be blue, green, pink, brown or black. It is the hardest substance known, and the one which refracts light the most strongly. Its index of refraction is 2.47 to 2.75. It is very brittle; a bad conductor of heat and of electricity; sp. gr. 3.50 to 3.55. When very strongly heated in vacuo, it swells up, and is converted into a black mass, resembling coke.

Graphite is a form of carbon almost as pure as the diamond, capable of crystallizing in hexagonal plates; sp. gr. 2.2; dark gray in color; opaque; soft enough to be scratched by the nail; and a good conductor of electricity. It is also known as **black lead** or **plumbago.** It has been obtained artificially, by allowing molten cast-iron, containing an excess of carbon, to cool slowly, and dissolving the iron in HCl.

Amorphous carbon is met with in a great variety of forms, natural and artificial, in all of which it is black; sp. gr. 1.6–2.0; more or less porous; and a conductor of electricity.

Anthracite coal is hard and dense; it does not flame when burning; is difficult to kindle, but gives great heat with a suitable draught. It contains 80–90 per cent. of carbon. **Bituminous** coal differs from anthracite in that, when burning, it gives off gases, which produce a flame. Some varieties are quite soft, while others, such as **jet,** are hard enough to assume a high polish. It is usually compact in texture, and, very frequently, contains impressions of leaves, and other parts of plants. It contains about 75 per cent. of carbon.

Charcoal, carbo ligni, U. S., is obtained by burning woody fibre, with an insufficient supply of air. It is brittle and sonorous; has the form of the wood from which it was obtained, and retains all the mineral matter present in the woody tissue Its sp. gr. is about 1.57. It has the power of condensing within its pores odorous substances, and large quantities of gases; 90 volumes of ammonia, 55 of hydrogen sulfid, 9.25 of oxygen. This property is taken advantage of in a variety of ways. Its power of absorbing odorous bodies renders it valuable as a disinfecting, and filtering agent, and in the prevention of putrefaction and fermentation of certain liquids. The efficacy of charcoal as a filtering material is due also, in a great measure, to the oxidizing action of the oxygen condensed in its pores; indeed, if charcoal be boiled with dilute HCl, dried, and heated to redness, the oxidizing action of the oxygen, which it thus condenses, is very energetic.

Lamp-black is obtained by incomplete combustion of some resinous or tarry substance, or natural gas, the smoke or soot from which is directed into suitable condensing-chambers. It is a light, amorphous powder, and contains a notable quantity of oily and tarry material, from which it may be freed by heating in a covered vessel. It is used in the manufacture of printer's ink.

Coke is the substance remaining in gas-retorts, after the distillation of bituminous coal, in the manufacture of illuminating gas. It is a hard, grayish substance, usually very porous, dense, and sonorous. When iron retorts are used, a portion of the gaseous products are decomposed by contact with the hot iron surface, upon which there is then deposited a layer of very hard, compact, grayish carbon, which is a good conductor of electricity, and furnishes the best material for making the carbons of galvanic batteries and the points for the electric light. It does not form when gas is made in clay retorts.

Animal charcoal is obtained by calcining animal matters in closed vessels. If prepared from bones it is known as **bone-black**, **carbo animalis, U. S.**; if from ivory, **ivory black.** The latter is used as a pigment, the former as a decolorizing agent. Bones yield about 60 per cent. of bone-black, which contains, besides carbon, nitrogen and the phosphates and other mineral subtances of the bones. It possesses in a remarkable degree the power of absorbing coloring matters. When its decolorizing power is lost by saturation with pigmentary bodies, it may be restored, although not completely, by calcination. For certain purposes purified animal charcoal, *i.e.*, freed from mineral matter, **carbo animalis purificatus, U. S.**, is required, and is obtained by extracting the commercial article with HCl, and washing it thoroughly. Its decolorizing power is diminished by this treatment. Animal charcoal has the power of removing from a solution certain crystalline substances, notably the alkaloids, and a method has been suggested for separating these bodies from organic mixtures by its use.

All forms of carbon are insoluble in any known liquid.

Chemical.—All forms of C combine with O at high temperatures, with light and heat. The product of the union is carbon dioxid if the supply of air or O be sufficient; but if O be present in limited quantity, carbon monoxid is formed. The affinity of C for O renders it a valuable reducing agent. Many metallic oxids are reduced, when heated with C, and steam is decomposed when passed over red-hot C: $H_2O+C=CO+H_2$. At elevated temperatures C also combines directly with S, to form carbon disulfid. With H, carbon also combines directly, under the influence of the voltaic arc.

FOR COMPOUNDS OF CARBON SEE PAGE 222.

SILICON.

Symbol=**Si**—*Atomic weight*=28—*Molecular weight*=56 (?)—*Discovered by Davy* 1807—*Name from* silex=*flint.*

Also known as **silicium**; occurs in three allotropic forms: **Amorphous silicon,** formed when silicon chlorid is passed over heated K or Na, is a dark brown powder, heavier than water. When heated in air, it burns with a bright flame to the dioxid. It dissolves in potash and in hydrofluoric acid, but is not attacked by other acids. **Graphitoid silicon** is obtained by fusing potassium fluosilicate with aluminium. It forms hexagonal plates, of sp. gr. 2.49, which do not burn when heated to whiteness in O, but may be oxidized at that temperature, by a mixture of potassium chlorate and nitrate. It dissolves slowly in alkaline solutions, but not in acids. **Crystallized silicon,** corresponding to the diamond, forms crystalline needles, which are only attacked by a mixture of nitric and hydrofluoric acids.

Silicon, although closely related to C, exists in nature in comparatively few compounds. It has been caused to form artificial combinations, however, which indicate its possible capacity to exist in substances, corresponding to those C compounds commonly known as organic, *e.g.*, **silicichloroform** and **silicibromoform,** $SiHCl_3$ and $SiHBr_3$.

Hydrogen silicid—SiH_4—32—is obtained as a colorless, insoluble, spontaneously inflammable gas, by passing the current of a galvanic battery of twelve cells through a solution of common salt, using a plate of aluminium, alloyed with silicon, as the positive electrode.

Silicon chlorid—$SiCl_4$—170—a colorless, volatile liquid, having an irritating odor; sp. gr. 1.52; boils at 59° (138°.2 F.); formed when Si is heated to redness in Cl.

Silicic oxid—*Silicic anhydrid—Silex*—**SiO_2**—60—is the most important of the compounds of silicon. It exists in nature in the different varieties of quartz, and in the rocks and sands containing that mineral, in agate, carnelian, flint, etc. Its purest native form is **rock crystal.** Its hydrates occur in the opal, and in solution in natural waters. When crystallized, it is fusible with difficulty. When heated to redness with the alkaline carbonates it forms **silicates,** which solidify to glass-like masses, on cooling. It unites with H_2O to form a number of acid hydrates. The normal hydrate, H_4SiO_4, has not been isolated, although it probably exists in the solution, obtained by adding an excess of HCl to a solution of sodium silicate. A gelatinous hydrate, soluble in water and in acids and alkalies, is obtained by adding a small quantity of HCl to a concentrated solution of sodium silicate.

Hydrofluosilicic acid—**H_2SiF_6**—144—is obtained in solution by passing the gas, disengaged by gently heating a mixture of equal parts of fluorspar and pounded glass, and 6 pts. H_2SO_4, through water; the disengagement tube being protected from moisture by a layer of mercury. It is used in analysis as a test for K and Na.

VI. VANADIUM GROUP.

VANADIUM—COLUMBIUM—TANTALUM.

The elements of this group resemble those of the N group, but are usually quadrivalent.

Vanadium—**V**—51.3—a brilliant, crystalline metal; sp. gr.=5.5; which forms a series of oxids similar to those of N. No salts of V are known, but salts of vanadyl (VO) are numerous, and are used in the manufacture of anilin black.

Columbium—**Nb**—94—a bright, steel-gray metal; sp. gr. 7.06; which burns in air to Nb_2O_5 and in Cl to $NbCl_5$; not attacked by acids.

Tantalum—**Ta**—182—closely resembles Nb in its chemical characters.

VII. MOLYBDENUM GROUP.

MOLYBDENUM—TUNGSTEN—OSMIUM.

The position of this group is doubtful: and it is probable that the lower oxids will be found to be basic in character: in which case the group should be transferred to the third class.

Molybdenum—**Mo**—95.5—a brittle white metal. The oxid MoO_3, *molybdic anhydrid*, combines with H_2O to form a number of acids; the ammonium salt of one of which is used as a reagent for H_3PO_4; with which it forms a conjugate acid, *phosphomolybdic acid*, used as a reagent for the alkaloids.

Tungsten—*Wolfram*—**W**—183.6—a hard, brittle metal; sp. gr.

17.4. The oxid, WO_3, *tungstic anhydrid*, is a yellow powder, forming with H_2O several acid hydrates; one of which, *metatungstic acid*, is used as a test for the alkaloids, as are also the conjugate *silicotungstic* and *phosphotungstic acids*. Tissues impregnated with *sodium tungstate* are rendered uninflammable.

Osmium—Os—198.5—occurs in combination with Ir in Pt ores; combustible and readily oxidized to OsO_4. This oxid, known as *osmic acid*, forms colorless crystals, soluble in H_2O, which give off intensely irritating vapors. It is used as a staining agent by histologists, and also in dental practice.

CLASS III.—AMPHOTERIC ELEMENTS.

Elements whose Oxids Unite with Water, Some to Form Bases, Others to Form Acids. Which Form Oxysalts.

I. GOLD GROUP.

GOLD.

Symbol = **Au** (**AURUM**)—*Atomic weight* = 196.2—*Molecular weight* = 392.4 (?)—*Sp. gr.* = 19.258–19.367—*Fuses at* 1200° (2192° F.).

This, the only member of the group, forms two series of compounds; in one, AuCl, it is univalent; in the other, $AuCl_3$, trivalent. Its hydroxid, **auric acid,** $Au(OH)_3$, corresponds to the oxid Au_2O_3. Its oxysalts are unstable.

It is yellow or red by reflected light, green by transmitted light, reddish-purple when finely divided; not very tenacious; softer than silver; very malleable and ductile. It is not acted on by H_2O or air, at any temperature, nor by any single acid. It combines directly with Cl, Br, I, P, Sb, As, and Hg. It dissolves in nitromuriatic acid as auric chlorid. It is oxidized by alkalies in fusion on contact with air.

Auric chlorid—*Gold trichlorid*—$\mathbf{AuCl_3}$—302.7—obtained by dissolving Au in aqua regia, evaporating at 100° (212° F.), and purifying by crystallization from H_2O. Deliquescent, yellow prisms, very soluble in H_2O, alcohol and ether; readily decomposed, with separation of Au, by contact with P, or with reducing agents. Its solution, treated with the chlorids of tin, deposits a purple double stannate of Sn and Au, called "purple of cassius." With alkaline chlorids it forms double chlorids, **chloraurates** (**auri et sodii chloridum, U. S.**).

Analytical Characters.—(1.) With H_2S, from neutral or acid solution, a blackish-brown ppt. in the cold; insoluble in HNO_3 and HCl; soluble in aqua regia, and in yellow NH_4HS. (2.) With stannous chlorid and a little chlorin water, a purple-red ppt., insoluble in HCl. (3.) With ferrous sulfate a brown deposit, which assumes the lustre of gold when dried and burnished.

II. IRON GROUP.

CHROMIUM—MANGANESE—IRON.

The elements of this group form two series of compounds. In one they are bivalent, as in $Fe''Cl_2$ or $Mn''SO_4$, while in the other they are quadrivalent; but when quadrivalent, the atoms do not enter into combination singly, but grouped, two together, to form a hexavalent unit $\left[\begin{matrix}\text{Fe}\equiv \\ | \\ \text{Fe}\equiv\end{matrix}\right]^{vi}$, as in $(Fe_2)^{vi}Cl_6$, $(Cr_2)^{vi}O_3$. They form several oxids; of which the oxid MO_3 is an anhydrid, corresponding to which are acids and salts. Most of the other oxids are basic.

CHROMIUM.

Symbol = **Cr**—*Atomic weight* = 52.06—*Molecular weight* = 104.12 (?)—*Sp. gr.* = 6.8—*Discovered by Vauquelin*, 1797—*Name from* *χρῶμα* = color.

Occurs in nature principally as chrome ironstone, a double oxid of Cr and Fe. The element is separated with difficulty by reduction of its oxid by charcoal, or of its chlorid by sodium. It is a hard, crystalline, almost infusible metal. Combines with O only at a red heat. It is not attacked by acids, except HCl; is readily attacked by alkalies.

Chromic Oxid—*Sesquioxid, or green oxid of chromium*—Cr_2O_3—152.8—obtained, amorphous, by calcining a mixture of potassium dichromate and starch, or, crystallized, by heating neutral potassium chromate to redness in Cl.

It is green; insoluble in H_2O, acids, and alkalies; fusible with difficulty, and not decomposed by heat; not reduced by H. At a red heat in air, it combines with alkaline hydroxids, and nitrates, to form chromates. It forms two series of salts, the terms of one of which are green, those of the other violet. The alkaline hydroxids separate a bluish-green hydrate from solutions of the green salts, and a bluish-violet hydrate from those of the violet salts.

Chromium green, or **emerald green,** is a green hydrate, formed by decomposing a double borate of chromium and potassium by H_2O. It is used in the arts as a substitute for the arsenical greens, and is non-poisonous.

Chromic Anhydrid—Acidum chromicum (U. S.)—CrO_3—100.4—is formed by decomposing a solution of potassium dichromate by excess of H_2SO_4, and crystallizing.

It crystallizes in deliquescent crimson prisms, very soluble in H_2O, and in dilute alcohol. It is a powerful oxidant, capable of igniting strong alcohol.

The true chromic acid has not been isolated, but salts are known which correspond to three acid hydrates: H_2CrO_4 = **chromic acid**; $H_2Cr_2O_7$ = **dichromic acid**; and $H_2Cr_3O_{10}$ = **trichromic acid.**

Chlorids.—Two chlorids and one oxychlorid of chromium are known. **Chromous chlorid,** $CrCl_2$, is a white solid, soluble, with a blue color, in H_2O. **Chromic chlorid,** $(Cr_2)Cl_6$, forms large, red crystals, insoluble in H_2O when pure.

Sulfates.—A *violet* sulfate crystallizes in octahedra, $(Cr)_2(SO_4)_3 +$ 15 Aq, and is very soluble in H_2O. At 100° it is converted into a *green* salt, $(Cr)_2(SO_4)_3 + 5$ Aq, soluble in alcohol; which, at higher temperatures, is converted into the red, insoluble, anhydrous salt. Chromic sulfate forms double sulfates, containing 24 Aq, with the alkaline sulfates. (See Alums.)

Analytical Characters.—CHROMOUS SALTS.—(1.) Potash, a brown ppt. (2.) Ammonium hydroxid, greenish-white ppt. (3.) Alkaline sulfids, black ppt. (4.) Sodium phosphate, blue ppt.

CHROMIC SALTS.—(1.) Potash, green ppt.; an excess of precipitant forms a green solution, from which Cr_2O_3 separates on boiling. (2.) Ammonium hydroxid, greenish-gray ppt. (3.) Ammonium sulfhydrate, greenish ppt.

CHROMATES.—(1.) H_2S in acid solution, brownish color, changing to green. (2.) Ammonium sulfhydrate, greenish ppt. (3.) Barium chlorid, yellowish ppt. (4.) Silver nitrate, brownish-red ppt., soluble in HNO_3 or NH_4HO. (5.) Lead acetate, yellow ppt., soluble in potash, insoluble in acetic acid.

Action on the Economy.—*Chromic anhydrid* oxidizes organic substances, and is used as a caustic.

The *chromates*, especially potassium dichromate (*q. v.*), are irritants, and have a distinctly poisonous action as well. Workmen handling the dichromate are liable to a form of chronic poisoning.

In acute chromium-poisoning, emetics, and subsequently magnesium carbonate in milk, are to be given.

MANGANESE.

Symbol = **Mn**—*Atomic weight* = 54—*Molecular weight* = 108 (?) —*Sp. gr.* = 7.138–7.206.

Occurs chiefly in pyrolusite, MnO_2, hausmanite, Mn_3O_4, braunite, Mn_2O_3, and manganite, Mn_2O_3, H_2O. A hard, grayish, brittle metal; fusible with difficulty; obtained by reduction of its oxids by C at a white heat. It is not readily oxidized by cold, dry air; but is superficially oxidized when heated. It decomposes H_2O, liberating H; and dissolves in dilute acids.

Oxids.—Manganese forms six oxids or compounds representing them: **Manganous oxid,** MnO; **manganoso-manganic oxid,** Mn_3O_4; **manganic oxid,** Mn_2O_3; **permanganic oxid,** MnO_2, and **permanganic anhydrid,** Mn_2O_7, are known free. **Manganic anhydrid,** MnO_3, has not been isolated. MnO and Mn_2O_3 are basic; Mn_3O_4

and MnO_2 are indifferent oxids; and MnO_3 and Mn_2O_7 are anhydrids, corresponding to the **manganates** and **permanganates.**

Permanganic Oxid—*Manganese dioxid, or black oxid*—**Mangani oxidum nigrum (U. S.)—Manganesii ox. nig. (Br.)—MnO_2**—86—exists in nature as **pyrolusite,** the principal ore of manganese, in steel gray, or brownish-black, imperfectly crystalline masses.

At a red heat it loses 12 per cent. of O : $3MnO_2 = Mn_3O_4 + O_2$; and, at a white heat, a further quantity of O is given off: $2Mn_3O_4 = 6MnO + O_2$. Heated with H_2SO_4, it gives off O, and forms manganous sulfate: $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$. With HCl it yields manganous chlorid, H_2O and Cl : $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$. It is not acted on by HNO_3.

Chlorids.—Two chlorids of Mn are known: **manganous chlorid,** $MnCl_2$, a pink, deliquescent, soluble salt, occurring, mixed with ferric chlorid, in the waste liquid of the preparation of Cl; and **manganic chlorid,** Mn_2Cl_6.

Salts of Manganese.—Manganese forms two series of salts: **Manganous salts,** containing Mn''; and **manganic salts,** containing $(Mn_2)^{vi}$; the former are colorless or pink, and soluble in water; the latter are unstable.

Manganous Sulfate—Mangani sulfas (U. S.)—$MnSO_4 + n$Aq—$150 + n18$—is formed by the action of H_2SO_4 on MnO_2. Below 6° (42°.8 F.) it crystallizes with 7 Aq, and is isomorphous with ferrous sulfate; between 7°–20° (44°.6–68° F.) it forms crystals with 5 Aq, and is isomorphous with cupric sulfate; between 20°–30° (68°–86° F.), it crystallizes with 4 Aq. It is rose-colored, darker as the proportion of Aq increases, soluble in H_2O, insoluble in alcohol. With the alkaline sulfates it forms double salts, with 6 Aq.

Analytical Characters.—MANGANOUS.—(1.) Potash, white ppt., turning brown. (2.) Alkaline carbonates, white ppts. (3.) Ammonium sulfhydrate, flesh-colored ppt., soluble in acids, sparingly soluble in excess of precipitant. (4.) Potassium ferrocyanid, faintly reddish-white ppt., in neutral solution; soluble in HCl. (5.) Potassium cyanid, rose-colored ppt., forming brown solution with excess.

MANGANIC.—(1.) H_2S, ppt. of sulfur. (2.) Ammonium sulfhydrate, flesh-colored ppt. (3.) Potassium ferrocyanid, greenish ppt. (4.) Potassium ferricyanid, brown ppt. (5.) Potassium cyanid, light brown ppt.

MANGANATES—are green salts, whose solutions are only stable in presence of excess of alkali, and turn brown when diluted and acidulated.

PERMANGANATES—form red solutions, which are decolorized by SO_2, other reducing agents, and many organic substances.

IRON.

Symbol = **Fe** (**FERRUM**)—*Atomic weight* = 55.9—*Molecular weight* = 111.8 (?)—*Sp. gr.* = 7.25-7.9—*Fuses at* 1600° (2912° F.)—*Name from the Saxon*, iren.

Occurrence.—Free, in small quantity only, in platinum ores and meteorites. As Fe_2O_3 in *red hæmatite* and *specular iron;* as hydrates of Fe_2O_3 in *brown hæmatite* and *oölitic iron;* as Fe_3O_4 in *magnetic iron;* as $FeCO_3$ in *spathic iron*, *clay ironstone* and *bog ore;* and as FeS_2 in *pyrites.* It is also a constituent of most soils and clays, exists in many mineral waters, and in the red blood pigment of animals.

Preparation.—In working the ores, reduction is first effected in a *blast-furnace*, into which alternate layers of ore, coal and limestone are fed from the top, while air is forced in from below. In the lower part of the furnace CO_2 is produced, at the expense of the coal; higher up it is reduced by the incandescent fuel to CO, which, at a still higher point, reduces the ore. The fused metal, so liberated, collects at the lowest point, under a layer of *slag;* and is drawn off to be cast as *pig iron.* This product is then purified, by burning out impurities, in the process known as *puddling.*

Pure iron is prepared by reduction of ferrous chlorid, or of ferric oxid, by H at a temperature approaching redness.

Varieties.—*Cast iron* is a brittle, white or gray, crystalline metal, consisting of Fe 89-90%; C 1-4.5%; and Si, P, S, and Mn. As *pig iron*, it is the product of the blast-furnace.

Wrought, or *bar iron*, is a fibrous, tough metal, freed in part from the impurities of cast iron, by *refining* and *puddling.*

Steel is Fe combined with a quantity of C, less than that existing in cast iron, and greater than that in bar iron. It is prepared by *cementation;* which consists in causing bar iron to combine with C; or by the *Bessemer method;* which, as now used, consists in burning the C out of molten cast iron, to which the proper proportion of C is then added in the shape of *spiegel eisen*, an iron rich in Mn and C.

The purest forms of commercial iron are those used in piano-strings, the teeth of carding machines, and electro-magnets; known as *soft iron.*

Reduced iron—**Ferrum reductum** (**U. S.**)—**Fer. redactum** (**Br.**)—is Fe, more or less mixed with Fe_2O_3 and Fe_3O_4, obtained by heating Fe_2O_3 in H.

Properties.—*Physical.*—Pure iron is silver-white; quite soft; crystallizes in cubes or octahedra. *Wrought iron* is gray, hard, very tenacious, fibrous, quite malleable and ductile, capable of being welded, highly magnetic, but only temporarily so. *Steel* is gray, very hard and brittle if *tempered*, soft and tenacious if not, permanently magnetic.

Chemical.—Iron is not altered by dry air at the ordinary temperature. At a red heat it is oxidized. In damp air it is converted into a hydrate, *iron rust*. *Tinplate* is sheet iron, coated with tin; *galvanized iron* is coated with zinc, to preserve it from the action of damp air.

Iron unites directly with Cl, Br, I, S, N, P, As, and Sb. It dissolves in HCl as ferrous chlorid, while H is liberated. Heated with strong H_2SO_4, it gives off SO_2; with dilute H_2SO_4, H is given off and ferrous sulfate formed. Dilute HNO_3 dissolves Fe, but the concentrated acid renders it *passive*, when it is not dissolved by either concentrated or dilute HNO_3, until the passive condition is destroyed by contact with Pt, Ag or Cu, or by heating to 40° (104° F.).

Compounds of Iron.—Oxids.—Three oxids of iron exist free: FeO; Fe_2O_3; Fe_3O_4.

Ferrous Oxid—*Protoxid of iron*—**FeO**—71.9—is formed by heating Fe_2O_3 in CO or CO_2.

Ferric Oxid—*Sesquioxid or peroxid of iron—Colcothar—Jeweller's rouge—Venetian red*—$\mathbf{Fe_2O_3}$—159.8—occurs in nature (see above; and is formed when ferrous sulfate is strongly heated, as in the manufacture of pyrosulfuric acid. It is a reddish, amorphous solid, is a weak base, and is decomposed at a white heat into O and Fe_3O_4.

Magnetic Oxid—*Black oxid—Ferri oxidum magneticum* (*Br.*)—$\mathbf{Fe_3O_4}$—231.7—is the **natural loadstone**, and is formed by the action of air, or steam, upon iron at high temperatures. It is probably a compound of ferrous and ferric oxids (FeO, Fe_2O_3), as acids produce with it mixtures of ferrous and ferric salts.

Hydrates.—Ferrous.—When a solution of a ferrous salt is decomposed by an alkaline hydroxid, a greenish-white hydroxid, FeH_2O_2, is deposited; which rapidly absorbs O from the air, with formation of ferric hydroxid.

Ferric.—When an alkali is added to a solution of a ferric salt, a brown, gelatinous precipitate is formed, which is the **normal ferric hydroxid,** $(Fe)_2H_6O_6$ = **Ferri peroxidum hydratum (U. S.)**; **Fer. perox. humidum (Br.)**. It is not formed in the presence of fixed organic acids, or of sugar in sufficient quantity. If preserved under H_2O, it is partly oxidized, forming an oxyhydrate which is incapable of forming ferrous arsenate with As_2O_3.

If the hydroxid, $(Fe_2)H_6O_6$, be dried at 100° (212° F.), it loses $2H_2O$, and is converted into $(Fe_2)O_2$, H_2O_2, which is the *Ferri peroxidum hydratum* (*Br.*).

If the **normal** hydroxid be dried *in vacuo*, it is **converted into** $(Fe_2)_2H_6O_9$, and this, when boiled for some hours with H_2O, is converted into the **colloid** or **modified hydrate** $(Fe_2)H_2O_4$ (?), which is brick-red in color, almost insoluble in HNO_3 and HCl, gives no Prussian blue reaction, and forms a turbid solution with acetic acid. If recently precipitated ferric hydroxid be dissolved in solution of ferric chlorid or acetate, and subjected to dialysis, almost all the acid passes out, leaving in the dialyzer a dark red solution, which probably contains this colloid hydrate, and which is instantly coagulated by a trace of H_2SO_4, by alkalies, many salts, and by heat; **dialyzed iron.**

Ferric Acid.—$H_2Fe_2O_4$.—Neither the free acid nor the oxid, FeO_3, are known in the free state; the **ferrates,** however, of Na, K, Ba, Sr, and Ca are known.

Sulfids. — Ferrous Sulfid — *Protosulfid of iron*—**FeS** — 87.9—is formed:

(1) By heating a mixture of finely divided Fe and S to redness; (2) by pressing roll-sulfur on white-hot iron; (3) in a hydrated condition, FeS,H_2O, by treating a solution of a ferrous salt with an alkaline sulfhydrate.

The dry sulfid is a brownish, brittle, magnetic solid, insoluble in H_2O, soluble in acids with evolution of H_2S. The hydrate is a black powder, which absorbs O from the air, turning yellow, by formation of Fe_2O_3, and liberation of S. It occurs in the fæces of persons taking chalybeate waters or preparations of iron.

Ferric Sulfid—*Sesquisulfid*—**Fe_2S_3**—207.8—occurs in nature in *copper pyrites*, and is formed when the disulfid is heated to redness.

Ferric Disulfid—FeS_2—119.9—occurs in the *white* and *yellow Martial pyrites*, used in the manufacture of H_2SO_4. When heated in air, it is decomposed into SO_2 and *magnetic pyrites*: $3FeS_2 + 2O_2 = Fe_3S_4 + 2SO_2$.

Chlorids.—Ferrous Chlorid—*Protochlorid*—**$FeCl_2$**—129.9—is produced: (1) by passing dry HCl over red-hot Fe; (2) by heating ferric chlorid in H; (3), as a hydrate, $FeCl_2, 4H_2O$, by dissolving Fe in HCl.

The anhydrous compound is a yellow, crystalline, volatile, and very soluble solid. The hydrated is in greenish, oblique rhombic prisms, deliquescent and very soluble in H_2O and alcohol. When heated in air it is converted into ferric chlorid, and an oxychlorid.

Ferric Chlorid—*Sesquichlorid*—*Perchlorid*—**Ferri chloridum (U. S.)—Fe_2Cl_6**—324.8—is produced, in the anhydrous form, by heating Fe in Cl. As a hydrate, $Fe_2Cl_6,4H_2O$, or $Fe_2Cl_6,6H_2O$, it is formed: (1) by solution of the anhydrous compound; (2) by dissolving Fe in aqua regia; (3) by dissolving ferric hydroxid in

HCl; (4) by the action of Cl or of HNO_3 on solution of ferrous chlorid. It is by the last method that the pharmaceutical product is obtained.

The anhydrous compound forms reddish-violet, crystalline plates, very deliquescent. The hydrates form yellow, nodular, imperfectly crystalline masses, or rhombic plates, very soluble in H_2O, soluble in alcohol and ether. In solution, it is converted into $FeCl_2$ by reducing agents. The **Liq. ferri chloridi** (**U. S.**) = **Liq. fer. perchloridi** (**Br.**) is an aqueous solution of this compound, containing excess of acid. The **Tinct. fer. chlor.** (**U. S.**) and **Tinct. fer. perchl.** (**Br.**) are the solution, diluted with alcohol; and contain ethyl chlorid and ferrous chlorid.

Bromids.—Ferrous Bromid—$FeBr_2$—215.9—is formed by the action of Br on excess of Fe, in presence of H_2O.

Ferric Bromid—Fe_2Br_6—591.8—is prepared by the action of excess of Br on Fe.

Iodids.—Ferrous Iodid—Ferri iodidum (**U. S.; Br.**)—**FeI_2**—309.9—is obtained, with $4H_2O$, by the action of I upon excess of Fe in the presence of warm H_2O. When anhydrous, it is a white powder; hydrated, it is in green crystals. In air it is rapidly decomposed, more slowly in the presence of sugar.

Ferric Iodid—Fe_2I_6—873.8—is formed by the action of excess of I on Fe.

Salts of Iron.—Sulfates.—Ferrous Sulfate—*Protosulfate*—**Green vitriol—Copperas—Ferri sulfas** (**U. S.; Br.**)—**$FeSO_4+7$ Aq**—151.9 + 126—is formed: (1) by oxidation of the sulfid, Fe_3S_4, formed in the manufacture of H_2SO_4; (2) by dissolving Fe in dilute H_2SO_4.

It forms green, efflorescent, oblique rhombic prisms, quite soluble in H_2O, insoluble in alcohol. It loses 6 Aq at 100° (212° F.) (**Ferr. sulf. exsiccatus, U. S.**); and the last Aq at about 300° (572° F.). At a red heat it is decomposed into Fe_2O_3; SO_2 and SO_3. By exposure to air it is gradually converted into a basic ferric sulfate, $(Fe_2)(SO_4)_2,5Fe_2O_3$.

Ferric Sulfates are quite numerous, and are formed by oxidations of ferrous sulfate under different conditions. The normal sulfate, $(Fe_2)(SO_4)_3$, is formed by treating solution of $FeSO_4$ with HNO_3, and evaporating, after addition of one molecule of H_2SO_4 for each two molecules of $FeSO_4$. The **Liq. fer. tersulfatis** (**U.S.**) contains this salt. It is a yellowish-white, amorphous solid.

Of the many **basic ferric sulfates**, the only one of medical interest is **Monsel's salt**, $5(Fe_2)(SO_4)_2+4Fe_2O_3$, which exists in the **Liq. ferri subsulfatis** (**U. S.**) and **Liq. fer. persulfatis** (**Br.**). Its solution is decolorized, and forms a white deposit with excess of H_2SO_4.

Nitrates.—Ferrous Nitrate—$Fe(NO_3)_2$—179.9—a greenish, unstable salt, formed by double decomposition between barium nitrate and ferrous sulfate; or by the action of HNO_3 on FeS.

Ferric Nitrates—The *normal nitrate*—**$(Fe_2)(NO_3)_6$**—483.8—is obtained in solution by dissolving Fe in HNO_3 of sp. gr. 1.115; or by dissolving ferric hydroxid in HNO_3. It therefore exists in the *Liq. ferri nitratis* (*U. S.*). It crystallizes in rhombic prisms with 18 Aq, or in cubes with 12 Aq.

Several basic nitrates are known, all of which are uncrystallizable, and by their presence (as when Fe is dissolved in HNO_3 to saturation) prevent the crystallization of the normal salt.

Phosphates.—Triferrous Phosphate—$Fe_3(PO_4)_2$—357.7.—A white precipitate, formed by adding disodic phosphate to a solution of a ferrous salt, in presence of sodium acetate. By exposure to air it turns blue; a part being converted into ferric phosphate. The *ferri phosphas* (*Br.*) is such a mixture of the two salts. It is insoluble in H_2O; sparingly soluble in H_2O containing carbonic or acetic acid.

It is probably this phosphate, capable of turning blue, which sometimes occurs in the lungs in phthisis, in blue pus, and in long-buried bones.

Ferric Phosphate—$(Fe_2)(PO_4)_2$—301.8—is produced by the action of an alkaline phosphate on ferric chlorid. It is soluble in HCl, HNO_3, citric and tartaric acids, insoluble in phosphoric acid and in solution of hydrosodic phosphate. The **ferri phosphas** (**U. S.**) is a compound, or mixture of this salt with disodic citrate, which is soluble in water.

There exist quite a number of basic ferric phosphates.

Ferric Pyrophosphate—$(Fe_2)_2(P_2O_7)_3$—745.6—is precipitated by decomposition of a solution of a ferric compound by sodium pyrophosphate; an excess of the Na salt dissolves the precipitate when warmed, and, on evaporation, leaves scales of a double salt, $(Fe_2)_2(P_2O_7)_3$, $Na_8(P_2O_7)_2 + 20$ Aq.

The **ferri pyrophosphas** (**U. S.**) is a mixture of ferric pyrophosphate, trisodic citrate, and ferric citrate.

Acetates.—Ferrous Acetate—$Fe(C_2H_3O_2)_2$—173.9—is formed by decomposition of ferrous sulfate by calcium acetate, in soluble, silky needles.

Ferric Acetates.—The *normal salt*, $(Fe_2)(C_2H_3O_2)_6$, is obtained by adding slight excess of ferric sulfate to lead acetate, and decanting after twenty-four hours. It is dark red, uncrystallizable, very soluble in alcohol, and in H_2O. If its solution be heated it darkens suddenly, gives off acetic acid, and contains a basic acetate. When boiled, it loses all its acetic acid, and deposits ferric hydrate. When heated in closed vessels to 100° (212° F.), and treated with a trace of mineral acid, it deposits the modified ferric hydrate.

Ferrous Carbonate—$FeCO_3$—115.9—occurs as an ore of iron, and is obtained, in a hydrated form, by adding an alkaline carbonate to a ferrous salt. It is a greenish, amorphous powder, which on exposure to air, turns red by formation of ferric hydrate; a change which is retarded by the presence of sugar, hence the addition of that substance in the **ferri carbonas saccharatus** (**U. S.; Br.**). It is insoluble in pure H_2O, but soluble in H_2O containing carbonic acid, probably as **ferrous bicarbonate**, $H_2Fe(CO_3)_2$, in which form it occurs in chalybeate waters.

Ferrous Lactate—Ferri lactas (**U. S.**)—**$Fe(C_3H_5O_3)_2+3Aq$**—233.9+54—is formed when iron filings are dissolved in lactic acid. It crystallizes in greenish-yellow needles; soluble in H_2O; insoluble in alcohol; permanent in air when dry.

Ferrous Oxalate—Ferri oxalas (**U. S.**) **FeC_2O_4+Aq**—143.9+36—is a yellow, crystalline powder; sparingly soluble in H_2O; formed by dissolving iron filings in solution of oxalic acid.

Tartrates—Ferrous Tartrate—$FeC_4H_4O_6+2Aq$—203.9+36.—A white, crystalline powder; formed by dissolving Fe in hot concentrated solution of tartaric acid.

Ferric Tartrate—$Fe_2(C_4H_4O_6)_3+3Aq$—555.8+54—A dirty yellow, amorphous mass, obtained by dissolving recently precipitated ferric hydroxid in tartaric acid solution, and evaporating below 59° (122° F.).

A number of double tartrates, containing the group $(Fe_2O_2)''$ are also known. Such are: **Ferrico-ammonic tartrate = ferri et ammonii tartras** (**U. S.**), $(C_4H_4O_6)_2(Fe_2O_2)$, $(NH)_4+4Aq$, and **Ferrico-potassic tartrate = ferri et potassii tartras** (**U. S.**), $(C_4H_4O_6)_2(Fe_2O_2)K_2$. They are prepared by dissolving recently precipitated ferric hydroxid in hot solutions of the hydro-alkaline tartrate. They only react with ferrocyanids and sulfocyanates after addition of a mineral acid.

Citrates.—Ferric Citrate—Ferri citras (**U. S.**)—**$(Fe_2)(C_6H_5O_7)_2+6Aq$**—489.8+108—is in garnet-colored scales, obtained by dissolving ferric hydrate in solution of citric acid, and evaporating the solution at about 60° (140° F.). It loses 3 Aq at 120° (248° F.), and the remainder at 150° (302° F.). If a small quantity of ammonium hydroxid be added, before the evaporation, the product consists of the **modified citrate = ferri et ammonii citras** (**U. S.**), which only reacts with potassium ferrocyanid after addition of HCl.

The various citrates of iron and alkaloids are not definite compounds.

Ferric Ferrocyanid—Prussian blue—$(Fe_2)_2(FeC_6N_6)_3+18Aq$—859.3+324—is a dark blue precipitate, formed when potassium ferrocyanid is added to a ferric salt. It is insoluble in H_2O, alcohol and dilute acids; soluble in oxalic acid solution (blue ink). Alkalies turn it brown.

Ferrous Ferricyanid—Turnbull's blue—$Fe_3(Fe_2C_{12}N_{12})+n$Aq— 591.5+*n*18—is a dark blue substance produced by the action of potassium ferricyanid on ferrous salts. Heated in air it is converted into Prussian blue and ferric oxid.

Analytical Characters.—FERROUS—Are acid; colorless when anhydrous; pale green when hydrated; oxidized by air to basic ferric compounds. (1.) Potash: greenish-white ppt.; insoluble in excess; changing to green or brown in air. (2.) Ammonium hydroxid: greenish ppt.; soluble in excess; not formed in presence of ammoniacal salts. (3.) Ammonium sulfhydrate: black ppt.; insoluble in excess; soluble in acids. (4.) Potassium ferrocyanid (in absence of ferric salts): white ppt.; turning blue in air. (5.) Potassium ferricyanid: blue ppt.; soluble in KHO; insoluble in HCl.

FERRIC—Are acid, and yellow or brown. (1.) Potash, or ammonium hydroxid: voluminous, red-brown ppt.; insoluble in excess. (2.) Hydrogen sulfid: in acid solution; milky ppt. of sulfur; ferric reduced to ferrous compound. (3.) Ammonium sulfhydrate: black ppt.; insoluble in excess; soluble in acids. (4.) Potassium ferrocyanid: dark blue ppt.; insoluble in HCl; soluble in KHO. (5.) Potassium sulfocyanate: dark-red color; prevented by tartaric or citric acid; discharged by mercuric chlorid. (6.) Tannin: blue-black color.

III. ALUMINIUM GROUP.

GLUCINIUM—ALUMINIUM—SCANDIUM—GALLIUM—INDIUM.

This group is placed in the third class by virtue of the existence of the aluminates, and of the relations between the compounds of these elements and some of those of the previous group. They form one series of compounds, corresponding to the ferric, containing the group $(M_2)^{vi}$, but no compounds corresponding to the ferrous M'' are known. Indeed, certain organic compounds, such as aluminium acetylacetonate, $Al(C_5H_7O_2)_3$, seem to contain single, trivalent atoms of the metal. No acids or salts of the members of the group, other than aluminium, are known; yet their resemblances in other points are such as to forbid their separation.

GLUCINIUM.

Symbol = **Gl** or **Be** (*Beryllium*)—*Atomic weight* = 9—*Sp. gr.* = 2.1.

A rare element occurring in the emerald and beryl. The metal resembles aluminium and its compounds resemble those of Al, and, in some respects, those of Mg. Its soluble salts are sweet in taste (γλυκύς = sweet).

ALUMINIUM.

Symbol = **Al**—*Atomic weight* = 27—*Molecular weight* = 55 (?)—*Sp. gr.* = 2.56–2.67—*Fuses at about* 700° (1292° F.)—*Name from* alumen=*alum*—*Discovered by Wöhler*, 1827.

Occurrence.—Exceedingly abundant in the clays as *silicate*.

Preparation.—(1.) By decomposing vapor of aluminium chlorid by Na or K(Wöhler). (2.) Aluminium hydroxid, mixed with sodium chlorid and charcoal, is heated in Cl, by which a double chlorid of Na and Al (2NaCl, Al_2Cl_6) is formed. This is then heated with Na, when Al and NaCl are produced. (The industrial process.)

Properties.—*Physical.*—A bluish-white metal; hard; quite malleable, and ductile, when annealed from time to time; slightly magnetic; a good conductor of electricity; non-volatile; very light, and exceedingly sonorous.

Chemical.—It is not affected by air or O, except at very high temperatures, and then only superficially. If, however, it contain Si, it burns readily in air, forming aluminium silicate. It does not decompose H_2O at a red heat; but in contact with Cu, Pt, or I, it does so at 100° (212° F.). It combines directly with B, Si, Cl, Br, and I. It is attacked by HCl, gaseous or in solution, with evolution of H, and formation of Al_2Cl_6. It dissolves in alkaline solutions, with formation of **aluminates**, and liberation of H. It alloys with Cu to form a golden yellow metal (**aluminium bronze**).

Aluminium Oxid—*Alumina*—$\mathbf{Al_2O_3}$—102—occurs in nature, nearly pure, as *corundum*, *emery*, *ruby*, *sapphire* and *topaz;* and is formed artificially, by calcining the hydrate, or ammonia alum, at a red heat.

It is a light, white, odorless, tasteless powder; fuses with difficulty; and, on cooling, solidifies in very hard crystals. Unless it have been heated to bright redness, it combines with H_2O, with elevation of temperature. It is almost insoluble in acids and alkalies. H_2SO_4, diluted with an equal bulk of H_2O, dissolves it slowly as $(Al_2)(SO_4)_3$. Fused potash and soda combine with it to form aluminates. It is not reduced by charcoal.

Aluminium Hydroxid—*Aluminium hydrate*—**Aluminii hydras (U. S.)**—$\mathbf{Al_2H_6O_6}$—156—is formed when a solution of an aluminium salt is decomposed by an alkali, or alkaline carbonate. It constitutes a gelatinous mass, which, when dried, leaves an amorphous, translucid mass; and, when pulverized, a white, tasteless, amorphous powder. When the liquid in which it is formed contains coloring matters, these are carried down with it, and the dried deposits are used as pigments, called **lakes**.

When freshly precipitated, it is insoluble in H_2O; soluble in acids, and in solutions of the fixed alkalies. When dried at a temperature above 50° (122° F.), or after 24 hours' contact with the mother liquor, its solubility is greatly diminished. With acids it forms salts of aluminium; and with alkalies, aluminates of the alkaline metal. Heated to near redness, it is decomposed into Al_2O_3 and H_2O. A soluble modification is obtained by dialyzing a solution of $Al_2H_6O_6$ in Al_2Cl_6, or by heating a dilute solution of aluminium acetate for 24 hours.

Aluminates are for the most part crystalline, soluble compounds, obtained by the action of metallic oxids or hydroxids upon alumina. **Potassium aluminate,** $K_2Al_2O_4+3Aq$, is formed by dissolving recently precipitated aluminium hydroxid in potash solution. It forms white crystals; very soluble in H_2O, insoluble in alcohol; caustic and alkaline. By a large quantity of H_2O it is decomposed into aluminium hydroxid, and a more alkaline salt, $K_6Al_4O_9$.

Sodium Aluminate.—The aluminate $Na_2Al_2O_4$ is not known. That having the composition $Na_6Al_4O_9$ is prepared by heating to redness a mixture of 1 pt. sodium carbonate and 2 pts. of a native ferruginous aluminium hydrate (beauxite). It is insoluble in H_2O, and is decomposed by carbonic acid, with precipitation of aluminium hydroxid.

Aluminium Chlorid—Al_2Cl_6—267—is prepared by passing Cl over a mixture of Al_2O_3 and C, heated to redness; or by heating clay in a mixture of gaseous HCl and vapor of CS_2.

It crystallizes in colorless, hexagonal prisms; fusible; volatile; deliquescent; very soluble in H_2O and in alcohol. From a hot, concentrated solution, it separates in prisms with 12 Aq.

The disinfectant called **chloralum** is a solution of impure Al_2Cl_6.

Aluminium Sulfate—Aluminii sulfas (U.S.)—$(Al_2)(SO_4)_3 + 18$ Aq—342 + 324—is obtained by dissolving $Al_2H_6O_6$ in H_2SO_4; or (industrially) by heating clay with H_2SO_4.

It crystallizes, with difficulty, in thin, flexible plates; soluble in H_2O; very sparingly soluble in alcohol. Heated, it fuses in its Aq, which it gradually loses up to 200° (392° F.), when a white, amorphous powder, $(Al_2)(SO_4)_3$, remains; this is decomposed at a red heat, leaving a residue of pure alumina.

Alums—are double sulfates of the alkaline metals, and the higher sulfates of this, or the preceding group. When crystallized, they have the general formula: $(M_2)^{vi}(SO_4)_3, R'_2SO_4 + 24$ Aq, in which (M) may be (Fe_2), (Mn_2), (Cr_2), (Al_2), or (Ga_2); and R_2 may be K_2, Na_2, Rb_2, Cs_2, Tl_2, or $(NH_4)_2$. They are isomorphous with each other.

Alumen (U. S.)—$Al_2(SO_4)_3, K_2SO_4 + 24$ Aq—516 + 432—is manufactured from "alum shale," and is formed when solutions of the sulfates of Al and K are mixed in suitable proportion.

It crystallizes in large, transparent, regular octahedra; has a sweetish, astringent taste, and is readily soluble in H_2O. Heated, it fuses in its Aq at 92° (197°.6 F.); and gradually loses 45.5 per cent. of its weight of H_2O, as the temperature rises to near redness. The product, known as **burnt alum** = **alumen exsiccatum (U. S.)**, is $(Al)_2(SO_4)_3$, K_2SO_4, and is slowly, but completely soluble in 20–30 pts. H_2O. At a bright red heat, SO_2 and O are given off, and Al_2O_3 and potassium sulfate remain; at a higher temperature, potassium aluminate is formed. Its solutions are acid in reaction; dissolve Zn and Fe with evolution of H; and deposit $Al_2H_6O_6$ when treated with ammonium hydroxid.

Alumen (Br.)—$Al_2(SO_4)_3,(NH_4)_2SO_4 + 24\ Aq$—474 + 432—is the compound now usually met with as **alum**, both in this country and in England. It differs from potash alum in being more soluble in H_2O, between 20°–30° (68°–86° F.), and less soluble at other temperatures; and in the action of heat upon it. At 92° (197°.6 F.) it fuses in its Aq; at 205° (401° F.) it loses its ammonium-sulfate, leaving a white, hygroscopic substance, very slowly and incompletely soluble in H_2O. More strongly heated, it leaves **alumina.**

Silicates—are very abundant in the different varieties of *clay*, *feldspar*, *albite*, *labradorite*, *mica*, etc. The clays are hydrated aluminium silicates, more or less contaminated with alkaline and earthy salts and iron, to which last certain clays owe their color. The purest is **kaolin,** or porcelain clay, a white or grayish powder. They are largely used in the manufacture of the different varieties of bricks, terra cotta, pottery, and porcelain. *Porcelain* is made from the purer clays, mixed with sand and feldspar; the former to prevent shrinkage, the latter to bring the mixture into partial fusion, and to render the product translucent. The fashioned articles are subjected to a first baking. The porous, baked clay is then coated with a *glaze*, usually composed of oxid of lead, sand, and salt. During a second baking, the glaze fuses, and coats the article with a hard, impermeable layer. The coarser articles of pottery are glazed by throwing sodium chlorid into the fire; the salt is volatilized, and, on contact with the hot aluminium silicate, deposits a coating of the fusible sodium silicate, which hardens on cooling.

Analytical Characters.—(1.) Potash, or soda; white ppt.; soluble in excess. (2.) Ammonium hydroxid; white ppt.; almost insoluble in excess, especially in presence of ammoniacal salts. (3.) Sodium phosphate; white ppt.; readily soluble in KHO and NaHO, but not in NH_4HO; soluble in mineral acids, but not in acetic acid. (4.) Blowpipe—on charcoal does not fuse, and moistened with cobalt nitrate solution turns dark sky-blue.

SCANDIUM.

Symbol = **Sc**—*Atomic weight* = 44.9—*Discovered by Nilson* (1879) —*Name from* Scandia.

Occurs in minute traces in gadolinite and euxenite. It forms an oxid, Sc_2O_3; a light, white, infusible powder; sp. gr. 3.8; resembling alumina.

GALLIUM.

Symbol = **Ga**—*Atomic weight* = 68.8—*Sp. gr.* = 5.9—*Fuses at* 36° (86° *F.*)—*Name from* Gallia—*Discovered by Lecoq de Boisbaudran* (1876).

Occurs in very small quantity in certain zinc blendes. It is a hard, white metal; soluble in hot HNO_3, in HCl, and in KHO solution. In chemical characters it closely resembles Al; forms an oxid, Ga_2O_3, and a series of alums.

The discovery of Sc and Ga affords most flattering verifications of predictions based upon purely theoretical considerations.

It has been observed that there exist numerical relations between the atomic weights of the elements, which, in groups of allied elements, differ from each other by (approximately) some multiple of eight. Upon this variation Mendelejeff has based what is known as the **Periodic Law,** to the effect that: **"The properties of elements, the constitution of their compounds, and the properties of the latter, are periodic functions of the atomic weights of the elements."**

In accordance with this law the elements may be thus arranged:

Series.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group. VIII.
	R_2O	RO	R_2O_3	RH_4 RO_2	RH_3 R_2O_5	RH_2 RO_3	RH R_2O_7	(R_2H) (RO_4)
1..............	H=1							....
2..............	Li=7	Be=9	B=11	C=12	N=14	O=16	F=19	....
3..............	Na=23	Mg=24	Al=27	Si=28	P=31	S=32	Cl=35	Cu=63 Fe=56 Co=59 Ni=59
4..............	K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=52	Mn=55	
5..............	(Cu=63)	Zn=65	Ga=69	Ge=72	As=75	Se=78	Br=80	Ru=104 Rh=104 Pd=106 Ag=108
6..............	Rb=85	Sr=87	Yt=88	Zr=90	Nb=94	Mo=96	?=100	
7..............	(Ag=108)	Cd=112	In=113	Sn=118	Sb=120	Te=125	I=127	....
8..............	Cs=133	Ba=137	La=139	Ce=142	Di=145	Sm=150	Da=154	....
9..............	....	....	E=166	....	....	....	....	Os=195 Ir=193 Pt=195 Au=197
10..............	....	....	Yb=173	....	Ta=182	W=184	?=190	
11..............	(Au=196)	Hg=200	Tl=204	Pb=207	Bi=208	....	....	....
12..............	....	....	....	Th=231	....	U=238	....	....

The atomic weights and chemical characters, which were announced by Mendelejeff in 1870 as those of the undiscovered elements which would occupy the positions 4 and 5 in group III. have been since found to be those of Sc and Ga. Still later, the vacant positions 10, III., 5, IV., 8, VI., and 8, VII., have been filled by the discovery of Yb, Ge, Sm, and Da.

INDIUM.

Symbol = **In**—*Atomic weight* = 113.4—*Sp. gr.* = 7.42—*Fuses at* 176° (348°.8 F.)—*Discovered by Reich and Richter in* 1863.

A soft, silver-white, ductile metal, which occurs in small quantity in certain zinc blendes. It is characterized spectroscopically by two principal lines—$\lambda = 4511$ and 4101.

IV. URANIUM GROUP.

URANIUM.

Symbol = **Ur**—*Atomic weight* = 238.5—*Sp. gr.* = 18.4—*Discovered by Klaproth* (1789).

This element is usually classed with Fe and Cr, or with Ni and Co. It does not, however, form compounds resembling the ferric; it forms a series of well-defined *uranates*, and a series of compounds of the radical *uranyl* $(UO)''$. Standard solutions of its acetate or nitrate are used for the quantitative determination of H_3PO_4.

V. LEAD GROUP.

LEAD.

Symbol = **Pb** (**PLUMBUM**)—*Atomic weight* = 206.9—*Molecular weight* = 413.8 (?)—*Sp. gr.* = 11.445—*Fuses at* 325° (617° F.)—*Name from* lœd = heavy (*Saxon*).

Lead is usually classed with Cd, Bi, or Cu and Hg. It differs, however, from Bi in being bivalent or quadrivalent, but not trivalent, and in forming no compounds, resembling those of bismuthyl (BiO); from Cd, in the nature of its O compounds; and from Cu and Hg in forming no compounds similar to the mercurous and cuprous salts. Indeed, the nature of the Pb compounds is such that the element is best classed in a group by itself, which finds a place in this class by virtue of the existence of potassium plumbate.

Occurrence.—Its most abundant ore is **galena**, PbS. It also occurs in **white lead ore**, $PbCO_3$, in **anglesite**, $PbSO_4$, and in **horn lead**, $PbCl_2$.

Preparation.—Galena is first roasted with a little lime. The mixture of PbO, PbS, and $PbSO_4$, so obtained, is strongly heated in a reverberatory furnace, when SO_2 is driven off. The impure *work lead*, so formed, is purified by fusion in air, and removal of the film of oxids of Sn and Sb. If the ore be rich in Ag, that metal is extracted, by taking advantage of the greater fusibility of an alloy of Pb and Ag, than of Pb alone; and subsequent oxidation of the remaining Pb.

Properties.—*Physical.*—It is a bluish-white metal; brilliant upon freshly cut surfaces; very soft and pliable; not very malleable or ductile; crystallizes in octahedra; a poor conductor of electricity; a better conductor of heat. When expanded by heat, it does not, on cooling, return to its original volume.

Chemical.—When exposed to air it is oxidized, more readily and completely at high temperatures. The action of H_2O on Pb varies with the conditions. Pure unaërated H_2O has no action upon it. By the combined action of air and moisture Pb is oxidized, and the oxid dissolved in the H_2O, leaving a metallic surface for the continuance of the action. The solvent action of H_2O upon Pb is increased, owing to the formation of basic salts, by the presence of nitrogenized organic substances, nitrates, nitrites, and chlorids. On the other hand, carbonates, sulfates, and phosphates, by their tendency to form insoluble coatings, diminish the corroding action of H_2O. Carbonic acid in small quantity, especially in presence of carbonates, tends to preserve Pb from solution, while H_2O highly charged with it (soda water) dissolves the metal readily. Lead is dissolved, as a nitrate, by HNO_3. H_2SO_4 when cold and moderately concentrated, does not affect it; but, when heated, dissolves it the more readily as the acid is more concentrated. It is attacked by HCl of sp. gr. 1.12, especially if heated. Acetic acid dissolves it as acetate, or, in the presence of CO_2, converts it into white lead.

Oxids.—**Lead Monoxid**—*Protoxid*—**Massicot**—**Litharge**—**Plumbi oxidum (U. S.; Br.)**—**PbO**—222.9—is prepared by heating Pb, or its carbonate, or nitrate, in air. If the product have been fused, it is **litharge**; if not, **massicot.** It forms copper-colored, mica-like plates, or a yellow powder; or crystallizes, from its solution in soda or potash, in white, rhombic dodecahedra, or in rose-colored cubes. It fuses near a red heat, and volatilizes at a white heat; sp. gr. 9.277–9.5. It is sparingly soluble in H_2O, forming an alkaline solution.

Heated in air to 300° (572° F.) it is oxidized to **minium.** It is readily reduced by H or C. With Cl it forms $PbCl_2$ and O. It is a strong base; decomposes alkaline salts, with liberation of the alkali. It dissolves in HNO_3, and in hot acetic acid, as nitrate or acetate. When ground up with oils it saponifies the glycerin ethers, the Pb combining with the fatty acids to form Pb soaps, one of which, **lead oleate,** is the **emplastrum plumbi, U. S.; Br.** It also combines with the alkalies and earths to form **plumbites. Calcium plumbite,** $CaPb_2O_3$, is a crystalline salt, formed by heating PbO with milk of lime, and used in solution as a hair-dye.

Plumboso-plumbic Oxid—*Red oxid*—**Minium—Red lead—Pb_3O_4**—684.7—is prepared by heating massicot to 300° (572° F.) in air. It ordinarily has the composition Pb_3O_4, and has been considered as composed of PbO_2, 2PbO; or as a basic lead salt of plumbic acid, PbO_3Pb, PbO. An orange-colored variety is formed when lead carbonate is heated to 300° (572° F.).

It is a bright red powder, sp. gr. 8.62. It is converted into PbO when strongly heated, or by the action of reducing agents. HNO_3 changes its color to brown, dissolving PbO and leaving PbO_2. It is decomposed by HCl, with formation of $PbCl_2$, H_2O and Cl.

Lead Dioxid—*Peroxid*, or *puce oxid*, or *brown oxid*, or *binoxid of lead—Plumbic anhydrid*—**PbO_2**—238.9—is prepared, either by dissolving the PbO out of red lead by dilute HNO_3, or by passing a current of Cl through H_2O, holding lead carbonate in suspension.

It is a dark, reddish-brown, amorphous powder; sp. gr. 8.903-9.190; insoluble in H_2O. Heated, it loses half its O, and is converted into PbO. It is a valuable oxidant. It absorbs SO_2 to form $PbSO_4$. It combines with alkalies to form **plumbates,** M_2PbO_3.

Plumbic Acid—PbO_3H_2—256.9—forms crystalline plates, at the + electrode, when alkaline solutions of the Pb salts are decomposed by a weak current.

Lead Sulfid—Galena—PbS—238.9—exists in nature. It is also formed by direct union of Pb and S; by heating PbO with S, or vapor of CS_2; or by decomposing a solution of a Pb salt by H_2S or an alkaline sulfid.

The native sulfid is a bluish-gray, and has a metallic lustre; sp. gr. 7.58; that formed by precipitation is a black powder; sp. gr. 6.924. It fuses at a red heat and is partly sublimed, partly converted into a subsulfate. Heated in air it is converted into $PbSO_4$, PbO and SO_2. Heated in H it is reduced. Hot HNO_3 oxidizes it to $PbSO_4$. Hot HCl converts it into $PbCl_2$. Boiling H_2SO_4 converts it into $PbSO_4$ and SO_2.

Lead Chlorid—$PbCl_2$—277.9—is formed by the action of Cl upon Pb at a red heat; by the action of boiling HCl upon Pb; and by double decomposition between a lead-salt and a chlorid.

It crystallizes in plates, or hexagonal needles; sparingly soluble in cold H_2O, less soluble in H_2O containing HCl; more soluble in hot H_2O, and in concentrated HCl.

Several oxychlorids are known. **Cassel, Paris, Verona, or Turner's yellow** is $PbCl_2$, 7PbO.

Lead Iodid—Plumbi iodidum (U. S.; Br.)—PbI_2—460.9—is deposited, as a bright yellow powder, when a solution of potassium iodid is added to a solution of a Pb salt. Fused in air, it is converted into an oxyiodid. Light and moisture decompose it, with liberation of I. It is almost insoluble in H_2O, soluble in solutions of ammonium chlorid, sodium hyposulfite, alkaline iodids, and potash.

Nitrates. — Lead Nitrate — Plumbi nitras — (U. S.; Br.)— $Pb(NO_3)_2$—330.9—is formed by solution of Pb, or of its oxids, in excess of HNO_3. It forms anhydrous crystals; soluble in H_2O. Heated, it is decomposed into PbO, O and NO_2.

Besides the neutral nitrate, basic lead nitrates are known, which seem to indicate the existence of nitrogen acids similar to those of phosphorus; $Pb_3(NO_4)_2$—**orthonitrate**; and $Pb_2N_2O_7$—**pyronitrate.**

Lead Sulfate—$PbSO_4$—302.9—is formed by the action of hot, concentrated H_2SO_4 on Pb; or by double decomposition between a sulfate and a Pb salt in solution. It is a white powder, almost insoluble in H_2O, soluble in concentrated H_2SO_4, from which it is deposited by dilution.

Lead Chromate—Chrome yellow—$PbCrO_4$—323.3—is formed by decomposing $Pb(NO_3)_2$ with potassium chromate. It is a yellow, amorphous powder, insoluble in H_2O, soluble in alkalies.

Acetates.—Neutral Lead Acetate—Salt of Saturn—Sugar of Lead—Plumbi acetas (U.S.; Br.)—$Pb(C_2H_3O_2)_2+3Aq$—324.9+54—is formed by dissolving PbO in acetic acid; or by exposing Pb in contact with acetic acid to air.

It crystallizes in large, oblique rhombic prisms, sweetish, with a metallic after-taste; soluble in H_2O and alcohol; its solutions being acid. In air it effloresces, and is superficially converted into carbonate. It fuses at 75°.5 (167°.9 F.); loses Aq, and a part of its acid at 100° (212° F.), forming the sesquibasic acetate; at 280° (536° F.) it enters into true fusion, and, at a slightly higher temperature, is decomposed into CO_2; Pb, and acetone. Its aqueous solution dissolves PbO, with formation of basic acetates.

Sexbasic Lead Acetate—$Pb(C_2H_3O_2)OH$, 2PbO—728.7—is the main constituent of **Goulard's extract = Liq. plumbi subacetatis (U. S.; Br.)**, and is formed by boiling a solution of the neutral acetate with PbO in fine powder. The solution becomes milky on addition of ordinary H_2O, from formation of the sulfate and carbonate.

Lead Carbonate—$PbCO_3$—266.9—occurs in nature as **cerusite**; and is formed, as a white, insoluble powder, when a solution of a Pb compound is decomposed by an alkaline carbonate, or by passing CO_2 through a solution containing Pb.

The **plumbi carbonas** (**U. S.**; **Br.**), or **white lead** or **ceruse**, is a basic carbonate $(PbCO_3)_2$, PbH_2O_2—774.7—mixed with varying proportions of other basic carbonates. It is usually prepared by the action of CO_2 on a solution of the subacetate, prepared by the action of acetic acid on Pb and PbO. It is a heavy, white powder; insoluble in H_2O, except in the presence of CO_2; soluble in acids with effervescence; and decomposed by heat into CO_2 and PbO.

Analytical Characters.—(1.) Hydrogen sulfid, in acid solution: a black ppt.; insoluble in alkaline sulfids, and in cold, dilute acids. (2.) Ammonium sulfhydrate: black ppt.; insoluble in excess. (3.) Hydrochloric acid: white ppt.; in not too dilute solution; soluble in boiling H_2O. (4.) Ammonium hydroxid: white ppt.; insoluble in excess. (5.) Potash: white ppt.; soluble in excess, especially when heated. (6.) Sulfuric acid: white ppt.; insoluble in weak acids, soluble in solution of ammonium tartrate. (7.) Potassium iodid: yellow ppt.; sparingly soluble in boiling H_2O; soluble in large excess. (8.) Potassium chromate: yellow ppt.; soluble in KHO solution. (9.) Iron or zinc separate the element from solution of its salts.

Action on the Economy.—All the soluble compounds of Pb, and those which, although not soluble, are readily convertible into soluble compounds by H_2O, air, or the digestive fluids, are actively poisonous. Some are also injurious by their local action upon tissues with which they come in contact; such are the acetate, and, in less degree, the nitrate.

The **chronic** form of lead intoxication, **painter's colic**, etc., is purely poisonous, and is produced by the continued absorption of minute quantities of Pb, either by the skin, lungs, or stomach. The **acute** form presents symptoms referable to the local, as well as to the poisonous, action of the Pb salt, and is usually caused by the ingestion of a single dose of the acetate or carbonate.

Metallic Pb, although probably not poisonous of itself, causes chronic lead-poisoning by the readiness with which it is convertible into compounds capable of absorption. The principal sources of poisoning by metallic Pb are: the contamination of drinking water which has been in contact with the metal (see p. 72); the use of articles of food, or of chewing tobacco, which has been packed in tin-foil, containing an excess of Pb; the drinking of beer or other beverages which have been in contact with pewter; or the handling of the metal and its alloys.

Almost all the compounds of Pb may produce painter's colic. The carbonate, in painters, artists, manufacturers of white lead, and in persons sleeping in newly painted rooms; the oxids, in the manufactures of glass, pottery, sealing-wax, and litharge, and by the use of lead-glazed pottery; by other compounds, by the inhalation of the dust of cloth factories, and by the use of lead hair-dyes.

Acute lead-poisoning is of by no means as common occurrence as the chronic form, and usually terminates in recovery. It is caused by the ingestion of a single large dose of the acetate, subacetate, carbonate, or of red lead. In such cases the administration of magnesium sulfate is indicated; it enters into double decomposition with the Pb salt to form the insoluble $PbSO_4$.

Lead, once absorbed, is eliminated very slowly, it becoming fixed by combination with the albuminoids, a form of combination which is rendered soluble by potassium iodid. The channels of elimination are by the perspiration, urine and bile.

In the analysis for mineral poisons (see p. 136), the major part of the Pb is precipitated as PbS in the treatment by H_2S. The PbS remains upon the filter after extraction with ammonium sulfhydrate. It is treated with warm HCl, which decolorizes it by transforming the sulfid into chlorid. The $PbCl_2$ thus formed is dissolved in hot H_2O, from which it crystallizes on cooling. The solution still contains $PbCl_2$ in sufficient quantity to respond to the tests for the metal.

Although Pb is not a normal constituent of the body, the every-day methods by which it may be introduced into the economy, and the slowness of its elimination, are such as to render the greatest caution necessary in drawing conclusions from the detection of Pb in the body after death.

VI. BISMUTH GROUP.

BISMUTH.

Symbol = **Bi**—*Atomic weight* = 207.5—*Molecular weight* = 420 (?)—*Sp. gr.* = 9.677-9.935—*Fuses at* 268° (514°.4 *F.*).

This element is usually classed with Sb; by some writers among the metals, by others in the phosphorus group. We are led to class Bi in our third class, and in a group alone, because: (1) while the so-called salts of Sb are not salts of the element, but of the radical $(SbO)'$, *antimonyl*, Bi enters into saline combination, not only in the radical **bismuthyl** $(BiO)'$, but also as an element; (2) while the compounds of the elements of the N group in which those elements are quinquivalent are, as a rule, more stable than those in which they are trivalent, Bi is trivalent in all its known compounds except one, which is very unstable, in which it is quinquivalent; (3) the hydrates of the N group are strongly acid, and their corresponding salts are stable and well defined; but those hydrates of Bi which are acid are but feebly so, and the bismuthates are unstable; (4) no compound of Bi and H is known.

Occurrence.—Occurs principally free, also as Bi_2O_3 and Bi_2S_3.

Properties.—Crystallizes in brilliant, metallic rhombohedra; hard and brittle.

It is only superficially oxidized in cold air. Heated to redness in air, it becomes coated with a yellow film of oxid. In H_2O, containing CO_2, it forms a crystalline subcarbonate. It combines directly with Cl, Br, and I. It dissolves in hot H_2SO_4 as sulfate, and in HNO_3 as nitrate.

It is usually contaminated with As, from which it is best purified by heating to redness a mixture of powdered bismuth, potassium carbonate, soap and charcoal, under a layer of charcoal. After an hour the mass is cooled; the button is separated and fused until its surface begins to be coated with a yellowish-brown oxid.

Oxids.—Four oxids are known: Bi_2O_2; Bi_2O_3; Bi_2O_4; and Bi_2O_5.

Bismuth Trioxid—*Bismuthous oxid*—*Protoxid*—$\mathbf{Bi_2O_3}$—468—is formed by heating Bi, or its nitrate, carbonate, or hydrate. It is a pale yellow, insoluble powder; sp. gr. 8.2; fuses at a red heat; soluble in HCl, HNO_3 and H_2SO_4 and in fused potash.

Hydrates.—Bismuth forms at least four hydrates.

Bismuthous Hydroxid—$\mathbf{BiH_3O_3}$—261—is formed, as a white precipitate, when potash or ammonium hydroxid is added to a cold solution of a Bi salt. When dried, it loses H_2O, and is converted into **bismuthyl hydroxid** (BiO)HO.

Bismuthic Acid—$(\mathbf{BiO_2})HO$—259—is deposited, as a red powder, when Cl is passed through a boiling solution of potash, holding bismuthous hydroxid in suspension. When heated it is converted into the **pentoxid**, Bi_2O_5.

Pyrobismuthic Acid—$\mathbf{H_4Bi_2O_7}$—536—is a dark brown powder, precipitated from solution of bismuth nitrate by potassium cyanid.

Bismuth Trichlorid—*Bismuthous chlorid*—$\mathbf{BiCl_3}$—316.5—is formed by heating Bi in Cl; by distilling a mixture of Bi and mercuric chlorid; or by distilling a solution of Bi in aqua regia. It is a fusible, volatile, deliquescent solid; soluble in dilute HCl. On contact with H_2O it is decomposed with formation of **bismuthyl chlorid** (BiO)Cl, or **pearl white**.

Bismuth Nitrate—$Bi(NO_3)_3+5$ Aq—396+90—obtained by dissolving Bi in HNO_3. It crystallizes in large, colorless prisms ; at 150° (302° F.), or by contact with H_2O, it is converted into bismuthyl nitrate ; at 260° (500° F.) into Bi_2O_3.

Bismuthyl Nitrate—*Trisnitrate* or *subnitrate of bismuth—Flake white*—**Bismuthi subnitras (U. S. ; Br.)—$(BiO)NO_3H_2O$**—306—is formed by decomposing a solution of $Bi(NO_3)_3$ with a large quantity of H_2O. It is a white, heavy, faintly acid powder ; soluble to a slight extent in H_2O when freshly precipitated, the solution depositing it again on standing. It is decomposed by pure H_2O, but not by H_2O containing $\frac{1}{500}$ ammonium nitrate. It usually contains 1 Aq, which it loses at 100° (212° F.).

Bismuth subnitrate, as well as the subcarbonate, is liable to contamination with arsenic, which accompanies bismuth in its ores. The method for separating this dangerous impurity, directed by the British Pharmacopœia, is more perfect than that usually followed in this country. The metal is first purified by fusion with potassium nitrate, which dissolves any arsenic present in the form of sodium arsenite, and the purified metal is then converted into nitrate by solution in HNO_3, and this in turn into subnitrate by decomposition with a large volume of H_2O.

The maximum amount of arsenic which has been found in commercial bismuth subnitrate is one-tenth of one per cent.

To detect the presence of arsenic, the subnitrate (or subcarbonate) is boiled for half an hour with an equal weight of *pure* sodium carbonate, dissolved in ten times its weight of H_2O. The solution is filtered ; the filtrate evaporated to dryness ; the residue strongly heated ; and, after cooling, cautiously decomposed with strong H_2SO_4. The mass is then gradually heated, during stirring, until dense white fumes are given off. The cooled residue is finally treated with water and the liquid introduced into a Marsh apparatus. (See page 133.)

Bismuthyl Subcarbonate—Bismuthi subcarbonas (U. S.)—Bismuthi carbonas (Br.)—$(BiO)_2CO_3H_2O$—530—is a white or yellowish, amorphous powder, formed when a solution of an alkaline carbonate is added to a solution of $Bi(NO_3)_3$. It is odorless and tasteless, and insoluble in H_2O and in alcohol.

When heated to 100° (212° F.), it loses H_2O, and is converted into $(BiO)_2CO_3$. At a higher temperature it is further decomposed into Bi_2O_3 and CO_2.

Analytical Characters.—(1.) Water : white ppt., even in presence of tartaric acid, but not of HNO_3, HCl, or H_2SO_4. (2.) Hydrogen sulfid: black ppt.; insoluble in dilute acids and in alkaline sulfids. (3.) Ammonium sulfhydrate : black ppt.; insoluble in excess. (4.) Potash, soda, or ammonia : white ppt., insoluble in excess, and in tartaric acid; turns yellow when the liquid is boiled. (5.) Potassium ferrocyanid: yellowish ppt.; insoluble in HCl. (6.) Potassium ferricyanid: yellowish ppt.; soluble in HCl. (7.) Infusion of galls: orange ppt. (8.) Potassium iodid: brown ppt.; soluble in excess. (9.) Reacts with Reinsch's test (*q. v.*), but gives no sublimate in the glass tube.

Action on the Economy.—Although the medicinal compounds of bismuth are probably poisonous, if taken in sufficient quantity, the ill effects ascribed to them are in most, if not all cases, referable to contamination with arsenic. Symptoms of arsenical poisoning have been frequently observed when the subnitrate has been taken internally, and also when it has been used as a cosmetic.

When preparations of bismuth are administered, the alvine discharges contain bismuth sulfid, as a dark brown powder.

VII. TIN GROUP.

TITANIUM. ZIRCONIUM. TIN.

Ti and Sn are bivalent in one series of compounds, $SnCl_2$, and quadrivalent in another, $SnCl_4$. Zr, so far as known, is always quadrivalent. Each of these elements forms an acid (or salts corresponding to one) of the composition H_2MO_3, and a series of oxysalts of the composition $M^{iv}(NO_3)_4$.

TITANIUM.

Symbol = **Ti**—*Atomic weight* = 48—*Sp. gr.* = 5.3.

Occurs in clays and iron ores, and as TiO_2 in several minerals. **Titanic anhydrid,** TiO_2, is a white, insoluble, infusible powder, used in the manufacture of artificial teeth; dissolves in fused KHO, as potassium titanate. Titanium combines readily with N, which it absorbs from air when heated. When NH_3 is passed over red-hot TiO_2, it is decomposed with formation of the violet nitrid, TiN_2. Another compound of Ti and N forms hard, copper-colored, cubical crystals.

ZIRCONIUM.

Symbol = **Zr**—*Atomic weight* = 89.6—*Sp. gr.* = 4.15.

Occurs in zircon and hyacinth. Its oxid, **zirconia,** ZrO_2, is a white powder, insoluble in KHO. Being infusible, and not altered by exposure to air, it is used in pencils to replace lime in the calcium light.

TIN.

Symbol = **Sn** (**STANNUM**)—*Atomic weight* = 117.7—*Molecular weight* = 235.4 (?)—*Sp. gr.* = 7.285–7.293—*Fuses at* 228° (442°.4 F.).

Occurrence.—As **tinstone** (SnO_2) or **cassiterite,** and in **stream tin.**

Preparation.—The commercial metal is prepared by roasting the ore, extracting with H_2O, reducing the residue by heating with charcoal, and refining.

Pure tin is obtained by dissolving the metal in HCl; filtering; evaporating; dissolving the residue in H_2O; decomposing with ammonium carbonate; and reducing the oxid with charcoal.

Properties.—A soft, malleable, bluish-white metal; but slightly tenacious; emits a peculiar sound, the **tin-cry,** when bent. A good conductor of heat and electricity. Air affects it but little, except when it is heated; more rapidly if Sn be alloyed with Pb. It oxidizes slowly in H_2O, more rapidly in the presence of sodium chlorid. Its presence with Pb accelerates the action of H_2O upon the latter. It dissolves in HCl as $SnCl_2$. In presence of a small quantity of H_2O, HNO_3 converts it into metastannic acid. Alkaline solutions dissolve it as metastannates. It combines directly with Cl, Br, I, S, P, and As.

Tin plates are thin sheets of Fe, coated with Sn. **Tin foil** consists of thin laminæ of Sn, frequently alloyed with Pb. Copper and iron vessels are **tinned** after brightening, by contact with molten Sn. Pewter, bronze, bell metal, gun metal, britannia metal, speculum metal, type metal, solder, and fusible metal contain Sn.

Oxids.—**Stannous Oxid**—*Protoxid*—**SnO**—133.7—obtained by heating the hydroxid or oxalate without contact of air. It is a white, amorphous powder, soluble in acids, and in hot concentrated solution of potash. It absorbs O readily.

Stannic Oxid.—*Binoxid of tin*—SnO_2—149.7—occurs native as *tinstone* or *cassiterite*, and is formed when Sn or SnO is heated in air. It is used as a polishing material, under the name of **putty powder.**

Hydrates.—**Stannous Hydroxid**—SnH_2O_2—151.7—is a white precipitate, formed by alkaline hydroxids and carbonates in solutions of $SnCl_2$.

Stannic Acid.—H_2SnO_3—167.7—is formed by the action of alkaline hydroxids on solutions of $SnCl_4$. It dissolves in solutions of the alkaline hydroxids, forming **stannates.**

Metastannic Acid.—$H_2Sn_5O_{11}$—766.5—is a white, insoluble powder, formed by acting on Sn with HNO_3.

Chlorids.—**Stannous Chlorid**—*Protochlorid*—**Tin crystals**—$SnCl_2 + 2\ Aq$—188.7 + 36—is obtained by dissolving Sn in HCl. It crystallizes in colorless prisms; soluble in a small quantity of H_2O; decomposed by a large quantity, unless in the presence of free HCl, with formation of an oxychlorid. Loses its Aq at 100° (212° F.). In air it is transformed into stannic chlorid and oxychlorid. Oxidizing and chlorinating agents convert it into $SnCl_4$. It is a strong reducing agent.

Stannic Chlorid—*Bichlorid—Liquid of Libavius*—**$SnCl_4$**—259.7—is formed by acting on Sn or $SnCl_2$ with Cl, or by heating Sn in aqua regia. It is a fuming yellowish liquid; sp. gr. 2.28; boils at 120° (248° F.).

Analytical Characters.—STANNOUS.—(1.) Potash or soda: white ppt.; soluble in excess; the solution deposits Sn when boiled. (2.) Ammonium hydroxid: white ppt.; insoluble in excess; turns olive-brown when the liquid is boiled. (3.) Hydrogen sulfid: dark brown ppt.; soluble in KHO, alkaline sulfids, and hot H_2O. (4.) Mercuric chlorid: white ppt.; turning gray and black. (5.) Auric chlorid: purple or brown ppt., in presence of small quantity of HNO_3. (6.) Zinc: deposit of Sn.

STANNIC.—(1.) Potash or ammonia: white ppt.; soluble in excess. (2.) Hydrogen sulfid: yellow ppt.; soluble in alkalies, alkaline sulfids, and hot HCL. (3.) Sodium hyposulfite: yellow ppt. when heated.

VIII. PLATINUM GROUP.

PALLADIUM. PLATINUM.

IX. RHODIUM GROUP.

RHODIUM. RUTHENIUM. IRIDIUM.

The elements of these two groups, together with osmium, are usually classed as "metals of the platinum ores." They all form hydrates (or salts representing them) having acid properties. Osmium has been removed, because the relations existing between its compounds, and those of molybdenum and tungsten, are much closer than those which they exhibit to the compounds of these groups. The separation of the remaining platinum metals into two groups is based upon resemblances in the composition of their compounds, as shown in the following table:

Chlorids.

$PdCl_2$	$PtCl_2$	$RhCl_2$	$RuCl_2$	?
$PdCl_4$	$PtCl_4$	——	$RuCl_4$	$IrCl_4$
——	——	Rh_2Cl_6	Ru_2Cl_6	Ir_2Cl_6

Oxids.

PdO	PtO	RhO	RuO	IrO
——	——	Rh_2O_3	Ru_2O_3	Ir_2O_3
PdO_2	PtO_2	RhO_2	RuO_2	IrO_2
——	——	RhO_3	RuO_3	IrO_3
——	——	——	RuO_4	——

PLATINUM.

Symbol = **Pt**—*Atomic weight* = 194.4—*Molecular weight* = 388.8 (?)—*Sp. gr.* = 21.1–21.5.

Occurrence.—Free and alloyed with Os, Ir, Pd, Rh, Ru, Fe, Pb, Au, Ag, and Cu.

Properties.—The compact metal has a silvery lustre; softens at a white heat; may be welded; fuses with difficulty; highly malleable, ductile and tenacious. **Spongy platinum** is a grayish, porous mass, formed by heating the double chlorid of Pt and NH_4. **Platinum black** is a black powder, formed by dissolving $PtCl_2$ in solution of potash, and heating with alcohol. Both platinum black and platinum sponge are capable of condensing large quantities of gas, and act as indirect oxidants.

Platinum is not oxidized by air or O; it combines directly with Cl, P, As, Si, S, and C; is not attacked by acids, except aqua regia, in which it dissolves as $PtCl_4$. It forms fusible alloys when heated with metals or reducible metallic oxids. It is attacked by mixtures liberating Cl, and by contact with heated phosphates, silicates, hydroxids, nitrates, or carbonates of the alkaline metals.

Platinic chlorid—*Tetrachlorid* or *perchlorid of platinum*—**$PtCl_4$**—336.4—is obtained by dissolving Pt in aqua regia, and evaporating. It crystallizes in very soluble, deliquescent, yellow needles. Its solution is used as a test for compounds of NH_4 and K.

PALLADIUM.

Symbol = **Pd**—*Atomic weight* = 105.7—*Molecular weight* = 211.4 (?)—*Sp. gr.* = 11.5.

A white metal, resembling Pt in appearance; but usually exhibiting a reddish reflection. It is harder, much lighter, and more readily fusible than Pt. It dissolves in HNO_3, as $Pd(NO_3)_2$. It possesses the property of occluding gases, notably hydrogen, in a much more marked degree than any other metal. One volume of palladium condenses 640 volumes of hydrogen at 100° (212° F.).

RHODIUM.

Symbol = **Rh** — *Atomic weight* = 104.1 — *Molecular weight* = 208.2 (?)—*Sp. gr.* = 11.4.

A hard, malleable, white metal, insoluble in aqua regia. Its compounds are mostly red, whence its name, from *ῥόδον*, a rose.

RUTHENIUM.

Symbol = **Ru**—*Atomic weight* = 104.2—*Sp. gr.* = 11.4.

A hard, brittle, very difficultly fusible metal, not dissolved by aqua regia, occurring in small quantity in platinum ores.

IRIDIUM.

Symbol = **Ir**—*Atomic weight* = 192.7—*Sp. gr.* = 22.3.

A hard, brittle metal which occurs in nature in platinum ores, and alloyed with osmium. It is not attacked by aqua regia. It is used to make an alloy with platinum, which is less fusible, more rigid, harder, denser, and less readily attacked chemically than pure platinum.

CLASS IV.—BASYLOUS ELEMENTS.

Elements whose Oxids Unite with Water to form Bases; never to form Acids. Which form Oxysalts.

I. SODIUM GROUP.

Alkali Metals.

LITHIUM—SODIUM—POTASSIUM—RUBIDIUM—CÆSIUM—SILVER.

Each of the elements of this group forms a single chlorid, $M'Cl$, and one or more oxids, the most stable of which has the composition M'_2O; they are, therefore, univalent. Their hydroxids, $M'HO$, are more or less alkaline and have markedly basic characters. Silver resembles the other members of the group in chemical properties, although it does not in physical characters.

LITHIUM.

Symbol = **Li**—*Atomic weight* = 7—*Molecular weight* = 14 (?)—*Sp. gr.* = 0.589—*Fuses at* 180° (356° F.)—*Discovered by Arfvedson in* 1817—*Name from* λίθειος = stony.

Occurrence.—Widely distributed in small quantity; in many minerals and mineral waters; in the ash of tobacco and other plants; in the milk and blood.

Properties.—A silver-white, ductile, volatile metal; the lightest of the solid elements; burns in air with a crimson flame; decomposes H_2O at ordinary temperatures, without igniting.

Lithium Oxid—**Li_2O**—30—is a white solid, formed by burning Li in dry O. It dissolves slowly in H_2O to form **lithium hydroxid**—$LiHO$.

Lithium Chlorid—**$LiCl$**—43.5—crystallizes in deliquescent, regular octahedra; very soluble in H_2O and in alcohol.

Lithium Bromid—**Lithii bromidum (U.S.)**—**$LiBr$**—87—is formed by decomposing lithium sulfate with potassium bromid; or by saturating a solution of HBr with lithium carbonate. It crystallizes in very deliquescent, soluble needles.

Lithium Carbonate—**Lithii carbonas (U. S.; Br.)**—**Li_2CO_3**—74—is a white, sparingly soluble, alkaline, amorphous powder. With uric acid it forms lithium urate (*q. v.*).

Analytical Characters.—(1.) Ammonium carbonate: white ppt. in concentrated solutions; not in dilute solutions, or in presence of ammoniacal salts. (2.) Sodium phosphate: white ppt. in neutral or alkaline solution; soluble in acids and in solutions of ammoniacal salts. (3.) It colors the Bunsen flame red; and exhibits a spectrum of two lines—λ = 6705 and 6102 (Fig. 16, No. 4).

SODIUM.

Symbol = **Na** (**NATRIUM**)—*Atomic weight* = 23—*Molecular weight* = 46 (?)—*Sp. gr.* = 0.972—*Fuses at* 95°.6 (204°.1 F.)—*Boils at* 742° (1368° F.)—*Discovered by Davy*, 1807.

Occurrence.—As chlorid, very abundantly and widely distributed; also as carbonate, nitrate, sulfate, borate, etc.

Preparation.—By heating a mixture of dry sodium carbonate, chalk, and charcoal to whiteness in iron retorts, connected with suitable condensers, in which the distilled metal collects, under a layer of coal naphtha.

Properties.—A silver-white metal, rapidly tarnished, and coated with a yellow film in air. Waxy at ordinary temperatures; volatile at a white heat, forming a colorless vapor, which burns in air with a yellow flame.

In air it is gradually oxidized from the surface, but may be kept in closed vessels, without the protection of a layer of naphtha. It decomposes H_2O, sometimes explosively. Burns with a yellow flame. Combines directly with Cl, Br, I, S, P, As, Pb, and Sn.

Oxids.—Two oxids are known: **Sodium monoxid**—Na_2O—a grayish-white mass; formed when Na is burnt in dry air, or by the action of Na on NaHO. **Sodium dioxid**—Na_2O_2—a white solid, formed when Na is heated in dry air to 200° (392° F.).

Sodium Hydroxid—*Sodium-hydrate*—**Caustic Soda**—**Soda** (**U. S.**)—**Soda caustica** (**Br.**)—**NaHO**—40—is formed: (1) when H_2O is decomposed by Na; (2) by decomposing sodic carbonate by calcium hydroxid: $Na_2CO_3 + CaH_2O_2 = CO_3Ca + 2NaHO$ (soda by lime); (3) in the same manner as in (2), using barium hydroxid in place of lime (soda by baryta). It frequently contains considerable quantities of As.

It is an opaque, white, fibrous, brittle solid; fusible below redness; sp. gr. 2.00; very soluble in H_2O, forming strongly alkaline and caustic solutions (**soda lye** and **liq. sodæ**). When exposed to air, solid or in solution, it absorbs H_2O and CO_2, and is converted into carbonate. Its solutions attack glass.

Sodium chlorid—**Common salt**—**Sea salt**—**Table salt**—**Sodii chloridum** (**U. S.**, **Br.**)—**NaCl**—58.5—occurs very abundantly in nature, deposited in the solid form as **rock salt**; in solution in all natural waters, especially in sea and mineral spring waters; in suspension in the atmosphere; and as a constituent of almost all animal and vegetable tissues and fluids. It is formed in an infinite variety of chemical reactions. It is obtained from rock salt, or from the waters of the sea or of saline springs; and is the source from which all the Na compounds are usually obtained, directly or indirectly.

It crystallizes in anhydrous, white cubes, or octahedra ; sp. gr. 2.078 ; fuses at a red heat, and crystallizes on cooling ; sensibly volatile at a white heat ; quite soluble in H_2O, the solubility varying but slightly with the variations of temperature. Dilute solutions yield almost pure ice on freezing. It is precipitated from concentrated solutions by HCl. It is insoluble in absolute alcohol ; sparingly soluble in dilute spirit. It is decomposed by H_2SO_4 with formation of HCl and sodium sulfate: $2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$.

PHYSIOLOGICAL.—Sodium chlorid exists in every animal tissue and fluid, and is present in the latter, especially the blood, in tolerably constant proportion. It is introduced with the food, either as a constituent of the alimentary substances, or as a condiment. In the body it serves to aid the phenomena of osmosis, and to maintain the solution of the albuminoids. It is probable, also, that it is decomposed in the gastric mucous membrane with formation of free hydrochloric acid.

It is discharged from the economy by all the channels of elimination, notably by the urine, when the supply by the food is maintained. If, however, the food contain no salt, it disappears from the urine before it is exhausted from the blood.

The amount of Cl (mainly in the form of NaCl) voided by a normal male adult in 24 hours is about 10 grams (154 grains), corresponding to 16.5 grams (255 grains) of NaCl. When normal or excessive doses are taken, the amount eliminated by the urine is less than that taken in ; when small quantities are taken, the elimination is at first in excess of the supply. The hourly elimination increases up to the seventh hour, when it again diminishes. The amount of NaCl passed in the urine is less than the normal in acute, febrile diseases ; in intermittent fever it is diminished during the paroxysms, but not during the intervals. In diabetes it is much increased, sometimes to 29 grams (448 grains) per diem.

Quantitative determination of chlorids in urine.—The process is based upon the formation of the insoluble silver chlorid, and upon the formation of the brown silver chromate in neutral liquids, in the absence of soluble chlorids. The solutions required are : (1) *A solution of silver nitrate* of known strength, made by dissolving 29.075 grams of pure, fused silver nitrate (see p. 193) in a litre of water ; (2) *a solution of neutral potassium chromate.*

To conduct the determination, 5–10 c.c. of the urine are placed in a platinum basin, 2 grams of sodium nitrate (free from chlorid) are added ; the whole is evaporated to dryness over the water-bath, and the residue heated gradually until a colorless, fused mass remains. This, on cooling, is dissolved in H_2O, the solution placed in a small beaker, treated with pure, dilute HNO_3 to faintly acid reaction, and neutralized with calcium carbonate. Two or three drops of the chromate solution are added, and then the silver solution from a burette, during constant stirring of the liquid in the beaker, until a faint reddish tinge remains permanent. Each c.c. of the silver solution used represents 10 milligrams NaCl (or 6.065 milligrams Cl) in the amount of urine used.

Example.—5 c.c. urine used; 6 c.c. silver solution added; 1,200 c.c. urine passed in 24 hours: $\therefore \frac{0.01 \times 6}{5} \times 1{,}200 = 14.4$ grams NaCl in 24 hours.

If the urine contain iodids or bromids, they must be removed, by acidulating the solution or the residue of incineration with H_2SO_4, removing the iodin or bromin by shaking with carbon disulfid, neutralizing the aqueous solution with calcium carbonate and proceeding as above.

Sodium Bromid—Sodii bromidum (U. S.)—NaBr—103—is formed by dissolving Br in solution of NaHO to saturation; evaporating; calcining at dull redness; redissolving; filtering; and crystallizing. It crystallizes in anhydrous cubes; quite soluble in H_2O, soluble in alcohol.

Sodium Iodid—Sodii iodidum (U. S.)—NaI—150—is prepared by heating together H_2O, Fe, and I in fine powder; filtering; adding an equivalent quantity of sodium sulfate, and some slacked lime; boiling; decanting and evaporating. Crystallizes in anhydrous cubes; very soluble in H_2O; soluble in alcohol.

Sodium Nitrate—Cubic or Chili saltpetre—Sodii nitras (U. S.)—Sodæ nitras (Br.)—$NaNO_3$—85—occurs in natural deposits in Chili and Peru. It crystallizes in anhydrous, deliquescent rhombohedra; cooling and somewhat bitter in taste; fuses at 310° (590° F.); very soluble in H_2O. Heated with H_2SO_4, it is decomposed, yielding HNO_3 and hydrosodic sulfate: $H_2SO_4 + NaNO_3 = HNaSO_4 + HNO_3$. This reaction is that used for obtaining HNO_3.

Sulfates.—Monosodic sulfate—*Hydrosodic sulfate—Acid sodium sulfate—Bisulfate*—**$HNaSO_4$**—120—crystallizes in long, four-sided prisms; is unstable and decomposed by air, H_2O or alcohol, into H_2SO_4 and Na_2SO_4. Heated to dull redness it is converted into **sodium pyrosulfate**, $Na_2S_2O_7$, corresponding to Nordhausen sulfuric acid.

Disodic Sulfate—*Sodic sulfate—Neutral sodium sulfate*—**Glauber's salt—Sodii sulfas (U. S.)—Sodæ sulfas (Br.)—$Na_2SO_4 + n$ Aq**—$142 + n\ 18$—occurs in nature in solid deposits, and in solution in natural waters. It is obtained as a secondary product in the manufacture of HCl, by the action of H_2SO_4 on NaCl, the decomposition occurring according to the equation: $2\ NaCl + H_2SO_4 = Na_2SO_4 + 2\ HCl$, if the temperature be raised sufficiently. At lower temperatures, the monosodic salt is produced, with only half the yield of HCl: $NaCl + H_2SO_4 = NaHSO_4 + HCl$.

It crystallizes with 7 Aq, from saturated or supersaturated solutions at 5° (41° F.); or, more usually, with 10 Aq. As usually met with it is in large, colorless, oblique rhombic prisms with 10 Aq; which effloresce in air, and gradually lose all their Aq. It fuses at 33° (91°.4 F.) in its Aq, which it gradually loses. If fused at 33° (91°.4 F.), and allowed to cool, it remains liquid in *supersaturated* solution, from which it is deposited, the entire mass becoming solid, on contact with a small particle of solid matter. It dissolves in HCl with considerable diminution of temperature.

PHYSIOLOGICAL.—The neutral sulfates of Na and K seem to exist in small quantity in all animal tissues and fluids, with the exception of milk, bile, and gastric juice; certainly in the blood and urine. They are partially introduced with the food, and partly formed as a result of the metamorphosis of those constituents of the tissues which contain S in organic combination.

The principal elimination of the sulfates is by the urine. All the sulfuric acid in the urine is not in simple combination with the alkali metals. A considerable amount exists in the form of the alkaline salts of conjugate, monobasic, ether acids, which, on decomposition, yield an aromatic organic compound. The amount of H_2SO_4 discharged by the urine in 24 hours, in the form of alkaline sulfates, is from 2.5 to 3.5 grams (38.5–54 grains). That eliminated in the salts of conjugate acids, 0.617 to 0.094 gram (9.5–1.5 grains).

Sodium Sulfite—Sodii sulfis (U. S.)—$Na_2SO_3 + 7\ Aq$—126 + 126—is formed by passing SO_2 over crystallized Na_2CO_3. It crystallizes in efflorescent, oblique prisms; quite soluble in H_2O, forming an alkaline solution. It acts as a reducing agent.

Sodium Thiosulfate—*Sodium hyposulfite*—**Sodii hyposulfis (U. S.)—$Na_2S_2O_3 + 5\ Aq$**—158 + 90—is obtained by dissolving S in hot concentrated solution of Na_2SO_3, and crystallizing.

It forms large, colorless, efflorescent prisms; fuses at 45° (113° F.); very soluble in H_2O; insoluble in alcohol. Its solutions precipitate alumina from solutions of Al salts, without precipitating Fe or Mn; they dissolve many compounds insoluble in H_2O; cuprous hydroxid, iodids of Pb, Ag and Hg, sulfids of Ca and Pb. It acts as a disinfectant and antiseptic. H_2SO_4 and most other acids decompose $Na_2S_2O_3$ according to the equation: $Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + SO_2 + S + H_2O$. Oxalic, and a few other acids, decompose the thiosulfate with formation of H_2S as well as SO_2 and S.

Silicates.—Quite a number of silicates of Na are known. If silica and Na_2CO_3 be fused together, the residue extracted with H_2O, and the solution evaporated, a transparent, glass-like mass, soluble in warm water, remains; this is **soluble glass** or **water glass.** Exposed to air in contact with stone, it becomes insoluble, and forms an impermeable coating.

Phosphates.—Trisodic Phosphate—*Basic sodium phosphate*—**Na_3PO_4 + 12 Aq**—164 + 216—is obtained by adding NaHO to disodic phosphate solution, and crystallizing. It forms six-sided prisms; quite soluble in H_2O. Its solution is alkaline, and, on exposure to air, absorbs CO_2, with formation of HNa_2PO_4 and Na_2CO_3.

Disodic Phosphate—*Hydro-disodic phosphate—Neutral sodium phosphate—Phosphate of soda*—**Sodii phosphas (U. S.)—Sodæ phosphas (Br.)—HNa_2PO_4 + 12 Aq**—142 + 216—is obtained by converting tricalcic phosphate into monocalcic phosphate, and decomposing that salt with sodium carbonate: $Ca(PO_4H_2)_2 + 2Na_2CO_3 = CaCO_3 + H_2O + CO_2 + 2HNa_2PO_4$.

Below 30° (86° F.) it crystallizes in oblique rhombic prisms, with 12 Aq; at 33° (91°.4 F.) it crystallizes with 7 Aq. The salt with 12 Aq effloresces in air, and parts with 5 Aq; and is very soluble in H_2O. The salt with 7 Aq is not efflorescent, and less soluble in H_2O. Its solutions are faintly alkaline.

Monosodic Phosphate—*Acid sodium phosphate*—**H_2NaPO_4 + Aq**—120 + 18—crystallizes in rhombic prisms; forming acid solutions. At 100° (212° F.) it loses Aq; at 200° (392° F.) it is converted into **acid pyrophosphate**, $Na_2H_2P_2O_7$; and at 204° (399°.2 F.) into the **metaphosphate**, $NaPO_3$.

PHYSIOLOGICAL.—All the sodium phosphates exist, accompanied by the corresponding K salts, in the animal economy. The disodic and dipotassic phosphates are the most abundant, and of these two the former. They exist in every tissue and fluid of the body, and are more abundant in the fluids of the carnivora than in those of the herbivora. In the blood, in which the Na salt predominates in the plasma, and the K salt in the corpuscles, they serve to maintain an alkaline reaction. With strictly vegetable diet the proportion of phosphates in the blood diminishes, and that of the carbonates (the predominating salts in the blood of the herbivora) increases.

The monosodic and monopotassic phosphates exist in the urine, the former predominating, and to their presence the acid reaction of that fluid is largely due. They are produced by decomposition of the neutral salts by uric acid. The urine of the herbivora, whose blood is poor in phosphates, is alkaline in reaction.

The greater part of the phosphates in the body are introduced with the food. A portion is formed in the economy by the oxidation of phosphorized organic substances, the lecithins.

Disodic Tetraborate—*Sodium pyroborate—Borate of sodium*—**Borax**—*Tincal*—**Sodii boras (U. S.)—Borax (Br.)—$Na_2B_4O_7$+10 Aq**—202+180—is prepared by boiling boric acid with Na_2CO_3 and crystallizing. It crystallizes in hexagonal prisms with 10 Aq; permanent in moist air, but efflorescent in dry air; or in regular octahedra with 5 Aq, permanent in dry air. Either form, when heated, fuses in its Aq, swells considerably; at a red heat becomes anhydrous; and, on cooling, leaves a transparent, glass-like mass. When fused, it is capable of dissolving many metallic oxids, forming variously colored masses, hence its use as a flux and in blow-pipe analysis.

Sodium Hypochlorite—NaClO—74.5—only known in solution—**Liq. sodæ chloratæ (U. S.; Br.)** or **Labarraque's solution**—obtained by decomposing a solution of chlorid of lime by Na_2CO_3. It is a valuable source of Cl, and is used as a bleaching and disinfecting agent.

Sodium Manganate—Na_2MnO_4+10 Aq—164+180—faintly colored crystals, forming a green solution with H_2O—**Condy's green disinfectant.**

Sodium Permanganate—$Na_2Mn_2O_8$—282—prepared in the same way as the K salt (*q. v.*), which it resembles in its properties. It enters into the composition of **Condy's fluid**, and of "**chlorozone**," which contains $Na_2Mn_2O_8$ and NaClO.

Sodium Acetate—Sodii acetas (U. S.)—Sodæ acetas (Br.)—$NaC_2H_3O_2$+3Aq—82+54—crystallizes in large, colorless prisms; acid and bitter in taste; quite soluble in H_2O; soluble in alcohol; loses its Aq in dry air, and absorbs it again from moist air. Heated with soda lime, it yields marsh gas. The anhydrous salt, heated with H_2SO_4, yields glacial acetic acid.

Carbonates.—Three are known: Na_2CO_3; $HNaCO_3$, and $H_2Na_4(CO_3)_3$.

Disodic Carbonate — *Neutral carbonate* — *Soda* — **Sal soda—Washing soda—Soda crystals—Sodii carbonas (U. S.)—Sodæ carbonas (Br.)—Na_2CO_3+10 Aq**—106+180—industrially the most important of the Na compounds, is manufactured by Leblanc's or Solvay's processes; or from *cryolite*, a native fluorid of Na and Al.

Leblanc's process, in its present form, consists of three distinct processes: (1.) The conversion of NaCl into the sulfate, by decomposition by H_2SO_4. (2.) The conversion of the sulfate into carbonate, by heating a mixture of the sulfate with calcium carbonate and charcoal. The product of this reaction, known as **black ball soda**, is a mixture of sodium carbonate, with charcoal and calcium sulfid and oxid. (3.) The purification of the product obtained in (2). The ball black is broken up, disintegrated by steam, and lixiviated. The solution on evaporation yields the soda salt or soda of commerce.

Of late years Leblanc's process has been in great part replaced by Solvay's method, or the *ammonia process*, which is more economical, and yields a purer product. In this process sodium chlorid and ammonium bicarbonate react upon each other, with production of the sparingly soluble sodium bicarbonate, and the very soluble ammonium chlorid. The sodium bicarbonate is then simply collected, dried, and heated, when it is decomposed into Na_2CO_3, H_2O, and CO_2.

The anhydrous carbonate, *Sodii carbonas exsiccatus* (*U. S.*), Na_2CO_3, is formed, as a white powder, by calcining the crystals. It fuses at dull redness, and gives off a little CO_2. It combines with and dissolves in H_2O with elevation of temperature.

The crystalline sodium carbonate, Na_2CO_3+10 Aq, forms large rhombic crystals, which effloresce rapidly in dry air; fuse in their Aq at 34° (93°.2 F.); are soluble in H_2O, most abundantly at 38° (100°.4 F.). The solutions are alkaline in reaction.

Monosodic Carbonate—*Hydrosodic carbonate*—**Bicarbonate of soda**—*Acid carbonate of soda*—*Vichy salt*—**Sodii bicarbonas** (**U. S.**)—**Sodæ bicarbonas** (**Br.**)—$NaHCO_3$—84—exists in solution in many mineral waters. It is obtained by the action of CO_2 upon the disodic salt in the presence of H_2O; or, as above described, by the Solvay method.

It crystallizes in rectangular prisms, anhydrous and permanent in dry air. In damp air it gives off CO_2, and is converted into the **sesquicarbonate**, $Na_4H_2(CO_3)_3$. When heated, it gives off CO_2 and H_2O, and leaves the disodic carbonate. Quite soluble in water; above 70° (158° F.) the solution gives off CO_2. The solutions are alkaline.

PHYSIOLOGICAL.—The fact that the carbonates of Na and K are almost invariably found in the ash of animal tissues and fluids, is no evidence of their existence there in life, as the carbonates are produced by the incineration of the Na and K salts of organic acids. There is, however, excellent indirect proof of the existence of the alkaline carbonates in the blood, especially of the herbivora, in the urine of the herbivora at all times, and in that of the carnivora and omnivora, when food rich in the salts of the organic acids, with alkali metals, is taken. The carbonates in the blood are both the mono- and disodic, and potassic; and the carbonic acid in the plasma is held partially in simple solution, and partly in combination in the monometallic carbonates.

Analytical Characters.—(1.) Hydrofluosilicic acid: gelatinous ppt., if not too dilute. (2.) Potassium pyroantimonate: in neutral solution and in absence of metals, other than K and Li: a white flocculent ppt.; becoming crystalline on standing. (3.)

Periodic acid in excess: white ppt., in not too dilute solutions. (4.) Colors the Bunsen flame yellow, and shows a brilliant double line at $\lambda = 5895$ and 5889 (Fig. 16, No. 2).

POTASSIUM.

Symbol = **K** (**KALIUM**) — *Atomic weight* = 39 — *Molecular weight* = 78 (?)—*Sp. gr.* = 0.865—*Fuses at* 62°.5 (144°.5 F.)—*Boils at* 667° (1233° F.)—*Discovered by Davy*, 1807—*Names from* pot ash, *and* Kali = ashes (Arabic).

It is prepared by a process similar to that followed in obtaining Na; is a silver-white metal; brittle at 0° (32° F.); waxy at 15° (59° F.); fuses at 62°.5 (144°.5 F.); distils in green vapors at a red heat, condensing in cubic crystals.

It is the only metal which oxidizes at low temperatures in dry air, in which it is rapidly coated with a white layer of oxid or hydroxid, and frequently ignites, burning with a violet flame. It must, therefore, be kept under naphtha. It decomposes H_2O, or ice, with great energy, the heat of the reaction igniting the liberated H. It combines with Cl with incandescence, and also unites directly with S, P, As, Sb, and Sn. Heated in CO_2 it is oxidized, and liberates C.

Oxids.—Three are known: K_2O; K_2O_2; and K_2O_4.

Potassium hydroxid—Potassium hydrate—Potash—Potassa—*Common caustic*—**Potassa (U. S.)—Potassa caustica (Br.)—KHO—**56—is obtained by a process similar to that used in manufacturing NaHO. It is purified by solution in alcohol, evaporation and fusion in a silver basin, and casting in silver moulds—**potash by alcohol**; it is then free from KCl and K_2SO_4, but contains small quantities of K_2CO_3, and frequently As.

It is usually met with in cylindrical sticks, hard, white, opaque, and brittle. The KHO by alcohol has a bluish tinge, and a smoother surface than the common; sp. gr. 2.1; fuses at dull redness; is freely soluble in H_2O, forming a strongly alkaline and caustic liquid; less soluble in alcohol. In air, solid or in solution, it absorbs H_2O and CO_2, and is converted into K_2CO_3. Its solutions dissolve Cl, Br, I, S, and P. It decomposes the ammoniacal salts, with liberation of NH_3; and the salts of many of the metals, with formation of a K salt, and a metallic hydroxid. It dissolves the albuminoids, and, when heated, decomposes them with formation of leucin, tyrosin, etc. It oxidizes the carbohydrates with formation of potassium oxalate and carbonate. It decomposes the fats with formation of soft soaps.

Sulfids.—Five are known: K_2S, K_2S_2, K_2S_3, K_2S_4, and K_2S_5; also a sulfhydrate: KHS.

Potassium Monosulfid—K_2S—110—is formed by the action of KHO on KHS. **Potassium Disulfid**—K_2S_2—142—is an orange-colored solid, formed by exposing an alcoholic solution of KHS to the air. **Potassium Trisulfid**—K_2S_3—174—a brownish-yellow mass, obtained by fusing together K_2CO_3 and S in the proportion: $4K_2CO_3+10S=SO_4K_2+3K_2S_3+4CO_2$. **Potassium Pentasulfid**—K_2S_5—238—is formed, as a brown mass, when K_2CO_3 and S are fused together in the proportion: $4K_2CO_3 + 16S = 4CO_2 + 3K_2S_5 + K_2SO_4$. **Liver of Sulfur**—*hepar sulfuris*—**potassii sulfuratum** (**U. S.**; **Br.**)—is a mixture of K_2S_3 and K_2S_5.

Potassium Sulfhydrate—**KHS**—72—is formed by saturating a solution of KHO with H_2S.

Potassium Chlorid.—*Sal digestivum Sylvii*—**KCl**—74.5—exists in nature, either pure or mixed with other chlorids; principally as **carnallite,** KCl, $MgCl_2 + 6$ Aq. It crystallizes in anhydrous, permanent cubes, soluble in H_2O.

Potassium Bromid—**Potassii bromidum** (**U. S.**; **Br.**)—**KBr**—119—is formed, either by decomposing ferrous bromid by K_2CO_3, or by dissolving Br in solution of KHO. In the latter case the **bromate** formed is converted into KBr, by calcining the product. It crystallizes in anhydrous cubes or tables; has a sharp, salty taste; very soluble in H_2O, sparingly so in alcohol. It is decomposed by Cl with liberation of Br.

Potassium Iodid—**Potassii iodidum** (**U. S.**; **Br.**)—**KI**—166—is obtained by saturating KHO solution with I, evaporating, and calcining the resulting mixture of iodid and iodate with charcoal. It frequently contains iodate and carbonate. It crystallizes in cubes, transparent if pure; permanent in air; anhydrous; soluble in H_2O, and in alcohol. It is decomposed by Cl, HNO_3 and HNO_2, with liberation of I. It combines with other iodids to form double iodids. Its solutions dissolve iodin and many metallic iodids.

Potassium Nitrate—**Nitre**—**Saltpetre**—**Potassii nitras** (**U. S.**)—**Potassæ nitras** (**Br.**)—KNO_3—101—occurs in nature, and is produced artificially, as a result of the decomposition of nitrogenized organic substances. It is usually obtained by decomposing native $NaNO_3$ by boiling solution of K_2CO_3 or KCl.

It crystallizes in six-sided, rhombic prisms, grooved upon the surface; soluble in H_2O, with depression of temperature; more soluble in H_2O containing NaCl; very sparingly soluble in alcohol; fuses at 350° (662° F.) without decomposition; gives off O, and is converted into nitrite below redness; more strongly heated, it is decomposed into N, O, and a mixture of K oxids. It is a valuable oxidant at high temperatures; heated with charcoal it deflagrates.

Gunpowder is an intimate mixture of KNO_3 with S and C, in such proportion that the KNO_3 yields all the O required for the combustion of the S and C.

Potassium Chlorate—Potassii chloras (U. S.)—Potassæ chloras (Br.)—$KClO_3$—122.5—is prepared: (1) by passing Cl through a solution of KHO; (2) by passing Cl over a mixture of milk of lime and KCl, heated to 60° (140° F.). It crystallizes in transparent, anhydrous plates; soluble in H_2O; sparingly soluble in weak alcohol.

It fuses at 400° (752° F.). If further heated, it is decomposed into KCl and perchlorate, and at a still higher temperature the perchlorate is decomposed into KCl and O: $2KClO_3 = KClO_4 + KCl + O_2$ and $KClO_4 = KCl + 2O_2$. It is a valuable source of O, and a more active oxidant than KNO_3. When mixed with readily oxidizible substances, C, S, P, sugar, tannin, resins, etc., the mixtures explode when subjected to shock. With strong H_2SO_4 it gives off Cl_2O_4, an explosive yellow gas. It is decomposed by HNO_3 with formation of KNO_3, $KClO_4$, and liberation of Cl and O. Heated with HCl it gives off a mixture of Cl and Cl_2O_4, the latter acting as an energetic oxidant in solutions in which it is generated.

Potassium Hypochlorite—KClO—90.5—is formed in solution by imperfect saturation of a cooled solution of KHO with hypochlorous acid. An impure solution is used in bleaching: **Javelle water.**

Sulfates.—Dipotassic sulfate—*Potassium sulfate*—**Potassii sulfas (U. S.)—Potassæ sulfas (Br.)—K_2SO_4**—174—occurs native; in the ash of many plants; and in solution in mineral waters. It crystallizes in right rhombic prisms; hard; permanent in air; salt and bitter in taste; soluble in H_2O.

Monopotassic Sulfate—*Hydropotassic sulfate—Acid sulfate*—**$KHSO_4$**—136—is formed as a by-product in the manufacture of HNO_3. When heated it loses H_2O, and is converted into the **pyrosulfate,** $K_2S_2O_7$, which, at a higher temperature, is decomposed into K_2SO_4 and SO_3.

Dipotassic Sulfite—*Potassic sulfite*—**Potassii Sulfis (U. S.)—K_2SO_3**—158—is formed by saturating solution of K_2CO_3 with SO_2, and evaporating over H_2SO_4. It crystallizes in oblique rhombohedra; soluble in H_2O. Its solution absorbs O from air, with formation of K_2SO_4.

Potassium Dichromate—*Bichromate of potash*—**Potassii bichromas (U. S.)—Potassæ bichromas (Br.)—$K_2Cr_2O_7$**—294.8—is formed by heating a mixture of *chrome iron ore* with KNO_3, or K_2CO_3 in air; extracting with H_2O; neutralizing with dilute H_2SO_4; and evaporating. It forms large, reddish-orange colored prismatic crystals; soluble in H_2O; fuses below redness, and at a higher temperature is decomposed into O, potassium chromate, and sesquioxid of chromium. Heated with HCl, it gives off Cl.

Potassium Permanganate—Potassii permanganas (**U. S.**)—**Potassæ permanganas** (**Br.**)—**$K_2Mn_2O_8$**—314—is obtained by fusing a mixture of manganese dioxid, KHO, and $KClO_3$, and evaporating the solution to crystallization; K_2MnO_4 and KCl are first formed; on boiling with H_2O, the manganate is decomposed into $K_2Mn_2O_8$, KHO, and MnO_2.

It crystallizes in dark prisms, almost black, with greenish reflections, which yield a red powder when broken. Soluble in H_2O, communicating to it a red color, even in very dilute solution. It is a most valuable oxidizing agent. With organic matter its solution is turned to green, by the formation of the manganate, or deposits the brown sesquioxid of manganese, according to the nature of the organic substance. In some instances the reaction takes place best in the cold, in others under the influence of heat; in some better in acid solutions, in others in alkaline solutions. Mineral reducing agents act more rapidly. Its oxidizing powers render its solutions valuable as disinfectants.

Potassium Acetate—Potassii acetas (**U. S.**)—**Potassæ acetas** (**Br.**)—**$KC_2H_3O_2$**—110—exists in the sap of plants; and it is by its calcination that the major part of the carbonate of wood ashes is formed. It is prepared by neutralizing acetic acid with K_2CO_3 or $KHCO_3$.

It forms crystalline needles, deliquescent, and very soluble in H_2O; less soluble in alcohol. Its solutions are faintly alkaline.

Carbonates.—Dipotassic Carbonate—Potassic Carbonate—Salt of tartar—Pearl ash—Potassii Carbonas (**U. S.**)—**Potassæ carbonas** (**Br.**)—**K_2CO_3**—138—exists in mineral waters, and in the animal economy. It is prepared industrially, in an impure form, known as **potash** or **pearlash,** from wood ashes, from the molasses of beet-sugar, and from the native Stassfurth chlorid. It is obtained pure by decomposing the monopotassic salt, purified by several recrystallizations, by heat; or by calcining a potassium salt of an organic acid. Thus cream of tartar, mixed with nitre and heated to redness, yields a black mixture of C and K_2CO_3, called **black flux**; on extracting which with H_2O, a pure carbonate, known as **salt of tartar,** is dissolved.

Anhydrous, it is a white, granular, deliquescent, very soluble powder. At low temperatures it crystallizes with 2 Aq. Its solution is alkaline.

Monopotassic Carbonate—*Hydropotassic carbonate*—**Bicarbonate—Potassii bicarbonas**—(**U. S.**)—**Potassæ bicarbonas** (**Br.**)—**$HKCO_3$**—100—is obtained by dissolving K_2CO_3 in H_2O, and saturating the solution with CO_2. It crystallizes in oblique rhombic prisms, much less soluble than the carbonate. In solution, it is gradually converted into the dipotassic salt when heated, when brought into a vacuum, or when treated with an inert gas. The solutions are alkaline in reaction and in taste, but are not caustic.

The substance used in baking, under the name **salæratus,** is this or the corresponding Na salt, usually the latter. Its extensive use in some parts of the country is undoubtedly in great measure the cause of the prevalence of dyspepsia. When used alone in baking, it "raises" the bread by decomposition into carbon dioxid and dipotassic (or disodic) carbonate, the latter producing disturbances of digestion by its strong alkaline reaction.

Monopotassic oxalate—*Hydropotassic oxalate—Binoxalate of potash*—**HKC_2O_4**—128—forms transparent, soluble, acid needles. It occurs along with the **quadroxalate** $HKC_2O_4,H_2C_2O_4+2$ Aq, in **salt of lemon** or **salt of sorrel**, used in straw bleaching, and for the removal of ink-stains, etc. It closely resembles Epsom salt in appearance, and has been fatally mistaken for it.

Tartrates.—Dipotassic tartrate—*Potassic tartrate*—**Soluble tartar**—*Neutral tartrate of potash*—**Potassii tartras (U. S.)—Potassæ tartras (Br.)—$K_2C_4H_4O_6$**—226—is prepared by neutralizing the hydropotassic salt with potassium carbonate. It forms a white, crystalline powder, very soluble in H_2O, the solution being dextrogyrous, $[\alpha]_D = +28°.48$; soluble in alcohol. Acids, even acetic, decompose its solution, with precipitation of the monopotassic salt.

Monopotassic tartrate—*Hydropotassic tartrate*—**Cream of tartar—Potassii bitartras (U. S.)—Potassæ bitartras (Br.)—$HKC_4H_4O_6$**—188.—During the fermentation of grape juice, as the porportion of alcohol increases, crystalline crusts collect in the cask. These constitute the **crude tartar,** or **argol,** of commerce, which is composed, in great part, of monopotassic tartrate. The crude product is purified by repeated crystallization from boiling H_2O; digesting the purified tartar with HCl at 20° (68° F.); washing with cold H_2O, and crystallizing from hot H_2O.

It crystallizes in hard, opaque (translucent when pure), rhombic prisms, which have an acidulous taste, and are very sparingly soluble in H_2O, still less soluble in alcohol. Its solution is acid, and dissolves many metallic oxids with formation of double tartrates. When boiled with antimony trioxid, it forms tartar emetic.

It is used in the household, combined with monosodic carbonate, in baking, the two substances reacting upon each other to form Rochelle salt, with liberation of carbon dioxid.

Baking Powders are now largely used as substitutes for yeast in the manufacture of bread. Their action is based upon the decomposition of $HNaCO_3$ by some salt having an acid reaction, or by a weak acid. In addition to the bicarbonate and flour, or corn-starch (added to render the bulk convenient to handle and to diminish the rapidity of the reaction), they contain cream of tartar, tartaric acid, alum, or acid phosphates. Sometimes ammonium sesquicarbonate is used, in whole or in part, in place of sodium carbonate.

The reactions by which the CO_2 is liberated are:

$$1.\ \underset{\substack{\text{Monopotassic}\\ \text{tartrate.}}}{HKC_4H_4O_6} + \underset{\substack{\text{Monosodic}\\ \text{carbonate.}}}{NaHCO_3} = \underset{\substack{\text{Sodium potassium}\\ \text{tartrate.}}}{NaKC_4H_4O_6} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbon}\\ \text{dioxid.}}}{CO_2}$$

$$2.\ \underset{\text{Tartaric acid.}}{H_2C_4H_4O_6} + \underset{\substack{\text{Monosodic}\\ \text{carbonate.}}}{2NaHCO_3} = \underset{\text{Disodic tartrate.}}{Na_2C_4H_4O_6} + \underset{\text{Water.}}{2H_2O} + \underset{\substack{\text{Carbon}\\ \text{dioxid.}}}{2CO_2}$$

$$3.\ \underset{\substack{\text{Aluminium}\\ \text{potassium alum.}}}{Al_2(SO_4)_3,K_2SO_4} + \underset{\substack{\text{Monosodic}\\ \text{carbonate.}}}{6NaHCO_3} = \underset{\substack{\text{Dipotassic}\\ \text{sulfate.}}}{K_2SO_4} + \underset{\substack{\text{Disodic}\\ \text{sulfate.}}}{3Na_2SO_4} +$$

$$+ \underset{\substack{\text{Aluminium}\\ \text{hydroxid.}}}{Al_2H_6O_6} + \underset{\substack{\text{Carbon}\\ \text{dioxid.}}}{6CO_2}$$

$$4.\ \underset{\substack{\text{Aluminium}\\ \text{ammonium alum.}}}{Al_2(SO_4)_3,(NH_4)_2SO_4} + \underset{\substack{\text{Monosodic}\\ \text{carbonate.}}}{6NaHCO_3} = \underset{\substack{\text{Diammonic}\\ \text{sulfate.}}}{(NH_4)_2SO_4} + \underset{\substack{\text{Disodic}\\ \text{sulfate.}}}{3Na_2SO_4} +$$

$$+ \underset{\substack{\text{Aluminium}\\ \text{hydroxid.}}}{Al_2H_6O_6} + \underset{\substack{\text{Carbon}\\ \text{dioxid.}}}{6CO_2}$$

$$5.\ \underset{\substack{\text{Aluminium}\\ \text{sulfate.}}}{Al_2(SO_4)_3} + \underset{\substack{\text{Monosodic}\\ \text{carbonate.}}}{6NaHCO_3} = \underset{\substack{\text{Disodic}\\ \text{sulfate.}}}{3Na_2SO_4} + \underset{\substack{\text{Aluminium}\\ \text{hydroxid.}}}{Al_2H_6O_6} + \underset{\substack{\text{Carbon}\\ \text{dioxid.}}}{6CO_2}$$

$$6.\ \underset{\substack{\text{Monosodic}\\ \text{phosphate.}}}{NaH_2PO_4} + \underset{\substack{\text{Monosodic}\\ \text{carbonate.}}}{NaHCO_3} = \underset{\substack{\text{Disodic}\\ \text{phosphate.}}}{Na_2HPO_4} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbon}\\ \text{dioxid.}}}{CO_2}$$

Sodium Potassium Tartrate—Rochelle salt—*Sel de seignette*—**Potassii et sodii tartras (U. S.)—Soda tartarata (Br.)**—$NaKC_4H_4O_6 + 4\ Aq$—210 + 72—is prepared by saturating monopotassic tartrate with disodic carbonate. It crystallizes in large, transparent prisms, which effloresce superficially in dry air, and attract moisture in damp air. It fuses at 70°–80° (158°–176° F.), and loses 3 Aq at 100° (212° F.). It is soluble in H_2O, the solutions being dextrogyrous, $[\alpha]_D = +\ 29^\circ.67$.

Potassium Antimonyl Tartrate—*Tartarated antimony*—**Tartar emetic—Antimonii et potassii tartras (U. S.)—Antimonium tartaratum (Br.)**—$(SbO)KC_4H_4O_6$—323—is prepared by boiling a mixture of 3 pts. Sb_2O_3 and 4 pts. $HKC_4H_4O_6$ in H_2O for an hour, filtering, and allowing to crystallize. When required pure, it must be made from pure materials.

It crystallizes in transparent, soluble, right rhombic octahedra, which turn white in air. Its solutions are acid in reaction, have a nauseating, metallic taste, are lævogyrous, $[\alpha]_D = -156^\circ.2$, and are precipitated by alcohol. The crystals contain ½ Aq, which they lose entirely at 100° (212° F.), and, partially, by exposure to air. It is decomposed by the alkalies, alkaline earths, and alkaline carbonates, with precipitation of Sb_2O_3. The precipitate is redissolved by excess of soda or potash, or by tartaric acid. HCl, H_2SO_4 and HNO_3 precipitate corresponding antimonyl compounds from solutions of tartar emetic. It converts mercuric into mercurous chlorid. It forms double tartrates with the tartrates of the alkaloids.

Potassium Cyanid—Potassii cyanidum (U. S.)—KCN—65—is obtained by heating a mixture of potassium ferrocyanid and dry K_2CO_3, as long as effervescence continues; decanting and crystallizing.

It is usually met with in dull, white, amorphous masses. Odorless when dry, it has the odor of hydrocyanic acid when moist. It is deliquescent, and very soluble in H_2O; almost insoluble in alcohol. Its solution is acrid and bitter in taste, with an after-taste of hydrocyanic acid. It is very readily oxidized to the cyanate, a property which renders it valuable as a reducing agent. Solutions of KCN dissolve I, AgCl, the cyanids of Ag and Au, and many metallic oxids.

It is actively poisonous, and produces its effects by decomposition and liberation of hydrocyanic acid (*q. v.*).

Potassium Ferrocyanid—Yellow prussiate of potash—Potassii ferrocyanidum (U.S.)—Potassæ prussias flava (Br.)—$K_4[Fe(CN)_6]$ + 3 Aq—367.9 + 54.—This salt, the source of the other cyanogen compounds, is manufactured by adding organic matter (blood, bones, hoofs, leather, etc.) and iron to K_2CO_3 in fusion; or by other processes in which the N is obtained from the residues of the purification of coal-gas, from atmospheric air, or from ammoniacal compounds.

It forms soft, flexible, lemon-yellow crystals, permanent in air at ordinary temperatures. They begin to lose Aq at 60° (140° F.), and become anhydrous at 100° (212° F.). Soluble in H_2O; insoluble in alcohol, which precipitates it from its aqueous solution. When calcined with KHO or K_2CO_3, potassium cyanid and cyanate are formed, and Fe is precipitated. Heated with dilute H_2SO_4, it yields an insoluble white or blue salt, potassium sulfate, and hydrocyanic acid. Its solutions form with those of many of the metallic salts insoluble ferrocyanids; those of Zn, Pb, and Ag are white, cupric ferrocyanid is mahogany-colored, ferrous ferrocyanid is bluish-white, ferric ferrocyanid, **Prussian blue,** is dark blue. Blue ink is a solution of Prussian blue in a solution of oxalic acid.

Potassium Ferricyanid—Red prussiate of potash—$K_6Fe_2(CN)_{12}$—657.8—is prepared by acting upon the ferrocyanid with chlorin; or, better, by heating the white residue of the action of H_2SO_4 upon potassium ferrocyanid, in the preparation of hydrocyanic acid, with a mixture of 1 vol. HNO_3 and 20 vols. H_2O; the *blue* product is digested with H_2O, and potassium ferrocyanid, the solution filtered and evaporated. It forms red, oblique, rhombic prisms, almost insoluble in alcohol. With solutions of ferrous salts it gives a dark blue precipitate, **Turnbull's blue.**

Analytical Characters.—(1.) Platinic chlorid, in presence of HCl: yellow ppt.; crystalline if slowly formed; sparingly soluble in H_2O, much less so in alcohol. (2.) Tartaric acid, in not too dilute solution: white ppt.; soluble in alkalies and in concentrated acids. (3.) Hydrofluosilicic acid: translucent, gelatinous ppt.; forms slowly; soluble in strong alkalies. (4.) Perchloric acid: white ppt.; sparingly soluble in H_2O; insoluble in alcohol. (5.) Phosphomolybdic acid: white ppt.; forms slowly. (6.) Colors the Bunsen flame violet (the color is only observable through blue glass in presence of Na), and exhibits a spectrum of two bright lines: $\lambda = 7860$ and 4045 (Fig. 16, No. 3).

Action of the Sodium and Potassium Compounds on the Economy.—The hydroxids of Na and of K, and in a less degree the carbonates, disintegrate animal tissues, dead or living, with which they come in contact, and, by virtue of this action, act as powerful caustics upon a living tissue. Upon the skin, they produce a soapy feeling, and in the mouth a soapy taste. Like the acids, they cause death, either immediately, by corrosion or perforation of the stomach; or secondarily, after weeks or months, by closure of one or both openings of the stomach, due to thickening, consequent upon inflammation.

The treatment consists in the neutralization of the alkali by an acid, dilute vinegar. Neutral oils and milk are of service, more by reason of their emollient action than for any power they have to neutralize the alkali, by the formation of a soap, at the temperature of the body.

The other compounds of Na, if the acid be not poisonous, are without deleterious action, unless taken in excessive quantity. Common salt has produced paralysis and death in a dose of half a pound. The neutral salts of K, on the contrary, are by no means without true poisonous action when taken internally, or injected subcutaneously, in sufficient quantities; causing dyspnœa, convulsions, arrest of the heart's action, and death. In the adult human subject, death has followed the ingestion of doses of ℥ ss.–℥ i. of the nitrate, in several instances; doses of ʒ ij.–℥ ij. of the sulfate have also proved fatal.

Cesium—*Symbol* = **Cs**—*Atomic weight* = 132.6; and **Rubidium** —*Symbol*=**Rb**—*Atomic weight*=85.3—are two rare elements, discovered in 1860 by Kirchoff and Bunsen while examining spectroscopically the ash of a spring water. They exist in very small quantity in *lepidolite*. They combine with O and decompose H_2O even more energetically than does K, forming strongly alkaline hydroxids.

SILVER.

Symbol = **Ag** (**ARGENTUM**)—*Atomic weight* = 107.9—*Molecular weight* = 216 (?)—*Sp. gr.* = 10.4–10.54—*Fuses at* 1,000° (1,832° F.).

Although silver is usually classed with the "noble metals," it differs from Au and Pt widely in its chemical characters, in which it more closely resembles the alkaline metals.

When pure Ag is required, coin silver is dissolved in HNO_3 and the diluted solution precipitated with HCl. The silver chlorid is washed, until the washings no longer precipitate with silver nitrate; and reduced, either (1) by suspending it in dilute H_2SO_4 in a platinum basin, with a bar of pure Zn, and washing thoroughly, after complete reduction; or (2) by mixing it with chalk and charcoal (AgCl, 100 parts; C, 5 parts; $CaCO_3$, 70 parts), and gradually introducing the mixture into a red-hot crucible.

Silver is a white metal; very malleable and ductile; the best known conductor of heat and electricity. It is not acted on by pure air, but is blackened in air containing a trace of H_2S. It combines directly with Cl, Br, I, S, P, and As. Hot H_2SO_4 dissolves it as sulfate, and HNO_3 as nitrate. The caustic alkalies do not affect it. It alloys readily with many metals; its alloy with Cu is harder than the pure metal.

Silver seems to exist in a number of allotropic modifications, besides that in which it is ordinarily met with. In one of these it is brilliant, metallic, bluish-green in color, and dissolves in H_2O, forming a deep red solution; in another it has the color of burnished gold, when dry; and in still another it has also a bluish-green color, but is insoluble in water. Very dilute mineral acids immediately convert these modifications into normal gray silver, without evolution of any gas.

Oxids.—Three oxids of silver are known: Ag_4O, Ag_2O, and Ag_2O_2.

Silver Monoxid—*Protoxid*—**Argenti oxidum**—(**U. S.; Br.**)—**Ag_2O** —231.8—formed by precipitating a solution of silver nitrate with potash. It is a brownish powder; faintly alkaline and very slightly soluble in H_2O; strongly basic. It readily gives up its oxygen. On contact with ammonium hydroxid it forms a fulminating powder.

Chlorid—$AgCl$—143.4—formed when HCl or a chlorid is added to a solution containing silver. It is white; turns violet and black in sunlight; volatilizes at 260° (500° F.); sparingly soluble in HCl; soluble in solutions of the alkaline chlorids, hyposulfids, and cyanids, and in ammonium hydroxid. It crystallizes in octahedra on exposure of its ammoniacal solution.

Bromid—$AgBr$; and **Iodid**—AgI—are yellowish precipitates, formed by decomposing silver nitrate with potassium bromid and iodid. The former is very sparingly soluble in ammonium hydroxid, the latter is insoluble.

Argentic Nitrate—Argenti Nitras (U. S.; Br.)—$AgNO_3$—169.9—is prepared by dissolving Ag in HNO_3, evaporating, fusing, and recrystallizing. It crystallizes in anhydrous, right rhombic plates; soluble in H_2O. The solutions are colorless and neutral. In the presence of organic matter it turns black in sunlight.

The salt, fused and cast into cylindrical moulds, constitutes **lunar caustic, lapis infernalis; argenti nitras fusa (U. S.)**. If, during fusion, the temperature be raised too high, it is converted into nitrite, O, and Ag; and if sufficiently heated, leaves pure Ag.

Dry Cl and I decompose it, with liberation of anhydrous HNO_3. It absorbs NH_3, to form a white solid, $AgNO_3, 3NH_3$, which gives up its NH_3 when heated. Its solution is decomposed very slowly by H, with deposition of Ag.

Argentic Cyanid—Argenti Cyanidum (U. S.)—$AgCN$—133.9—is prepared by passing HCN through a solution of $AgNO_3$. It is a white, tasteless powder; gradually turns brown in daylight; insoluble in dilute acids; soluble in ammonium hydroxid, and in solutions of ammoniacal salts, cyanids, or hyposulfites. The strong mineral acids decompose it with liberation of HCN.

Analytical Characters.—(1.) Hydrochloric acid: white, flocculent ppt.; soluble in NH_4HO; insoluble in HNO_3. (2.) Potash or soda: brown ppt.; insoluble in excess; soluble in NH_4HO. (3.) Ammonium hydroxid, from neutral solutions: brown ppt.; soluble in excess. (4.) Hydrogen sulfid or ammonium sulfhydrate; black ppt.; insoluble in NH_4HS. (5.) Potassium bromid: yellowish-white ppt.; insoluble in acids, if not in great excess; soluble in NH_4HO. (6.) Potassium iodid: same as KBr, but the ppt. is less soluble in NH_4HO.

Action on the Economy.—Silver nitrate acts both locally as a corrosive and systemically as a true poison. Its local action is due to its decomposition, by contact with organic substances, resulting in the separation of elementary Ag, whose deposition causes a black stain, and liberation of free HNO_3, which acts as a caustic. When absorbed, it causes nervous symptoms, referable to its poisonous action. The blue coloration of the skin, observed in those to whom it is administered for some time, is due to the reduction of the metal, under the combined influence of light and organic matter; especially of the latter, as the darkening is observed, although it is less intense, in internal organs.

In acute poisoning by silver nitrate, sodium chlorid or white of egg should be given; and, if the case be seen before the symptoms of corrosion are far advanced, emetics.

AMMONIUM COMPOUNDS.

The ammonium theory.—Although the radical **ammonium, NH_4**, has probably never been isolated, its existence in the ammoniacal compounds is almost universally admitted. The ammonium hypothesis is based chiefly upon the following facts: (1) the close resemblance of the ammoniacal salts to those of K and Na; (2) when ammonia gas and an acid gas come together, they unite, *without liberation of hydrogen*, to form an ammoniacal salt; (3) the diatomic anhydrids unite directly with dry ammonia with formation of the ammonium salt of an amido acid:

$$\underset{\text{Sulfur trioxid.}}{SO_3} \quad + \quad \underset{\text{Ammonia.}}{2NH_3} \quad = \quad \underset{\text{Ammonium sulfamate.}}{SO_2(NH_2)(NH_4)}$$

(4) when solutions of the ammoniacal salts are subjected to electrolysis, a mixture, having the composition NH_3+H is given off at the negative pole; (5) amalgam of sodium, in contact with a concentrated solution of ammonium chlorid, increases much in volume, and is converted into a light, soft mass, having the lustre of mercury. This **ammonium amalgam** is decomposed gradually, giving off ammonia and hydrogen in the proportion NH_3+H; (6) if the gases NH_3+H, given off by decomposition of the amalgam, exist there in simple solution, the liberated H would have the ordinary properties of that element. If, on the other hand, they exist in combination, the H would exhibit the more energetic affinities of an element in the nascent state. The hydrogen so liberated is in the nascent state.

Ammonium Hydroxid—*Caustic ammonia*—**NH_4HO**—35—has never been isolated, probably owing to its tendency to decomposition; $NH_4HO=NH_3+H_2O$. It is considered as existing in the so-called aqueous solutions of ammonia. These are colorless liquids; of less sp. gr. than H_2O; strongly alkaline; and having the taste and odor of ammonia, which gas they give off on exposure to air, and more rapidly when heated. They are neutralized by acids, with elevation of temperature and formation of ammoniacal salts. The **Aqua ammoniæ** (**U. S.**) and **Liq. ammoniæ** (**Br.**) are such solutions.

Sulfids.—Four are known: $(NH_4)_2S$; $(NH_4)_2S_2$; $(NH_4)_2S_4$; and $(NH_4)_2S_5$; as well as a sulfhydrate $(NH_4)HS$.

Ammonium Sulfhydrate—$\mathbf{NH_4HS}$—51—is formed, in solution, by saturating a solution of NH_4HO with H_2S; or, anhydrous, by mixing equal volumes of dry NH_3 and dry H_2S.

The anhydrous compound is a colorless, transparent, volatile and soluble solid; capable of sublimation with decomposition. The solution, when freshly prepared, is colorless, but soon becomes yellow from oxidation, and formation of ammonium disulfid and hyposulfite, and finally deposits sulfur.

The sulfids and hydrosulfid of ammonium are also formed during the decomposition of albuminoids, and exist in the gases formed in burial vaults, sewers, etc.

Ammonium Chlorid—**Sal ammoniac**—**Ammonii chloridum** (**U.S.; Br.**)—$\mathbf{NH_4Cl}$—53.5—is obtained from the ammoniacal water of gas-works. It is a translucid, fibrous, elastic solid; salty in taste, neutral in reaction; volatile without fusion or decomposition; soluble in H_2O. Its solution is neutral, but loses NH_3 and becomes acid when boiled.

Ammonium chlorid exists in small quantity in the gastric juice of the sheep and dog; also in the perspiration, urine, saliva, and tears.

Ammonium Bromid—**Ammonii bromidum** (**U. S.**)—$\mathbf{(NH_4)Br}$—98—is formed either by combining NH_3 and HBr; by decomposing ferrous bromid with NH_4HO; or by double decomposition between KBr and $(NH_4)_2SO_4$. It is a white, granular powder, or crystallizes in large prisms, which turn yellow on exposure to air; quite soluble in H_2O; volatile without decomposition.

Ammonium Iodid—**Ammonii iodidum** (**U. S.**)—$\mathbf{NH_4I}$—145—is formed by union of equal volumes of NH_3 and HI; or by double decomposition of KI and $(NH_4)_2SO_4$. It crystallizes in deliquescent, very soluble cubes.

Ammonium Nitrate—**Ammonii nitras** (**U. S.**)—$\mathbf{(NH_4)NO_3}$—80—is prepared by neutralizing HNO_3 with ammonium hydroxid or carbonate. It crystallizes in flexible, anhydrous, six-sided prisms; very soluble in H_2O, with considerable diminution of temperature; fuses at 150° (302° F.), and decomposes at 210° (410° F.), with formation of nitrous oxid: $(NH_4)NO_3 = N_2O + 2H_2O$. If the heat be suddenly applied, or allowed to surpass 250° (482° F.), NH_3, NO, and N_2O are formed. When fused it is an active oxidant.

Sulfates.—**Diammonic Sulfate**—*Ammonic sulfate*—**Ammonii sulfas** (**U. S.**)—$\mathbf{(NH_4)_2SO_4}$—132—is obtained by collecting the distillate from a mixture of ammoniacal gas liquor and lime in H_2SO_4. It forms anhydrous, soluble, rhombic crystals; fuses at 140° (284° F.), and is decomposed at 200° (392° F.) into NH_3 and $H(NH_4)SO_4$.

Monoammonic Sulfate—*Hydroammonic sulfate—Bisulfate of ammonia*—**$H(NH_4)SO_4$**—115—is formed by the action of H_2SO_4 on $(NH_4)_2SO_4$. It crystallizes in right rhombic prisms, soluble in H_2O and in alcohol.

Ammonium Acetate—**$(NH_4)C_2H_3O_2$**—77—is formed by saturating acetic acid with NH_3, or with ammonium carbonate. It is a white, odorless, very soluble solid; fuses at 86° (186°.8 F.), and gives off NH_3; then acetic acid, and finally acetamid. **Liq. ammonii acetatis=Spirit of Mindererus** is an aqueous solution of this salt.

Carbonates.—Diammonic Carbonate—*Ammonic carbonate—Neutral ammonium carbonate*—**$(NH_4)_2CO_3+Aq$**—96+18—has been obtained as a white crystalline solid. In air it is rapidly decomposed into NH_3 and $H(NH_4)CO_3$.

Monoammonic Carbonate—*Hydroammonic carbonate—Acid carbonate of ammonia*—**$H(NH_4)CO_3$**—79—is prepared by saturating a solution of NH_4HO or ammonium sesquicarbonate with CO_2. It crystallizes in large, rhombic prisms; quite soluble in H_2O. At 60° (140° F.) it is decomposed into NH_3 and CO_2.

Ammonium Sesquicarbonate—Sal volatile—Preston salts—Ammonii carbonas (U. S.)—Ammoniæ carbonas (Br.)—**$(NH_4)_4H_2(CO_3)_3$**—254—is prepared by heating a mixture of NH_4Cl and chalk, and condensing the product. It crystallizes in rhombic prisms; has an ammoniacal odor and an alkaline reaction; soluble in H_2O. By exposure to air or by heating its solution, it is decomposed into H_2O, NH_3, and $H(NH_4)CO_3$.

Analytical Characters.—(1.) Entirely volatile at high temperatures. (2.) Heated with KHO, the ammoniacal compounds give off NH_3, recognizable: (*a*) by changing moist red litmus to blue; (*b*) by its odor; (*c*) by forming a white cloud on contact with a glass rod moistened with HCl. (3.) With platinic chlorid: a yellow, crystalline ppt. (4.) With hydrosodic tartrate, in moderately concentrated and neutral solution: a white crystalline ppt.

Action on the Economy.—Solutions of the hydroxid and carbonate act upon animal tissues in the same way as the corresponding Na and K compounds. They, moreover, disengage NH_3, which causes intense dyspnœa, irritation of the air-passages, and suffocation.

The treatment indicated is the neutralization of the alkali by a dilute acid. Usually the vapor of acetic acid or of dilute HCl must be administered by inhalation.

II. THALLIUM GROUP.

THALLIUM.

Symbol=**Tl**—*Atomic weight*=203.7—*Sp. gr.*=11.8-11.9—*Fuses at* 294° (561° *F.*)—*Discovered by Crookes* (1861).

A rare element, first obtained from the deposits in flues of sulfuric acid factories, in which pyrites from the Hartz were used. It resembles Pb in appearance and in physical properties, but differs entirely from that element in its chemical characters. It resembles Au in being univalent and trivalent, but differs from it, and resembles the alkali metals in being readily oxidized, in forming alums, and in forming no acid hydrate. It differs from the alkali metals in the thallic compounds, which contain Tl‴. It is characterized spectroscopically by a bright green line—λ=5349.

III. CALCIUM GROUP.

Metals of the Alkaline Earths.

CALCIUM—STRONTIUM—BARIUM.

The members of this group are bivalent in all their compounds; each forms two oxids: MO and MO_2; each forms a hydroxid, having well marked basic characters.

CALCIUM.

Symbol=**Ca**—*Atomic weight*=40—*Molecular weight*=80 (?)—*Sp. gr.*=1.984—*Discovered by Davy in* 1808—*Name from* calx=lime.

Occurs only in combination, as limestone, marble, chalk ($CaCO_3$); gypsum, selenite, alabaster ($CaSO_4$), and many other minerals. In bones, egg-shells, oyster-shells, etc., as $Ca_3(PO_4)_2$ and $CaCO_3$, and in many vegetable structures.

The element is a hard, yellow, very ductile, and malleable metal; fusible at a red heat; not sensibly volatile. In dry air it is not altered, but is converted into CaH_2O_2 in damp air; decomposes H_2O; burns when heated in air.

Calcium Monoxid—Quick lime—Lime—Calx (**U. S.; Br.**)—**CaO**—56—is prepared by heating a native carbonate (limestone); or, when required pure, by heating a carbonate, prepared by precipitation.

It occurs in white or grayish, amorphous masses; odorless; alkaline; caustic; almost infusible; sp. gr. 2.3. With H_2O it gives off great heat and is converted into the hydroxid (**slacking**). In air it becomes **air-slacked**, falling into a white powder, having the composition $CaCO_3,CaH_2O_2$.

Calcium Hydroxid—Slacked lime—Calcis hydras (**Br.**)—**CaH_2O_2**—74—is formed by the action of H_2O on CaO. If the quantity of H_2O used be one-third that of the oxid, the hydroxid remains as a dry, white, odorless powder; alkaline in taste and reaction; more soluble in cold than in hot H_2O. If the quantity of H_2O be greater, a creamy, or milky liquid remains, **cream** or **milk of lime;** a solution holding an excess in suspension. With a sufficient quantity of H_2O the hydroxid is dissolved to a clear solution, which is **lime water—Liquor calcis** (**U. S.**; **Br.**). The solubility of CaH_2O_2 is diminished by the presence of alkalies, and is increased by sugar or mannite: **Liq. calc. saccharatus** (**Br.**). Solutions of CaH_2O_2 absorb CO_2 with formation of a white deposit of $CaCO_3$.

Calcium Chlorid—Calcii chloridum (**U. S.**; **Br.**)—**$CaCl_2$**—111—is obtained by dissolving marble in HCl: $CaCO_3+2HCl=CaCl_2+H_2O+CO_2$. It is bitter; deliquescent; very soluble in H_2O; crystallizes with 6 Aq, which it loses when fused, leaving a white, amorphous mass; used as a drying agent.

Chloride of Lime—Bleaching powder—Calx chlorata (**U.S.**; **Br.**)—is a white or yellowish, hygroscopic powder, prepared by passing Cl over CaH_2O_2, maintained in excess. It is bitter and acrid in taste; soluble in cold H_2O; decomposed by boiling H_2O, and by the weakest acids, with liberation of Cl. It is decomposed by CO_2, with formation of $CaCO_3$, and liberation of hypochlorous acid, if it be moist; or of Cl, if it be dry. A valuable disinfectant.

Bleaching powder was formerly considered as a mixture of calcium chlorid and hypochlorite, formed by the reaction: $2CaO+2Cl_2=CaCl_2+Ca(ClO)_2$, but it is more probable that it is a definite compound having the formula CaCl(OCl), which is decomposed by H_2O into a mixture of $CaCl_2$ and $Ca(ClO)_2$; and by dilute HNO_3 or H_2SO_4 with formation of HClO.

Calcium Sulfate—$CaSO_4$—136—occurs in nature as *anhydrite;* and with 2 Aq in **gypsum,** *alabaster*, *selenite;* and in solution in natural waters. **Terra alba** is ground gypsum. It crystallizes with 2 Aq in right rhombic prisms; sparingly soluble in H_2O, more soluble in H_2O containing free acids or chlorids. When the hydrated salt (gypsum) is heated to 80° (176° F.), or, more rapidly, between 120°-130° (248°-266° F.), it loses its Aq and is converted into a white, opaque mass; which, when ground, is **plaster-of-Paris.**

The **setting** of plaster when mixed with H_2O, is due to the conversion of the anhydrous into the crystalline, hydrated salt. The ordinary plastering should never be used in hospitals, as, by reason of its irregularities and porosity, it soon becomes saturated with the transferrers of septic disease, be they germs or poisons, and cannot be thoroughly purified by disinfectants. Plaster surfaces may, however, be rendered dense, and be highly polished, so as to be smooth and impermeable, by adding glue and alum, or an alkaline silicate to the water used in mixing.

Phosphates.—Three are known: $Ca_3(PO_4)_2$; $Ca_2(HPO_4)_2$, and $Ca(H_2PO_4)_2$.

Tricalcic Phosphate—*Tribasic* or *neutral phosphate*—**Bone phosphate—Calcii phosphas præcipitatus (U. S.)—Calcis phosphas (Br.)—$Ca_3(PO_4)_2$**—310—occurs in nature, in soils, guano, *coprolites*, phosphorite, in all plants, and in every animal tissue and fluid. It is obtained by dissolving bone-ash in HCl, filtering, and precipitating with NH_4HO; or by double decomposition between $CaCl_2$ and an alkaline phosphate. When freshly precipitated it is gelatinous; when dry, a light, white, amorphous powder; almost insoluble in pure H_2O; soluble to a slight extent in H_2O containing ammoniacal salts, or NaCl or $NaNO_3$; readily soluble in dilute acids, even in H_2O charged with carbonic acid. It is decomposed by H_2SO_4 into $CaSO_4$ and $Ca(H_2PO_4)_2$. **Bone-ash** is an impure form of $Ca_3(PO_4)_2$, obtained by calcining bones, and used in the manufacture of P and of superphosphate.

Dicalcic Phosphate—$Ca_2(HPO_4)_2+2Aq$—272+36—is a crystalline, insoluble salt; formed by double decomposition between $CaCl_2$ and HNa_2PO_4 in acid solution.

Monocalcic Phosphate—*Acid calcium phosphate*—**Superphosphate of lime—$Ca(H_2PO_4)_2$**—234—exists in brain tissue, and in those animal liquids whose reaction is acid It is also formed when $Ca_3(PO_4)_2$ is dissolved in an acid, and is manufactured, for use as a manure, by decomposing bone-ash with H_2SO_4. It crystallizes in pearly plates; very soluble in H_2O. Its solutions are acid.

Physiological.—All three calicum phosphates, accompanied by the corresponding Mg salts, exist in the animal économy. The *tricalcic* salt occurs in all the solids of the body, and in all fluids not having an acid reaction, being held in solution in the latter by the presence of chlorids. In the fluids it is present in very small quantity, except in the milk, in which it is comparatively abundant; 2.5 to 3.95 parts per 1,000 in human milk, and 1.8 to 3.87 parts per 1,000 in cow's milk; constituting about 70 per cent. of the ash. The **bones** contain about 35 parts of organic matter, combined with 65 parts of mineral material. The average of human bone-ash is: $Ca_3(PO_4)_2$—83.89; $CaCO_3$—13.03; Ca, combined with Cl, F, and organic acids—0.35; F—0.23; Cl—0.18. The average quantity of $Ca_3(PO_4)_2$ in male adult bones is 57 per cent.; that of $CaCO_3$, 10 per cent.; and that of $Mg_3(PO_4)_2$, 1.3 per cent. In pathological conditions the composition of bone is modified as shown in the following table:

ANALYSES OF BONES.

In 100 parts.	Healthy male, aged 40; femur.	Osteomalacia, male, aged 40; femur.	Osteomalacia, male, aged 60; femur.	Osteomalacia, child; vertebra.	Rachitis; femur	Rachitis; humerus.	Caries; femur.	Caries, female, aged 40; vertebra.	Necrosis.
Collagen	......	48.83	32.54	75.22	72.20	81.12	35.69	41.42	19.58
Fats	......	29.18	4.15	6.12	7.20		3.00	8.36	1.22
Tricalcic phosphate	56.9	17.56	53.25	12.56	14.78	15.60	51.53	44.05	72.63
Calcium fluorid	......	......	......	......	1.00	......			
Calcium carbonate	10.2	3.04	7.49	3.20	3.00	2.66	5.44	3.45	4.03
Trimagnesic phosphate	1.3	0.23	1.22	0.92	0.80	*	3.43	1.02	1.93
Other salts	......	0.37	1.35	1.98	1.02	0.62	0.91	1.70	0.61
Organic matter	35.8	78.01	36.69	81.34	79.40	81.12	38.69	49.78	20.80
Ash	64.2	21.20	63.31	19.66	20.60	18.88	61.31	50.22	79.20
* Included in tricalcic phosphate.	Frémy.	Lehmann.	Von Bibra.	Marchand.	Marchand	Ragsky.	Becquerel and Rodier.	Becquerel and Rodier.	Von Bibra.

The **teeth** consist largely of $Ca_3(PO_4)_2$; the dentin of human molars containing 66.72 per cent., and the enamel 89.82 per cent.

From the **urine**, tricalcic phosphate is frequently deposited, either in the form of an amorphous, granular sediment, or as calculi. The *dicalcic* salt occurs occasionally in urinary sediments, in the form of needle-shaped crystals, arranged in rosettes, and also in urinary calculi. The *monocalcic* salt is always present in acid urine, constituting, with the corresponding magnesium salt, the **earthy phosphates.** The total elimination of H_3PO_4 by the urine is about 2.75 grams (42.5 grains) in 24 hours; of which two-thirds are in combination with Na and K; and one-third with Ca and Mg. The hourly elimination follows about the same variation as that of the chlorids. The total elimination is greater with animal than with vegetable food; is diminished during pregnancy; and is above the normal during excessive mental work. The elimination of earthy phosphates is greatly increased in osteomalacia, often so far that they are in excess of the alkaline phosphates.

So long as the urine is *acid*, it contains the soluble acid phosphates. When the reaction becomes alkaline, or even on loss of CO_2 by exposure to air, the acid phosphate is converted into the insoluble $Ca_3(PO_4)_2$. Alkaline urines are, for this reason, almost always turbid, and become clear on the addition of acid. It is in such urine that phosphatic calculi are invariably formed, usually about a nucleus of uric acid, or of a foreign body. If the alkalinity be due to the formation of ammonia, the trimagnesic phosphate is not formed, but ammonio-magnesian phosphate (*q.v.*).

Quantitative determination of phosphates in urine.—A process for determining the quantity of phosphates in urine is based upon the formation of the insoluble uranium phosphate, and upon the production of a brown color when a solution of a uranium salt is brought in contact with a solution of potassium ferrocyanid. Four solutions are required: (1) *a standard solution of disodic phosphate*, made by dissolving 10.085 grams of crystallized, non-effloresced HNa_2PO_4 in H_2O, and diluting to a litre; (2) *an acid solution of sodium acetate*, made by dissolving 100 grams sodium acetate in H_2O, adding 100 c.c. glacial acetic acid, and diluting with H_2O to a litre; (3) *a strong solution of potassium ferrocyanid;* (4) *a standard solution of uranium acetate*, made by dissolving 20.3 grams of yellow uranic oxid in glacial acetic acid, and diluting with H_2O to nearly a litre. Solution 1 serves to determine the true strength of this solution, as follows: 50 c.c. of Solution 1 are placed in a beaker, 5 c.c. of Solution 2 are added, the mixture heated on a water-bath, and the uranium solution gradually added, from a burette, until a drop from the beaker produces a brown color when brought in contact with a drop of the ferrocyanid solution. At this point the reading of the burette, which indicates the number of c.c. of the uranium solution, corresponding to 0.1—P_2O_5, is taken. A quantity of H_2O, determined by calculation from the result thus obtained, is then added to the remaining uranium solution, such as to render each c.c. equivalent to 0.005 gram P_2O_5.

To determine the **total phosphates** in a urine: 50 c.c. are placed in a beaker, 5 c.c. sodium acetate solution are added; the mixture is heated on the water-bath, and the uranium solution delivered from a burette, until a drop, removed from the beaker and brought in contact with a drop of ferrocyanid solution, produces a brown tinge. The burette reading, multiplied by 0.005, gives the amount of P_2O_5 in 50 c.c. urine; and this, multiplied by $\frac{1}{50}$ the amount of urine passed in 24 hours, gives the daily elimination.

To determine the **earthy phosphates**, a sample of 100 c.c. urine is rendered alkaline with NH_4HO, and set aside for 12 hours. The precipitate is then collected upon a filter, washed with ammoniacal water, brought into a beaker, dissolved in a small quantity of acetic acid; the solution diluted to 50 c.c. with H_2O, treated with 5 c.c. sodium acetate solution, and the amount of P_2O_5 determined as above.

Calcium Carbonate—**$CaCO_3$**—100—the most abundant of the natural compounds of Ca, exists as *limestone*, *calcspar*, *chalk*, *marble*, *Iceland spar*, and *arragonite;* and forms the basis of corals, shells of crustacea and of molluscs, etc.

The precipitated chalk—**Calcii carbonas præcipitata** (**U. S.**; **Br.**) —is prepared by precipitating a solution of $CaCl_2$ with one of

Na_2CO_3. **Prepared chalk—Creta præparata (U. S.; Br.)**—is native chalk, purified by grinding with H_2O, diluting, allowing the coarser particles to subside, decanting the still turbid liquid, collecting, and drying the finer particles. A process known as **elutriation.**

It is a white powder, almost insoluble in pure H_2O; much more soluble in H_2O containing carbonic acid, the solution being regarded as containing **monocalcic carbonate** $H_2Ca(CO_3)_2$. At a red heat it yields CO_2 and CaO. It is decomposed by acids with liberation of CO_2.

PHYSIOLOGICAL.—Calcium carbonate is much more abundant in the lower than in the higher forms of animal life. It occurs in the egg-shells of birds, in the bones and teeth of all animals; in solution in the saliva and urine of the herbivora, and deposited in the crystalline form, as **otoliths,** in the internal ear of man. It is deposited pathologically in calcifications, in parotid calculi, and occasionally in human urinary calculi and sediments.

Calcium Oxalate—*Oxalate of lime*—CaC_2O_4—128—exists in the sap of many plants, and is formed as a white, crystalline precipitate, by double decomposition, between a Ca salt and an alkaline oxalate. It is insoluble in H_2O, acetic acid, or NH_4HO; soluble in the mineral acids and in solution of H_2NaPO_4.

PHYSIOLOGICAL.—Calcium oxalate is taken into the body in vegetable food, and is formed in the economy, where its production is intimately connected with that of uric acid.

It occurs in the urine, in which it is increased in quantity when large amounts of vegetable food are taken; when sparkling wines or beers are indulged in; and when the carbonates of the alkalies, lime-water and lemon-juice, are administered. It is deposited as a urinary sediment in the form of small, brilliant octahedra, having the appearance of the backs of square letter-envelopes; or in dumb-bells. It is usually deposited from acid urine, and accompanied by crystals of uric acid. Sometimes, however, it occurs in urines undergoing alkaline fermentation, in which case it is accompanied by crystals of ammonio-magnesian phosphate.

The renal or vesical calculi of calcium oxalate, known as **mulberry calculi,** are dark brown or gray, very hard, occasionally smooth, generally tuberculated, soluble in HCl without effervescence; and when ignited, they blacken, turn white, and leave an alkaline residue. (See oxalic acid.)

Analytical Characters.—(1.) Ammonium sulfhydrate: nothing, unless the Ca salt be the phosphate, oxalate or fluorid, when it forms a white ppt. (2.) Alkaline carbonates: white ppt.; not prevented by the presence of ammoniacal salts. (3.) Ammonium oxalate: white ppt.; insoluble in acetic acid; soluble in HCl, or

HNO$_3$. (4.) Sulfuric acid: white ppt., either immediately or on dilution with three volumes of alcohol; very sparingly soluble in H_2O; insoluble in alcohol; soluble in sodium hyposulfite solution. (5.) Sodium tungstate: dense white ppt., even from dilute solutions. (6.) Colors the flame of the Bunsen burner reddish-yellow, and exhibits a spectrum of a number of bright bands, the most prominent of which are: λ=6265, 6202, 6181, 6044, 5982, 5933, 5543, and 5517.

STRONTIUM.

Symbol=**Sr**—*Atomic weight*=87.4—*Sp. gr.*=2.54.

An element, not as abundant as Ba, occurring principally in the minerals *strontianite* ($SrCO_3$) and *celestine* ($SrSO_4$). Its compounds resemble those of Ca and Ba. Its nitrate is used in making red fire.

Analytical Characters.—(1.) Behaves like Ba with alkaline carbonates and Na_2HPO_4. (2.) Calcium sulfate: a white ppt. which forms slowly; accelerated by addition of alcohol. (3.) The Sr compounds color the Bunsen flame red, or, as observed through blue glass, purple or rose color. The Sr flame gives a spectrum of many bands, of which the most prominent are: λ=6694, 6664, 6059, 6031, 4607.

BARIUM.

Symbol=**Ba**—*Atomic weight*=136.8—*Molecular weight*=273.6 (?)—*Sp. gr.*=4.0—*Discovered by Davy*, 1808—*Name from* βαρὺς= heavy.

Occurs only in combination, principally as *heavy spar* ($BaSO_4$) and *witherite* ($BaCO_3$). It is a pale yellow, malleable metal, quickly oxidized in air, and decomposing H_2O at ordinary temperatures.

Oxids.—Barium Monoxid—Baryta—BaO—152.8—is prepared by calcining the nitrate. It is a grayish-white or white, amorphous, caustic solid. In air it absorbs moisture and CO_2, and combines with H_2O as does CaO.

Barium Dioxid—*Barium peroxid*—**BaO$_2$**—168.8—is prepared by heating the monoxid in O. It is a grayish-white, amorphous solid. Heated in air it is decomposed: $BaO_2 = BaO + O$. Aqueous acids dissolve it with formation of a barytic salt and H_2O_2.

Barium Monohydroxid—Ba$_2$HO$_2$—170.8—is prepared by the action of H_2O on BaO. It is a white, amorphous solid, soluble in H_2O. Its aqueous solution, **baryta water**, is alkaline, and absorbs CO_2, with formation of a white deposit of $BaCO_3$.

Barium Chlorid—BaCl$_2$+2Aq—207.8+36—is obtained by treating BaS or $BaCO_3$ with HCl. It crystallizes in prismatic plates, permanent in air, soluble in H_2O.

Barium Nitrate—$Ba(NO_3)_2$—260.8—is prepared by neutralizing HNO_3 with $BaCO_3$. It forms octahedral crystals, soluble in H_2O.

Barium Sulfate—$BaSO_4$—232.8—occurs in nature as *heavy spar*, and is formed as an amorphous, white powder, insoluble in acids, by double decomposition between a Ba salt and a sulfite in solution. It is insoluble in H_2O and in acids. It is used as a pigment, **permanent white.**

Barium Carbonate—$BaCO_3$—196.8—occurs in nature as *witherite*, and is formed by double decomposition between a Ba salt and a carbonate in alkaline solution. It is a heavy, amorphous, white powder, insoluble in H_2O, soluble with effervescence in acids.

Analytical Characters.—(1.) Alkaline carbonates: white ppt., in alkaline solution. (2.) Sulfuric acid, or calcium sulfate: white ppt.; insoluble in acids. (3.) Sodium phosphate: white ppt.; soluble in HNO_3. (4.) Colors the Bunsen flame greenish-yellow, and exhibits a spectrum of several lines, the most prominent of which are: $\lambda=6108$, 6044, 5881, 5536.

Action on the Economy.—The oxids and hydroxid act as corrosives, by virtue of their alkalinity, and also as true poisons. All soluble compounds of Ba, and those which are readily converted into soluble compounds in the stomach, are actively poisonous. Soluble sulfids, followed by emetics, are indicated as antidotes. The sulfate, notwithstanding its insolubility in water, is poisonous to some animals.

IV. MAGNESIUM GROUP.

MAGNESIUM—ZINC—CADMIUM.

Each of these elements forms a single oxid—a corresponding basic hydroxid, and a series of salts in which its atoms are bivalent.

MAGNESIUM.

Symbol=**Mg**—*Atomic weight*=24—*Molecular weight*=48 (?)—*Sp. gr.*=1.75—*Fuses at* 1000° (1832° F.)—*Discovered by Davy*, 1808.

Occurs as carbonate in *dolomite* or *magnesian limestone*, and as silicate in *mica*, *asbestos*, *soapstone*, *meerschaum*, *talc*, and in other minerals. It also accompanies Ca in the forms in which it is found in the animal and vegetable worlds.

It is prepared by heating its chlorid with Na. It is a hard, light, malleable, ductile, white metal. It burns with great brilliancy when heated in air (magnesium light), but may be distilled in H. The flash light used by photographers is a mixture of powdered Mg with an oxidizing agent, $KClO_3$ or KNO_3. It decomposes vapor of H_2O when heated; reduces CO_2 with the aid of heat, and combines directly with Cl, S, P, As, and N. It dissolves in dilute acids, but is not affected by alkaline solutions.

Magnesium Oxid—Calcined magnesia—Magnesia (U. S.; Br.)—MgO—40—is obtained by calcining the carbonate, hydroxid, or nitrate. It is a light, bulky, tasteless, odorless, amorphous, white powder; alkaline in reaction; almost insoluble in H_2O; readily soluble without effervescence in acids.

Magnesium Hydroxid—MgH_2O_2—58—occurs in nature, and is formed when a solution of a Mg salt is precipitated with excess of NaHO, in absence of ammoniacal salts. It is a heavy, white powder, insoluble in H_2O; absorbs CO_2.

Magnesium Chlorid—$MgCl_2$—95—is formed when MgO or $MgCO_3$ is dissolved in HCl. It is an exceedingly deliquescent, soluble substance, which is decomposed into HCl and MgO when its aqueous solutions are evaporated to dryness. Like all the soluble Mg compounds it is bitter in taste, and accompanies the sulfate and bicarbonate in the *bitter waters.*

Magnesium Sulfate—Epsom salt—*Sedlitz salt*—**Magnesii sulfas (U. S.)—Magnesiæ sulfas** (**Br.**)—**$MgSO_4 + 7$ Aq**—120 + 126—exists in solution in sea-water and in the waters of many mineral springs, especially those known as **bitter waters.** It is formed by the action of H_2SO_4 on $MgCO_3$. It crystallizes in right rhombic prisms; bitter; slightly effervescent, and quite soluble in H_2O. Heated, it fuses and gradually loses 6 Aq up to 132° (269°.6 F.); the last Aq it loses at 210° (410° F.).

Phosphates.—Resemble those of Ca in their constitution and properties, and accompany them in the situations in which they occur in the animal body, but in much smaller quantity.

Magnesium also forms double phosphates, constituted by the substitution of one atom of the bivalent metal for two of the atoms of basic hydrogen, of a molecule of phosphoric acid, and of an atom of an alkaline metal, or of an ammonium group, for the remaining basic hydrogen.

Ammonio-Magnesian Phosphate—Triple phosphate—$Mg(NH_4)PO_4+6$ Aq—137+108—is produced when an alkaline phosphate and NH_4HO are added to a solution containing Mg. When heated it is converted into **magnesium pyrophosphate** $Mg_2P_2O_7$, in which form H_3PO_4 and Mg are usually weighed in quantitative analysis.

In the urine, alkaline phosphates and magnesium salts are always present, and consequently when, by decomposition of urea, the urine becomes alkaline, the conditions for the formation of this compound are fulfilled. Being practically insoluble, especially in the presence of excess of phosphates and of ammonia, it is deposited in crystals, usually tabular, sometimes feathery and stellate in form. When it is formed in the bladder, in the presence of some body to serve as a nucleus, the crystallization takes place upon the nucleus, and a **fusible calculus** is produced.

Carbonates.—Magnesium Carbonate—*Neutral carbonate*—**$MgCO_3$**—84—exists native in *magnesite*, and, combined with $CaCO_3$, in *dolomite*. It cannot be formed, like other carbonates, by decomposing a Mg salt with an alkaline carbonate, but may be obtained by passing CO_2 through H_2O holding tetramagnesic tricarbonate in suspension.

Trimagnesic Dicarbonate—**$(MgCO_3)_2MgH_2O_2+2Aq$**—226+36—is formed, in small crystals, when a solution of $MgSO_4$ is precipitated with excess of Na_2CO_3, and the mixture boiled.

Tetramagnesic Tricarbonate—Magnesia alba—Magnesii carbonas (U. S.)—Magnesiæ carbonas (Br.)—**$3(MgCO_3)MgH_2O_2+3Aq$**—310+54—occurs in commerce in light, white cubes, composed of a powder which is amorphous, or partly crystalline. It is prepared by precipitating a solution of $MgSO_4$ with one of Na_2CO_3. If the precipitation occur in cold, dilute solutions (**Magnesiæ carbonas lœvis, Br.**), very little CO_2 is given off; a light, bulky precipitate falls, and the solution contains magnesium, probably in the form of the bicarbonate $Mg(HCO_3)_2$. This solution, on standing, deposits crystals of the carbonate, $MgCO_3+3Aq$. If hot concentrated solutions be used, and the liquid be then boiled upon the precipitate, CO_2 is given off, and a denser, heavier precipitate is formed, which varies in composition, according to the length of time during which the boiling is continued, and to the presence or absence of excess of sodium carbonate. The pharmaceutical product frequently contains $4(MgCO_3),MgH_2O_2+4H_2O$, or even $2(MgCO_3),MgH_2O_2+2H_2O$. All of these compounds are very sparingly soluble in H_2O, but much more soluble in H_2O containing ammoniacal salts.

Analytical Characters.—(1.) Ammonium hydroxid: voluminous, white ppt. from neutral solutions. (2.) Potash or soda: voluminous, white ppt. from warm solutions; prevented by the presence of NH_4 salts, and of certain organic substances. (3.) Ammonium carbonate: slight ppt. from hot solutions; prevented by the presence of NH_4 salts. (4.) Sodium or potassium carbonate: white ppt., best from hot solution; prevented by the presence of NH_4 compounds. (5.) Disodic phosphate: white ppt. in hot, not too dilute solutions. (6.) Oxalic acid: nothing alone, but in presence of NH_4HO, a white ppt.; not formed in presence of salts of NH_4.

ZINC.

Symbol=**Zn**—*Atomic weight*=64.9—*Molecular weight*=64.9—*Sp. gr.*=6.862–7.215—*Fuses at* 415° (779° *F.*)—*Distils at* 1040° (1904° *F.*).

Occurs principally in *calamine* ($ZnCO_3$); and *blende* (ZnS); also as oxid and silicate; never free. It is separated from its ores by calcining, roasting, and distillation.

It is a bluish-white metal; crystalline, granular, or fibrous; quite malleable and ductile when pure. The commercial metal is usually brittle. At 130°-150° (266°–302° F.) it is pliable, and becomes brittle again above 200°–210° (392°–410° F.).

At 500° (932° F.) it burns in air, with a greenish-white flame, and gives off snowy white flakes of the oxid (*lana philosophica; nil album; pompholix*). In moist air it becomes coated with a film of hydrocarbonate. It decomposes steam when heated.

Pure H_2SO_4 and pure Zn do not react together in the cold. If the acid be diluted, however, it dissolves the Zn, with evolution of H, and formation of $ZnSO_4$, in the presence of a trace of Pt or Cu. The commercial metal dissolves readily in dilute H_2SO_4, with evolution of H, and formation of $ZnSO_4$, the action being accelerated in presence of Pt, Cu, or As. Zinc surfaces, thoroughly coated with a layer of an amalgam of Hg and Zn, are only attacked by H_2SO_4 if they form part of closed galvanic circuit; hence the zincs of galvanic batteries are protected by *amalgamation*. Zinc also decomposes HNO_3, HCl, and acetic acid.

When required for toxicological analysis, zinc must be perfectly free from As, and sometimes from P. It is better to test samples until a pure one is found, than to attempt the purification of a contaminated metal.

Zinc surfaces are readily attacked by weak organic acids. Vessels of *galvanized iron* or *sheet zinc* should therefore never be used to contain articles of food or medicines.

Zinc Oxid—Zinci oxidum (**U. S.; Br.**)—**ZnO**—80.9—is prepared either by calcining the precipitated carbonate, or by burning Zn in a current of air. An impure oxid, known as **tutty**, is deposited in the flues of zinc furnaces, and in those in which brass is fused. When obtained by calcination of the carbonate, it forms a soft, white, tasteless, and odorless powder. When produced by burning the metal, it occurs in light, voluminous, white masses. It is neither fusible, volatile, nor decomposable by heat, and is completely insoluble in neutral solvents. It dissolves in dilute acids, with formation of the corresponding salts.

It is used in the arts as a white pigment in place of lead carbonate, and is not darkened by H_2S.

Zinc Hydroxid—ZnH_2O_2—98.9—is not formed by union of ZnO and H_2O; but is produced when a solution of a Zn salt is treated with KHO. Freshly prepared, it is very soluble in alkalies, and in solutions of NH_4 salts.

Zinc Chlorid—Butter of zinc—Zinci chloridum (U. S.; Br.)—$ZnCl_2$ +Aq—135.9+18—is obtained by dissolving Zn in HCl; or by heating Zn in Cl. It is a soft, white, very deliquescent, fusible, volatile mass; very soluble in H_2O, somewhat less so in alcohol. Its solution has a burning metallic taste; destroys vegetable tissues; dissolves silk; and exerts a strong dehydrating action upon organic substances in general.

In dilute solution it is used as a disinfectant and antiseptic (*Burnett's fluid*), as a preservative of wood and as an embalming injection.

Zinc Sulfate—White vitriol—Zinci sulfas (U. S.; Br.)—$ZnSO_4$ +nAq—160.9+n18—is formed when Zn, ZnO, ZnS, or $ZnCO_3$ is dissolved in diluted H_2SO_4. It crystallizes below 30° (86° F.) with 7 Aq; at 30° (86° F.) with 6 Aq; between 40°–50° (104°–122° F.) with 5 Aq; at 0° (32° F.) from concentrated acid solution with 4 Aq. From a boiling solution it is precipitated by concentrated H_2SO_4 with 2Aq; from a saturated solution at 100° (212° F.) with 1 Aq; and anhydrous, when the salt with 1 Aq is heated to 238° (460° F.).

The salt usually met with is that with 7 Aq, which is in large, colorless, four-sided prisms; efflorescent; very soluble in H_2O; sparingly soluble in weak alcohol. Its solutions have a strong, styptic taste; coagulate albumin when added in moderate quantity, the coagulum dissolving in an excess; and form insoluble precipitates with the tannins.

Carbonates.—Zinc Carbonate—$ZnCO_3$—124.9—occurs in nature as *calamine*. If an alkaline carbonate be added to a solution of a Zn salt, the neutral carbonate, as in the case of Mg, is not formed, but an oxycarbonate, $nZnCO_3$, $nZnH_2O_2$ [**Zinci carbonas (U. S.; Br.)**], whose composition varies with the conditions under which it is formed.

Analytical Characters.—(1.) K, Na or NH_4 hydroxid: white ppt., soluble in excess. (2.) Carbonate of K or Na: white ppt., in absence of NH_4 salts. (3.) Hydrogen sulfid, in neutral solution: white ppt. In presence of an excess of a mineral acid, the formation of this ppt. is prevented, unless sodium acetate be also present. (4.) Ammonium sulfhydrate: white ppt., insoluble in excess, in KHO, NH_4HO, or acetic acid; soluble in dilute mineral acids. (5.) Ammonium carbonate: white ppt., soluble in excess. (6.) Disodic phosphate, in absence of NH_4 salts: white ppt., soluble in acids or alkalies. (7.) Potassium ferrocyanid: white ppt., insoluble in HCl.

Action on the Economy.—All the compounds of Zn which are soluble in the digestive fluids behave as true poisons; and solutions of the chlorid (in common use by tinsmiths, and in disinfecting fluids) have also well-marked corrosive properties. When Zn compounds are taken, it is almost invariably by mistake for other substances: the sulfate for Epsom salt, and solutions of the chlorid for various liquids, gin, fluid magnesia, vinegar, etc.

Metallic zinc is dissolved by solutions containing NaCl, or organic acids, for which reason articles of food kept in vessels of galvanized iron become contaminated with zinc compounds, and, if eaten, produce more or less intense symptoms of intoxication. For the same reason materials intended for analysis, in cases of supposed poisoning, *should never be packed in jars closed by zinc caps.*

CADMIUM.

Symbol=**Cd**—*Atomic weight*=111.8—*Molecular weight*=111.8—*Sp. gr.*=8.604—*Fuses at* 227°.8 (442° F.)—*Boils at* 860° (1580° F.).

A white metal, malleable and ductile at low temperature, brittle when heated; which accompanies Zn in certain of its ores. It resembles zinc in its physical as well as its chemical characters. It is used in certain fusible alloys, and its iodid is used in photography.

Analytical Characters.—Hydrogen sulfid: bright yellow ppt.; insoluble in NH_4HS, and in dilute acids and alkalies, soluble in boiling HNO_3 or HCl.

V. NICKEL GROUP.

NICKEL—COBALT.

These two elements bear some resemblance chemically to those of the Fe group; from which they differ in forming, so far as known, no compounds similar to the ferrates, chromates, and manganates, unless the barium cobaltite, recently described by Rousseau, be such. They form compounds corresponding to Fe_2O_3, but those corresponding to the ferric series are either wanting or exceedingly unstable.

NICKEL.

Symbol=**Ni**—*Atomic weight*=58—*Sp. gr.*=8.637.

Occurs in combination with S, and with S and As.

It is a white metal, hard, slightly magnetic, not tarnished in air. *German silver* is an alloy of Ni, Cu, and Zn. Nickel is now extensively used for plating upon other metals, and for the manufacture of dishes, etc., for use in the laboratory. Its salts are green.

Analytical Characters.—(1.) Ammonium sulfhydrate: black ppt.; insoluble in excess. (2.) Potash or soda: apple-green ppt., in absence of tartaric acid; insoluble in excess. (3.) Ammonium hydroxid: apple-green ppt.; soluble in excess; forming a violet solution, which deposits the apple-green hydrate, when heated with KHO.

COBALT.

Symbol=**Co**—*Atomic weight*=58.9—*Sp. gr.*=8.5–8.7.

Occurs in combination with As and S. Its salts are red when hydrated, and usually blue when anhydrous. Its phosphate is used as a blue pigment.

Analytical Characters.—(1.) Ammonium sulfhydrate: black ppt.; insoluble in excess. (2.) Potash: blue ppt.; turns red, slowly in the cold, quickly when heated; not formed in the cold in the presence of NH_4 salts. (3.) Ammonium hydroxid: blue ppt.; turns red in absence of air, green in its presence.

VI. COPPER GROUP.

COPPER—MERCURY.

Each of these elements forms two series of compounds. One contains compounds of the bivalent group $\left(\begin{array}{l}Cu\diagdown\\ \,| \quad\;\rangle\\ Cu\diagup\end{array}\right)''$ or $(Hg_2)''$, which are designated by the termination **ous**; the other contains compounds of single, bivalent atoms Cu″ or Hg″, which are designated by the termination ic.

COPPER.

Symbol = **Cu** (**CUPRUM**)—*Atomic weight* = 63.1—*Molecular weight*=127 (?)—*Sp. gr.*=8.914–8.952—*Fuses at* 1091° (1996° *F.*).

Occurrence.—It is found free, in crystals or amorphous masses, sometimes of great size; also a sulfid, *copper pyrites;* oxid, *ruby ore* and *black oxid;* and basic carbonate, *malachite.*

Properties.—*Physical.*—A yellowish-red metal; dark brown when finely divided; very malleable, ductile, and tenacious; a good conductor of heat and electricity; has a peculiar, metallic taste and a characteristic odor.

Chemical.—It is unaltered in dry air at the ordinary temperature; but, when heated to redness, is oxidized to CuO. In damp air it becomes coated with a brownish film of oxid; a green film of basic carbonate; or, in salt air, a green film of basic chlorid. Hot H_2SO_4 dissolves it with formation of $CuSO_4$ and SO_2. It is dissolved by HNO_3 with formation of $Cu(NO_3)_2$ and NO; and by HCl with liberation of H. Weak acids form with it soluble salts, in presence of air and moisture. It is dissolved by NH_4HO, in presence of air, with formation of a blue solution. It combines directly with Cl, frequently with light.

Oxids.—Cuprous Oxid—*Suboxid or red oxid of copper*—$(Cu_2)O$—142.4—is formed by calcining a mixture of $(Cu_2)Cl_2$ and Na_2CO_3; or a mixture of CuO and Cu. It is a red or yellow powder; permanent in air; sp. gr. 5.749-6.093; fuses at a red heat; easily reduced by C or H. Heated in air it is converted into CuO.

Cupric Oxid—*Binoxid or black oxid of copper*—**CuO**—79.2—is prepared by heating Cu to dull redness in air; or by calcining $Cu(NO_3)_2$; or by prolonged boiling of the liquid over a precipitate, produced by heating a solution of a cupric salt, in presence of glucose, with KHO. By the last method it is sometimes produced in Trommer's test for glucose, when an excessive quantity of $CuSO_4$ has been used.

It is a black, or dark reddish-brown, amorphous solid; readily reduced by C, H, Na, or K at comparatively low temperatures. When heated with organic substances, it gives up its O, converting the C into CO_2, and the H into H_2O: $C_2H_6O+6CuO=6Cu+2CO_2+3H_2O$; a property which renders it valuable in organic analysis, as by heating a known weight of organic substance with CuO, and weighing the amount of CO_2 and H_2O produced, the percentage of C and H may be obtained. It dissolves in acids with formation of salts.

Hydroxids.—Cuprous Hydroxid—$(Cu)_2H_2O_2$(?)—160.4 (?)—is formed as a yellow or red powder when mixed solutions of $CuSO_4$ and KHO are heated in presence of glucose. By boiling the solution it is rapidly dehydrated with formation of $(Cu_2)O$.

Cupric Hydroxid—CuH_2O_2—97.2—is formed by the action of KHO upon solution of $CuSO_4$, in absence of reducing agents and in the cold. It is a bluish, amorphous powder; very unstable, and readily dehydrated, with formation of CuO.

Sulfids.—Cuprous Sulfid—*Subsulfid or protosulfid of copper*—Cu_2S—158.4—occurs in nature as *copper glance* or *chalcosine*, and in many double sulfids, **pyrites**.

Cupric Sulfid—**CuS**—95.2—is formed by the action of H_2S, or of NH_4HS, on solutions of cupric salts. It is almost black when moist, greenish-brown when dry. Hot HNO_3 oxidizes it to Cu SO_4; hot HCl converts it into $CuCl_2$, with separation of S, and formation of H_2S. It is sparingly soluble in NH_4HS, its solubility being increased by the presence of organic matter.

Chlorids.—Cuprous Chlorid—*Subchlorid or protochlorid*—**$(Cu_2)Cl_2$**—197.4—is prepared by heating Cu with one of the chlorids of Hg; by dissolving $(Cu_2)O$ in HCl, without contact of air; or by the action of reducing agents on solutions of $CuCl_2$. It is a heavy, white powder; turns violet and blue by exposure to light; soluble in HCl; insoluble in H_2O. It forms a crystallizable compound with CO; and its solution in HCl is used in analysis to absorb that gas.

Cupric Chlorid—*Chlorid or deutochlorid*—**$CuCl_2$**—134.2—is formed by dissolving Cu in aqua regia. If the Cu be in excess, it reduces $CuCl_2$ to $(Cu_2)Cl_2$. It crystallizes in bluish-green, rhombic prisms with 2 Aq; deliquescent; very soluble in H_2O and in alcohol.

Cupric Nitrate—**$Cu(NO_3)_2$**—187.2—is formed by dissolving Cu, CuO, or $CuCO_3$ in HNO_3. It crystallizes at 20°-25° (68°-77° F.) with 3 Aq; below 20° (68° F.) with 6 Aq, forming blue, deliquescent needles. Strongly heated, it is converted into CuO.

Cupric Sulfate—Blue vitriol—Blue stone—Cupri sulfas (U. S.; Br.)—**$CuSO_4+5Aq$**—159.2+90—is prepared: (1) by roasting Cu S; (2) from the water of copper mines; (3) by exposing Cu, moistened with dilute H_2SO_4, to air; (4) by heating Cu with H_2SO_4.

As ordinarily crystallized, it is in fine, blue, oblique prisms; soluble in H_2O; insoluble in alcohol; efflorescent in dry air at 15° (59° F.), losing 2 Aq. At 100° (212° F.) it still retains 1 Aq, which it loses at 230° (446° F.), leaving a white, amorphous powder of the anhydrous salt, which, on taking up H_2O, resumes its blue color. Its solutions are blue, acid, styptic, and metallic in taste.

When NH_4HO is added to a solution of $CuSO_4$, a bluish-white precipitate falls, which redissolves in excess of the alkali, to form a deep blue solution. Strong alcohol floated over the surface of this solution separates long, right rhombic prisms, having the composition $CuSO_4,4NH_3+H_2O$, which are very soluble in H_2O. This solution constitutes **ammonio-sulfate of copper or aqua sapphirina.**

Arsenite—Scheele's green—Mineral green—is a mixture of cupric arsenite and hydrate; prepared by adding potassium arsenite to solution of $CuSO_4$. It is a grass-green powder, insoluble in H_2O; soluble in NH_4HO, or in acids. Exceedingly poisonous.

Schweinfurt Green—Mitis green or **Paris green**—is the most frequently used, and the most dangerous of the cupro-arsenical pigments. It is prepared by adding a thin paste of neutral cupric acetate with H_2O to a boiling solution of arsenious acid, and continuing the boiling during a further addition of acetic acid. It is an insoluble, green, crystalline powder, having the composition $(C_2H_3O_2)_2Cu+3(As_2O_4Cu)$. It is decomposed by prolonged boiling in H_2O, by aqueous solutions of the alkalies, and by the mineral acids.

Carbonates.—The existence of cuprous carbonate is doubtful. **Cupric carbonate**—**$CuCO_3$**—exists in nature, but has not been obtained artificially. **Dicupric carbonate**—**$CuCO_3,CuH_2O_2$**—exists in nature as **malachite.** When a solution of a cupric salt is decomposed by an alkaline carbonate, a bluish precipitate, having the composition $CuCO_3,CuH_2O_2+H_2O$, is formed, which, on drying, loses H_2O, and becomes green; it is used as a pigment under the name **mineral green.** **Tricupric carbonate**—*Sesquicarbonate of copper*—**$2(CuCO_3),CuH_2O_2$**—exists in nature as a blue mineral, called **azurite** or **mountain blue,** and is prepared by a secret process for use as a pigment known as **blue ash.**

Acetates.—**Cupric Acetate**—*Diacetate*—*Crystals of Venus*—**Cupri acetas** (**U. S.**)—**$Cu(C_2H_3O_2)_2+Aq$**—181.2+18—is formed when CuO or verdigris is dissolved in acetic acid; or by decomposition of a solution of $CuSO_4$ by $Pb(C_2H_3O_2)_2$. It crystallizes in large, bluish-green prisms, which lose their Aq at 140° (284° F.). At 240°-260° (464°-500° F.) they are decomposed with liberation of glacial acetic acid.

Basic Acetates.—**Verdigris**—is a substance prepared by exposing to air piles composed of alternate layers of grape-skins and plates of copper, and removing the bluish-green coating from the copper. It is a mixture, in varying proportions, of three different substances: $(C_2H_3O_2)_2CuH_2O_2+5Aq$; $[(C_2H_3O_2)_2Cu]_2,CuH_2O_2+5Aq$; and $(C_2H_3O_2)2Cu,2(CuH_2O_2)$.

Analytical Characters.—CUPROUS—are very unstable and readily converted into cupric compounds. (1.) Potash: white ppt.; turning brownish. (2.) Ammonium hydroxid, in absence of air: a colorless liquid; turns blue in air.

CUPRIC—are white when anhydrous; when soluble in H_2O they form blue or green, acid solutions. (1.) Hydrogen sulfid: black ppt.; insoluble in KHS or NaHS; sparingly soluble in NH_4HS; soluble in hot concentrated HNO_3 and in KCN. (2.) Alkaline sulfhydrates: same as H_2S. (3.) Potash or soda: pale blue ppt.; insoluble in excess. If the solution be heated over the ppt., the latter contracts and turns black. (4.) Ammonium hydroxid, in small quantity: pale blue ppt.; in larger quantity, deep blue solution. (5.) Potassium or sodium carbonate: greenish-blue ppt.; insoluble in excess; turning black when the liquid is boiled. (6.) Ammonium carbonate: pale blue ppt.; soluble with deep blue color in excess. (7.) Potassium cyanid: greenish-yellow ppt.; soluble in excess. (8.) Potassium ferrocyanid: chestnut-brown ppt.; insoluble in weak acids; decolorized by KHO. (9.) Iron is coated with metallic Cu.

Action on the Economy.—The opinion, until recently universal among toxicologists, that all the compounds of copper are poisonous, has been much modified by recent researches. Certain of the copper compounds, such as the sulfate, having a tendency to combine with albuminoid and other animal substances, produce symptoms of irritation by their direct local action, when brought in contact with the gastric or intestinal mucous membrane. One of the characteristic symptoms of such irritation is the vomiting of a greenish matter, which develops a blue color upon the addition of NH_4HO.

Cases are not wanting in which severe illness, and even death, has followed the use of food which has been in contact with imperfectly tinned copper vessels. Cases in which nervous and other symptoms referable to a truly poisonous action have occurred. As, however, it has also been shown that non-irritant, *pure* copper compounds may be taken in considerable doses with impunity, it appears at least probable that the poisonous action attributed to copper is due to other substances. The tin and solder used in the manufacture of copper utensils contain lead, and in some cases of so-called copper-poisoning, the symptoms have been such as are as consistent with lead-poisoning as with copper-poisoning. Copper is also notoriously liable to contamination with arsenic, and it is by no means improbable that compounds of that element are the active poisonous agents in some cases of supposed copper-intoxication. Nor is it improbable that articles of food allowed to remain exposed to air in copper vessels should undergo those peculiar changes which result in the formation of poisonous substances, such as the sausage- or cheese-poisons, or the ptomains.

The treatment, when irritant copper compounds have been taken, should consist in the administration of white of egg or of milk, with whose albuminoids an inert compound is formed by the copper salt. If vomiting do not occur spontaneously, it should be induced by the usual methods.

The detection of copper in the viscera after death is not without interest, especially if arsenic have been found, in which case its discovery or non-discovery enables us to differentiate between poisoning by the arsenical greens, and that by other arsenical compounds. The detection of mere traces of copper is of no significance, because, although copper is not a physiological constituent of the body, it is almost invariably present, having been taken with the food.

Pickles and canned vegetables are sometimes intentionally *greened* by the addition of copper; this fraud is readily detected by inserting a large needle into the pickle or other vegetable; if copper be present the steel will be found to be coated with copper after half an hour's contact.

MERCURY.

Symbol=**Hg** (**HYDRARGYRUM**)—*Atomic weight*=199.7—*Molecular weight*=199.7—*Sp. gr. of liquid*=13.596; *of vapor*=6.97—*Fuses at* −38°.8 (−37°.9 F.)—*Boils at* 350° (662° F.).

Occurrence.—Chiefly as *cinnabar* (HgS); also in small quantity free and as chlorid.

Preparation.—The commercial product is usually obtained by simple distillation in a current of air: $HgS+O_2=Hg+SO_2$. If required pure, it must be freed from other metals by distillation, and agitation of the redistilled product with mercurous nitrate solution, solution of Fe_2Cl_6, or dilute HNO_3.

Properties.—*Physical.*—A bright metallic liquid; volatile at all temperatures. Crystallizes in octahedra of sp. gr. 14.0. When pure, it rolls over a smooth surface in round drops. The formation of tear-shaped drops indicates the presence of impurities.

Chemical.—If pure, it is not altered by air at the ordinary temperature, but, if contaminated with foreign metals, its surface becomes dimmed. Heated in air, it is oxidized superficially to HgO. It does not decompose H_2O. It combines directly with Cl, Br, I and S. It alloys readily with most metals to form **amalgams.** It amalgamates with Fe and Pt only with difficulty. Hot, concentrated H_2SO_4 dissolves it, with evolution of SO_2, and formation of $HgSO_4$. It dissolves in cold HNO_3, with formation of a nitrate.

Elementary mercury is insoluble in H_2O, and probably in the digestive liquids. It enters, however, into the formation of three medicinal agents: **hydrargyrum cum creta** (**U.S.**; **Br.**); **massa hydrargyri** (**U. S.**)=**pilula hydrargyri** (**Br.**); and **unguentum hydrargyri** (**U. S.**; **Br.**), all of which owe their efficacy, not to the metal itself, but to a certain proportion of oxid, produced during their manufacture. The fact that blue mass is more active than mercury with chalk is due to the greater proportion of oxid contained in the former. It is also probable that absorption of vapor of Hg by cutaneous surfaces is attended by its conversion into $HgCl_2$.

Oxids.—**Mercurous Oxid**—*Protoxid or black oxid of mercury*—**$(Hg_2)O$**—415.4—is obtained by adding a solution of $(Hg_2)(NO_3)_2$ to an excess of solution of KHO. It is a brownish-black, tasteless powder; very prone to decomposition into HgO and Hg. It is converted into $(Hg_2)Cl_2$ by HCl; and by other acids into the corresponding mercurous salts.

It is formed by the action of CaH_2O_2 on mercurous compounds, and exists in **black wash.**

Mercuric Oxid—*Red, or binoxid of mercury*—**Hydrargyri oxidum flavum (U. S.; Br.)**—**Hydrargyri oxidum rubrum (U. S.; Br.)**—**HgO**—215.7—is prepared by two methods: (1) by calcining $Hg(NO_3)_2$, as long as brown fumes are given off (*Hydr. oxid. rubr.*); or, (2) by precipitating a solution of a mercuric salt by excess of KHO (*Hydr. oxid. flavum*). The products obtained, although the same in composition, differ in physical characters and in the activity of their chemical actions. That obtained by (1) is red and crystalline; that obtained by (2) is yellow and amorphous. The latter is much the more active in its chemical and medicinal actions.

It is very sparingly soluble in H_2O, the solution having an alkaline reaction, and a metallic taste. It exists both in solution and in suspension in **yellow wash**, prepared by the action of CaH_2O_2 on a mercuric compound.

Exposed to light and air, it turns black, more rapidly in presence of organic matter, giving off O, and liberating Hg: $HgO = Hg + O$. It decomposes the chlorids of many metallic elements in solution, with formation of a metallic oxid and mercuric oxychlorids. It combines with alkaline chlorids to form soluble double chlorids, called **chloromercurates** or **chlorhydrargyrates**; and forms similar compounds with alkaline iodids and bromids.

Sulfids.—**Mercurous Sulfid**—**$(Hg_2)S$**—431.4—a very unstable compound, formed by the action of H_2S on mercurous salts.

Mercuric Sulfid—*Red sulfid of mercury*—**Cinnabar**—**Vermilion**—**Hydrargyri sulfidum rubrum (U. S.)**—**HgS**—231.7—exists in nature in amorphous red masses, or in red crystals, and is the chief ore of Hg. If Hg and S be ground up together in the cold, or if a solution of a mercuric salt be completely decomposed by H_2S, a black sulfid is obtained, which is the **Æthiops mineralis of** the older pharmacists.

A red sulfid is obtained for use as a pigment (**vermilion**), by agitating for some hours at 60° (140° F.) a mixture of Hg, S, KHO, and H_2O. It is a fine, red powder, which turns brown, and finally black, when heated. Heated in air, it burns to SO_2 and Hg. It is decomposed by strong H_2SO_4, but not by HNO_3 or HCl.

Chlorids.—**Mercurous Chlorid**—*Protochlorid or mild chlorid of mercury*—**Calomel**—**Hydrargyri chloridum mite (U. S.)**—**Hydrargyri subchloridum (Br.)**—**$(Hg_2)Cl_2$**—470.4—is now principally obtained by mutual decomposition of NaCl and $(Hg_2)SO_4$. Mercuric sulfate is first obtained by heating together 2 pts. Hg and 3 pts. H_2SO_4; the product is then caused to combine with a quantity of Hg equal to that first used, to form $(Hg_2)SO_4$; which is then mixed with dry NaCl, and the mixture heated in glass vessels, connected with condensing chambers; $2NaCl + (Hg_2)SO_4 = Na_2SO_4 + (Hg_2)Cl_2$.

In practice, varying quantities of $HgCl_2$ are also formed, and must be removed from the product by washing with boiled, distilled H_2O, until the washings no longer precipitate with NH_4HO. The presence of $HgCl_2$ in calomel may be detected by the formation of a black stain upon a bright copper surface, immersed in the calomel, moistened with alcohol; or by the production of a black color by H_2S in H_2O which has been in contact with and filtered from calomel so contaminated.

Calomel is also formed in a number of other reactions: (1) by the action of Cl upon excess of Hg; (2) by the action of Hg upon Fe_2Cl_6; (3) by the action of HCl, or of a chlorid, upon $(Hg_2)O$, or upon a mercurous salt; (4) by the action of reducing agents, including Hg, upon $HgCl_2$.

Calomel crystallizes in nature, and when sublimed, in quadratic prisms. When precipitated it is deposited as a heavy, amorphous, white powder, faintly yellowish, and producing a yellowish mark when rubbed upon a dark surface. It sublimes, without fusing, between 420° and 500° (788°-932° F.), is insoluble in cold H_2O and in alcohol; soluble in boiling H_2O to the extent of 1 part in 12,000. When boiled with H_2O for some time, it suffers partial decomposition, Hg is deposited and $HgCl_2$ dissolves.

Although Hg_2Cl_2 is insoluble in H_2O, in dilute HCl, and in pepsin solution, it is dissolved at the body temperature in an aqueous solution of pepsin acidulated with HCl.

When exposed to light, calomel becomes yellow, then gray, owing to partial decomposition, with liberation of Hg and formation of $HgCl_2$: $(Hg_2)Cl_2=Hg+HgCl_2$. It is converted into $HgCl_2$ by Cl or aqua regia: $(Hg_2)Cl_2+Cl_2=2HgCl_2$. In the presence of H_2O, I converts it into a mixture of $HgCl_2$ and HgI_2: $(Hg_2)Cl_2+I_2=HgCl_2+HgI_2$. It is also converted into $HgCl_2$ by HCl and by alkaline chlorids: $(Hg_2)Cl_2=HgCl_2+Hg$. This change occurs in the stomach when calomel is taken internally, and that to such an extent when large quantities of NaCl is taken with the food, that calomel cannot be used in naval practice as it may be with patients who do not subsist upon salt provisions. It is converted by KI into $(Hg_2)I_2$: $(Hg_2)Cl_2+2KI=2KCl+(Hg_2)I_2$; which is then decomposed by excess of KI into Hg and HgI_2, the latter dissolving: $(Hg)_2I_2=Hg+HgI_2$. Solutions of the sulfates of Na, K, and NH_4 dissolve notable quantities of $(Hg_2)Cl_2$. The hydroxids and carbonates of K and Na decompose it with formation of $(Hg_2)O$: $(Hg_2)Cl_2+Na_2CO_3=(Hg_2)O+CO_2+2NaCl$; and the $(Hg_2)O$ so formed is decomposed into HgO and Hg. If alkaline chlorids be also present, they react upon the HgO so produced, with formation of $HgCl_2$.

Mercuric Chlorid—*Perchlorid or bichlorid of mercury*—**Corrosive sublimate—Hydrargyri chloridum corrosivum (U. S.)—Hy-**

drargyri perchloridum (**Br.**)—**$HgCl_2$**—270.7—is prepared by heating a mixture of 5 pts. dry $HgSO_4$ with 5 pts. dry NaCl, and 1 pt. MnO_2 in a glass vessel communicating with a condensing chamber.

It crystallizes by sublimation in octahedra, and by evaporation of its solutions in flattened, right rhombic prisms; fuses at 265° (509° F.), and boils at about 295° (563° F.); soluble in H_2O and in alcohol; very soluble in hot HCl, the solution gelatinizing on cooling. Its solutions have a disagreeable, acid, styptic taste, and are highly poisonous.

It is easily reduced to $(Hg_2)Cl_2$ and Hg, and its aqueous solutions are so decomposed when exposed to light; a change which is retarded by the presence of NaCl. Heated with Hg, it is converted into $(Hg_2)Cl_2$. When dry $HgCl_2$, or its solution, is heated with Zn, Cd, Ni, Fe, Pb, Cu, or Bi, those elements remove part or all of its Cl, with separation of $(Hg_2)Cl_2$ or Hg. Its solution is decomposed by H_2S, with separation of a yellow sulfochlorid, which, with an excess of the gas, is converted into black HgS. It is soluble without decomposition in H_2SO_4, HNO_3, and HCl. It is decomposed by KHO or NaHO, with separation of a brown oxychlorid if the alkaline hydroxid be in limited quantity; or of the orange-colored HgO if it be in excess. A similar decomposition is effected by CaH_2O_2 and MgH_2O_2; which does not, however, take place in presence of an alkaline chlorid, or of certain organic matters, such as sugar and gum. Many organic substances decompose it into $(Hg_2)Cl_2$ and Hg, especially under the influence of sunlight. Albumen forms with it a white precipitate, which is insoluble in H_2O, but soluble in an exces of fluid albumen and in solutions of alkaline chlorids. It readily combines with metallic chlorids, to form soluble double chlorids, called **chloromercurates** or **chlorhydrargyrates**. One of these, obtained in flattened, rhombic prisms, by the cooling of a boiling solution of $HgCl_2$ and NH_4Cl, has the composition $HgCl_2, 2(NH_4Cl)+Aq$, and was formerly known as *sal alembroth* or *sal sapientiæ*.

Mercurammonium Chlorid—*Mercury chloramidid*—*Infusible white precipitate*—*Ammoniated mercury*—**Hydrargyrum ammoniatum** (**U. S.**; **Br.**)—**NH_2HgCl**—251.1—is prepared by adding a slight excess of NH_4HO to a solution of $HgCl_2$. It is a white powder, insoluble in alcohol, ether, and cold H_2O; decomposed by hot H_2O, with separation of a heavy, yellow powder. It is entirely volatile, without fusion. The *fusible white precipitate* is formed in small crystals when a solution containing equal parts of $HgCl_2$ and NH_4Cl is decomposed by Na_2CO_3. It is **mercurdiammonium chlorid**, NH_2HgCl,NH_4Cl.

Iodids.—**Mercurous Iodid**—*Protoiodid* or *yellow iodid*—**Hydrargyri iodidum viride** (**U. S.**; **Br.**)—**Hg_2I_2**—653.4—is prepared by grinding together 200 pts. Hg and 127 pts. I with a little alcohol, until a green paste is formed. It is a greenish-yellow, amorphous powder, insoluble in H_2O and in alcohol. When heated, it turns brown, and volatilizes completely. When exposed to light, or even after a time in the dark, it is decomposed into HgI_2 and Hg. The same decomposition is brought about instantly by KI; more slowly by solutions of alkaline chlorids, and by HCl when heated. NH_4HO dissolves it with separation of a gray precipitate.

Mercuric Iodid—*Biniodid* or *red iodid*—**Hydrargyri iodidum rubrum** (**U. S.**; **Br.**)—**HgI_2**—453.7—is obtained by double decomposition between $HgCl_2$ and KI, care being had to avoid too great an excess of the alkaline iodid, that the soluble potassium iodhydrargyrate may not be formed.

It is sparingly soluble in H_2O; but forms colorless solutions with alcohol. It dissolves readily in many dilute acids, and in solutions of ammoniacal salts, alkaline chlorids, and mercuric salts; and in solutions of alkaline iodids. Iron and copper convert it into $(Hg_2)I_2$, then into Hg. The hydroxids of K and Na decompose it into oxid or oxyiodid, and combine with another portion to form iodhydrargyrates, which dissolve. NH_4HO separates from its solution a brown powder, and forms a yellow solution, which deposits white flocks.

Cyanids.—Mercuric Cyanid—Hydrargyri cyanidum (**U. S.**)—**$Hg(CN)_2$**—251.7—is best prepared by heating together, for a quarter of an hour, potassium ferrocyanid, 1 pt.; $HgSO_4$, 2 pts.; and H_2O, 8 pts. It crystallizes in quadrangular prisms; soluble in 8 pts. of cold H_2O, much less soluble in alcohol; highly poisonous. When heated dry it blackens, and is decomposed into $(CN)_2$ and Hg; if heated in presence of H_2O it yields HCN, Hg, CO_2, and NH_3. Hot concentrated H_2SO_4, and HCl, HBr, HI, and H_2S in the cold decompose it, with liberation of HCN. It is not decomposed by alkalies.

Nitrates.—There exist, besides the normal nitrates: $(Hg_2)(NO_3)_2$, and $Hg(NO_3)_2$, three basic mercurous nitrates, three basic mercuric nitrates, and a mercuroso-mercuric nitrate.

Mercurous Nitrate—**$(Hg_2)(NO_3)_2+2$ Aq**—523.4+36—is formed when excess of Hg is digested with HNO_3, diluted with $\frac{1}{2}$ vol. H_2O; until short, prismatic crystals separate.

It effloresces in air; fuses at 70° (158° F.); dissolves in a small quantity of hot H_2O, but with a larger quantity is decomposed with separation of the yellow, basic **trimercuric nitrate** $Hg(NO_3)_2$, $2HgO+Aq$.

Dimercurous Nitrate—**$(Hg_2)(NO_3)_2$, Hg_2O+Aq**—938.8+18—is formed by acting upon the preceding salt with cold H_2O until it turns lemon-yellow; or by extracting with cold H_2O the residue of evaporation of the product obtained by acting upon excess of Hg with concentrated HNO_3.

Trimercurous Nitrate—$(Hg_2)_2(NO_3)_4$, Hg_2O+3 Aq—1462.2+54—is obtained in large, rhombic prisms, when excess of Hg is boiled with HNO_3, diluted with 5 pts. H_2O, for 5-6 hours, the loss by evaporation being made up from time to time.

Mercuric Nitrate—$Hg(NO_3)_2$—323.7—is formed when Hg or HgO is dissolved in excess of HNO_3, and the solution evaporated at a gentle heat. A syrupy liquid is obtained, which, over quicklime, deposits large, deliquescent crystals, having the composition $2[Hg(NO_3)_2]+Aq$, while there remains an uncrystallizable liquid, $Hg(NO_3)_2+2$ Aq.

This salt is soluble in H_2O, and exists in the **Liq. hydrargyri nitratis (U. S.), Liq. hydrargyri nitratis acidus (Br.)**; in the volumetric standard solution used in *Liebig's process* for urea; and probably in *citrine ointment*=**Ung. hydrar. nitratis (U. S.; Br.)**.

Dimercuric Nitrate—$Hg(NO_3)_2$, $HgO+Aq$—539.4—is formed when HgO is dissolved to saturation in hot HNO_3, diluted with 1 vol. H_2O; and crystallizes on cooling. It is decomposed by H_2O into **trimercuric nitrate,** $Hg(NO_3)_2$, $2HgO$, and $Hg(NO_3)_2$.

Hexamercuric Nitrate—$Hg(NO_3)_2$, 5 HgO—1402.2—is formed as a red powder, by the action of H_2O on trimercuric nitrate.

Sulfates.—Mercurous Sulfate—$(Hg_2)SO_4$—495.4—is a white, crystalline powder, formed by gently heating together 2 pts. Hg and 3 pts. H_2SO_4, and causing the product to combine with 2 pts. Hg. Heated with NaCl it forms $(Hg_2)Cl_2$.

Mercuric Sulfate—Hydrargyri sulfas (Br.)—$HgSO_4$—295.7—is obtained by heating together Hg and H_2SO, or Hg, H_2SO_4, and HNO_3. It is a white, crystalline, anhydrous powder, which, on contact with H_2O, is decomposed with formation of **trimercuric sulfate,** $HgSO_4$, $2HgO$; a yellow, insoluble powder, known as **turpeth mineral = Hydrargyri subsulfas flavus (U. S.)**.

Analytical Characters.—MERCUROUS.—(1.) Hydrochloric acid: white ppt.; insoluble in H_2O and in acids; turns black with NH_4HO; when boiled with HCl, deposits Hg, while $HgCl_2$ dissolves. (2.) Hydrogen sulfid: black ppt.; insoluble in alkaline sulfhydrates, in dilute acids, and in KCN; partly soluble in boiling HNO_3. (3.) Potash: black ppt.; insoluble in excess. (4.) Potassium iodid: greenish ppt.; converted by excess into Hg, which is deposited, and HgI_2, which dissolves.

MERCURIC.—(1.) Hydrogen sulfid: black ppt. If the reagent be slowly added, the ppt. is first white, then orange, finally black. (2.) Ammonium sulfhydrate: black ppt.; insoluble in excess, except in the presence of organic matter. (3.) Potash or soda: yellow ppt.; insoluble in excess. (4.) Ammonium hydroxid: white ppt.; soluble in great excess and in solutions of NH_4 salts. (5.) Potassium carbonate: red ppt. (6.) Potassium iodid: yellow ppt., rapidly turning to salmon color, then to red; easily soluble in excess of KI, or in great excess of mercuric salt. (7.) Stannous chlorid: in small quantity white ppt.; in larger quantity gray ppt.; and when boiled, deposit of globules of Hg.

Action on the Economy.—Mercury, in the metallic form, is without action upon the animal economy so long as it remains such. On contact, however, with alkaline chlorids it is converted into a soluble double chlorid, and this the more readily the greater the degree of subdivision of the metal. The mercurials insoluble in dilute HCl are also inert until they are converted into soluble compounds.

Mercuric chlorid, a substance into which many other compounds of Hg are converted when taken into the stomach or applied to the skin, not only has a distinctly corrosive action, by virtue of its tendency to unite with albuminoids, but, when absorbed, it produces well-marked poisonous effects, somewhat similar to those of arsenical poisoning. Indeed, owing to its corrosive action, and to its greater solubility, and more rapid absorption, it is a more dangerous poison than As_2O_3. In poisoning by $HgCl_2$, the symptoms begin sooner after the ingestion of the poison than in arsenical poisoning, and those phenomena referable to the local action of the toxic are more intense.

The treatment should consist in the administration of white of egg, not in too great quantity, and the removal of the compound formed, by emesis, before it has had time to redissolve in the alkaline chlorids contained in the stomach.

Absorbed Hg tends to remain in the system in combination with albuminoids, from which it may be set free, or, more properly, brought into soluble combination, at a period quite removed from the date of last administration, by the exhibition of alkaline iodids.

Mercury is eliminated principally by the saliva and urine, in which it may be readily detected. The fluid is faintly acidulated with HCl, and in it is immersed a short bar of Zn, around which a spiral of dentist's gold-foil is wound in such a way as to expose alternate surfaces of Zn and Au. After 24 hours, if the saliva or urine contain Hg, the Au will be whitened by amalgamation; and, if dried and heated in the closed end of a small glass tube, will give off Hg, which condenses in globules, visible with the aid of a magnifier, in the cold part of the tube.

COMPOUNDS OF CARBON.

Organic Substances.

In the seventeenth and eighteenth centuries, chemists had observed that there might be extracted from animal and vegetable bodies substances which differed much in their properties from those which could be obtained from the mineral world; substances which burned without leaving a residue, and many of which were subject to the peculiar changes wrought by the processes of fermentation and putrefaction. It was not until the beginning of the present century, however, that chemistry was divided into the two sections of **inorganic** and **organic**.

In the latter class were included all such substances as existed only in the organized bodies of animals and vegetables, and which seemed to be of a different essence from that of mineral bodies, as chemists had been unable to produce any of these organic substances by artificial means. Later in the history of the science it was found that these bodies were all made up of a very few elements, and that they all contained carbon.

Gmelin at this time proposed to consider as organic substances all such as contained more than one atom of C, his object in thus limiting the minimum number of atoms of C being that substances containing one atom of C, such as carbon dioxid and marsh-gas, were formed in the mineral kingdom, and consequently, according to then existing views, could not be considered as *organic*. Such a distinction, still adhered to in text-books of very recent date, of necessity leads to most incongruous results. Under it the first terms of the homologous series (see p. 224) of saturated hydrocarbons, CH_4, alcohols, CH_4O, acids, CH_2O_2, and all of their derivatives are classed among mineral substances, while all the higher terms of the same series are organic. Under it urea, COH_4N_2, the chief product of excretion of the animal body, is a mineral substance, but ethene, C_2H_4, obtained from the distillation of coal, is organic.

The idea of organic chemistry conveyed by the definition: "that branch of the science of chemistry which treats of the carbon compounds containing hydrogen," adopted in a text-book of medical chemistry printed during the present year (1890), is still more fantastic. Under it hydrocyanic acid, CNH, is "organic," but the cyanids, CNK, are "mineral." Oxalic acid, $C_2O_4H_2$, is "organic," and potassium hydroxid, KHO, unquestionably "mineral." If these two act upon each other in the proportion of 90 parts of the former to 56 of the latter, the "organic" monopotassic oxalate, C_2O_4HK, is formed, but if the proportion of KHO be doubled, other conditions remaining the same, the "mineral" dipotassic oxalate, $C_2O_4K_2$, is produced. Similarly one of the sodium carbonates, Na_2CO_3, is "mineral;" the other, $NaHCO_3$, is "organic."

The notion that organic substances could only be formed by some mysterious agency, manifested only in organized beings, was finally exploded by the labors of Wöhler and Kolbe. The former obtained urea from ammonium cyanate; while the latter, at a subsequent period, formed acetic acid, using in its preparation only such unmistakably mineral substances as coal, sulfur, aqua regia, and water.

During the half-century following Wöhler's first synthesis, chemists have succeeded not only in making from mineral materials many of the substances previously only formed in the laboratory of nature, but have also produced a vast number of carbon compounds which were previously unknown, and which, so far as we know, have no existence in nature.

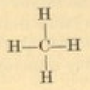
At the present time, therefore, **we must consider as an organic substance any compound containing carbon, whatever may be its origin and whatever its properties.** Indeed, the name *organic* is retained merely as a matter of convenience, and not in any way as indicating the origin of these compounds. Although, owing to the great number of the carbon compounds, it is still convenient to treat of them as forming a section by themselves, their relations with the compounds of other elements are frequently very close. Indeed, within the past few years, compounds of silicon have been obtained, which indicate the possibility that that element is capable of forming series of compounds as interesting in numbers and variety as those of carbon.

Nevertheless, there are certain peculiarities exhibited by C in its compounds, which are not possessed to a like extent by any other element, and which render the study of organic substances peculiarly interesting and profitable.

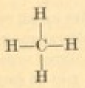
In the study of the compounds of the other elements, we have to deal with a small number of substances, relatively speaking, formed by the union with each other of a large number of elements. With the organic substances the reverse is the case. Although compounds have been formed which contain C along with each of the other elements, the great majority of the organic substances are made up of C, combined with a very few other elements; H, O and N occurring in them most frequently.

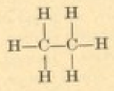
It is chiefly in the study of the carbon compounds that we have to deal with **radicals** (see p. 49). Among mineral substances there are many whose molecules consist simply of a combination of two atoms. Among organic substances there is none which does not contain a radical: indeed, organic chemistry has been defined as "the chemistry of compound radicals."

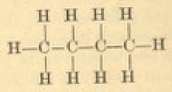
The atoms of carbon possess in a higher degree than those of any other element the power of uniting with each other, and in so doing of interchanging valences. Were it not for this property of the C atoms, we could have but one saturated compound of carbon and hydrogen, CH_4, or, expressed graphically:



There exist, however, a great number of such compounds, which differ from each other by one atom of C and two atoms of H. In these substances the atoms of C may be considered as linked together in a continuous chain, their free valences being satisfied by H atoms; thus:







If now one H atom be removed from either of these combinations, we have a group possessing one free valence, and consequently univalent. The decompositions of these substances show that they contain such radicals, and that their typical formulæ are:

$$\left.\begin{matrix}CH_3\\H\end{matrix}\right\};\qquad\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\};\qquad\left.\begin{matrix}C_4H_9\\H\end{matrix}\right\}.$$

Homologous Series.—It will be observed that these formulæ differ from each other by CH_2, or some multiple of CH_2, more or less. In examining numbers of organic substances, which are closely related to each other in their properties, we find that we can arrange the great majority of them in series, each term of which differs from the one below it by CH_2; such a series is called an **homologous series.** It will be readily understood that such an arrangement in series vastly facilitates the remembering of the composition of organic bodies. In the following table, for example, are given the saturated hydrocarbons, and their more immediate derivatives. At the head of each vertical column is an **algebraic formula,** which is the **general formula** of the entire series below it; *n* being equal to the numerical position in the series.

HOMOLOGOUS SERIES.

Saturated hydrocarbons, C_nH_{2n+2}.	Alcohols, $C_nH_{2n+2}O$.	Aldehydes, $C_nH_{2n}O$.	Acids, $C_nH_{2n}O_2$.	Ketones, $C_nH_{2n}O$.
CH_4	CH_4O	....	CO_2H_2	....
C_2H_6	C_2H_6O	C_2H_4O	$C_2O_2H_4$	....
C_3H_8	C_3H_8O	C_3H_6O	$C_3O_2H_6$	C_3H_6O
C_4H_{10}	$C_4H_{10}O$	C_4H_8O	$C_4O_2H_8$	C_4H_8O
C_5H_{12}	$C_5H_{12}O$	$C_5H_{10}O$	$C_5O_2H_{10}$	$C_5H_{10}O$
C_6H_{14}	$C_6H_{14}O$	$C_6H_{12}O$	$C_6O_2H_{12}$	....
C_7H_{16}	$C_7H_{16}O$	$C_7H_{14}O$	$C_7O_2H_{14}$	....
C_8H_{18}	$C_8H_{18}O$	$C_8H_{16}O$	$C_8O_2H_{16}$	....
C_9H_{20}	$C_9H_{20}O$	....	$C_9O_2H_{18}$	....
$C_{10}H_{22}$	$C_{10}H_{22}O$	....	$C_{10}O_2H_{20}$	....
$C_{11}H_{24}$	....	....	....	....
$C_{12}H_{26}$	....	....	$C_{12}O_2H_{24}$	....
$C_{13}H_{28}$	....	....	....	....
$C_{14}H_{30}$	....	....	$C_{14}O_2H_{28}$	....

But the arrangement in homologous series does more for us than this. The properties of substances in the same series are similar, or vary in regular gradation according to their position in the series. Thus, in the series of monoatomic alcohols (see above) each member yields on oxidation, first an aldehyde, then an acid. Each yields a series of compound ethers by the action of acids upon it. The boiling-points of the first six are, 66°.5, 78°.4, 96°.7, 111°.7, 132°.2, 153°.9; from which it will be seen that the boiling-point of any one of them can be determined, with a maximum error of 3°, by taking the mean of those of its neighbors above and below. In this way we may prophesy, to some extent, the properties of a wanting member in a series before its discovery.

The terms of any homologous series must all have the same **constitution**, *i.e.*, their constituent atoms must be similarly arranged within the molecule.

Isomerism—Metamerism—Polymerism.—Two substances are said to be isomeric, or to be isomeres of each other, when they have the same centesimal composition. If, for instance, we analyze acetic acid and methyl formiate, we find that each body consists of C, O and H, in the following proportions:

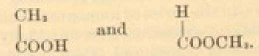
Carbon	40	$24 = 12 \times 2$
Oxygen	53.33	$32 = 16 \times 2$
Hydrogen.................	6.67	$4 = 1 \times 4$
	100.00	60

This similarity of centesimal composition may occur in two ways. The two substances may each contain in a molecule the same numbers of each kind of atom; or one may contain in each molecule the same kind of atoms as the other, but in a higher multiple. In the above instance, for example, each substance may have the composition $C_2H_4O_2$; or one may have that formula and the other, $C_6H_{12}O_6$, or $C_2H_4O_2 \times 3$. In the former case the substances are said to be **metameric,** in the latter **polymeric.** Whether two substances are metameric or polymeric can only be determined by ascertaining the weights of their molecules, which is usually accomplished by determining the sp. gr. of their vapors (see p. 37).

The sp. gr. of the vapor of acetic acid is the same as that of methyl formiate, and, consequently, each substance is made up of molecules, each containing $C_2H_4O_2$. But the two substances differ from each other greatly in their properties, and their differences are at once indicated by their typical or graphic formulæ:

$$\left.\begin{array}{r}(C_2H_3O)'\\ H\end{array}\right\}O \quad \text{and} \quad \left.\begin{array}{r}(CHO)'\\ (CH_3)'\end{array}\right\}O;$$

or graphically:



$$\begin{array}{l}CH_3\\ |\\ COOH\end{array} \quad \text{and} \quad \begin{array}{l}H\\ |\\ COOCH_3.\end{array}$$

Classification of Organic Substances.—The practically unlimited number of carbon compounds which are known to exist, or whose existence is possible according to accepted theories, imposes the necessity of a rational classification, that they may be satisfactorily studied and that their reactions and decompositions may be understood. Such a classification has been constructed, embracing not only known compounds, but capable of extension, to include in a systematic whole, any compounds which may be discovered in the future. The rules governing the naming of organic substances constitute a part of the system; and the names used, cumbrous and barbarous as they may seem to the uninitiated, indicate to the educated not only the constitution of the substance, but also its position in the classification, its relationship to other bodies, and the reactions and decompositions of which it is capable or incapable.

The simplest of the carbon compounds, the **hydrocarbons,** or substances consisting of carbon and hydrogen only, form the framework of the classification, and are divided into families and groups, according to the relations of the carbon and hydrogen atoms in the structure of the molecule:

Family I.—Arborescent, acyclic, or open chain hydrocarbons.—In the hydrocarbons of this family the number of hydrogen atoms, or this number, plus the number of univalent atoms that can be introduced into the molecule by addition (*i.e.*, by the introduction of other atoms without the removal of any already contained in the molecule) is equal to twice the number of carbon atoms plus two. Or, if $n =$ the number of carbon atoms, and $x =$ the number of univalent atoms which the molecule can receive by addition, these hydrocarbons will have the algebraic formula : $C_nH_{(2n+2-x)}$.

Group A—Paraffin, or Methane Series.—These are the most highly saturated hydrocarbons possible. Their algebraic formula is C_nH_{2n+2}. The graphic formulæ of the first, second and fourth are given on p. 224.

Group B—Olefin, Ethene, or Ethylene Series—contain two atoms of hydrogen less than the corresponding paraffins and have the algebraic formula C_nH_{2n}. No compound of this series containing a single C atom can exist. The first term is $H_2C = CH_2$.

Group C—Acetylene, or Ethine Series—contain two atoms of hydrogen less than the corresponding olefins. Their algebraic formula is C_nH_{2n-2}. The first term is $HC \equiv CH$.

Family II.—Cyclic or Closed Chain Hydrocarbons.—The compounds of this family all contain a "**nucleus**" or "**ring,**" in which every carbon atom is linked to at least two other carbon atoms, thus forming a "**cycle,**" or closed chain. The number of possible groups in this series is very large. Representatives of the following are known :

Group A — Paraffene Series — have the algebraic formula C_nH_{2n}. This is the simplest form of cyclic hydrocarbon, each carbon atom exchanging a valence with its neighbor on each side. Some representatives of the group exist in petroleum and have been formed synthetically. They are isomeric with the terms of Group B, Family I.

Group B — Terebenthic Series — have the algebraic formula C_nH_{2n-4}. The lower terms of the series are not well known. Among the higher terms are a great number of isomeres existing in nature among the essential oils.

Group C—Benzenic Series.—This series includes the most important of the closed chain hydrocarbons, and their derivatives. They have the algebraic formula C_nH_{2n-6}, and all contain the benzene nucleus C_6H_6, or some product of substitution thereof. The number of derivatives obtainable by substitution, by grafting together of two or more benzene nuclei, or by grafting of open-chain hydrocarbons, or of their derivatives, upon a benzene nucleus is apparently unlimited. They are all very stable substances.

The other carbon compounds may be regarded as derived from the hydrocarbons by the substitution or addition of an atom or group of atoms in or upon the hydrocarbon, the character, or **function** of the substance so produced depending upon the character and position of the substituted or added atom or group. This will be developed as we proceed.

ACYCLIC HYDROCARBONS AND THEIR DERIVATIVES.

FIRST SERIES OF HYDROCARBONS.

SERIES C_nH_{2n+2}.

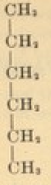
The hydrocarbons of this series at present known are the following :

Name.	Formula.	Specific Gravity of Liquid.	Boiling-point. Centigrade.
Methyl hydrid........	CH_3H	....	....
Ethyl hydrid..........	C_2H_5H	....	....
Propyl hydrid.........	C_3H_7H	....	....
Butyl hydrid..........	C_4H_9H	0.600 at 0°	0°
Amyl hydrid...........	$C_5H_{11}H$	0.628 at 18°	30°
Hexyl hydrid..........	$C_6H_{13}H$	0.669 at 18°	68°
Heptyl hydrid.........	$C_7H_{15}H$	0.690 at 18°	92°–94°
Octyl hydrid..........	$C_8H_{17}H$	0.726 at 18°	116°–118°
Nonyl hydrid.	$C_9H_{19}H$	0.741 at 18°	136°–138°
Decyl hydrid.........	$C_{10}H_{21}H$	0.757 at 18°	158°–162°
Undecyl hydrid	$C_{11}H_{23}H$	0.766 at 18°	180°–182°
Dodecyl hydrid........	$C_{12}H_{25}H$	0.778 at 18°	198°–200°
Tridecyl hydrid.......	$C_{13}H_{27}H$	0.796 at 18°	218°–220°
Tetradecyl hydrid....	$C_{14}H_{29}H$	0.809 at 18°	236°–240°
Pentadecyl hydrid....	$C_{15}H_{31}H$	0.825 at 18°	258°–262°
Hexadecyl hydrid.....	$C_{16}H_{33}H$	....	about 280°

They form an homologous series whose general formula is C_nH_{2n+2}, and are known as **paraffins** from their stability (*parum* = little, *affinis* = affinity). The *radicals* C_nH_{2n+1}, of which they are the **hydrids**, are sometimes designated as the radicals of the monoatomic alcohols, or monoatomic alcoholic radicals.

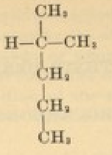
Corresponding to the higher terms of the series (those above the third) there are one or more isomeres, which may be arranged in four classes. (1.) The **normal paraffins**, or regularly formed series, in which each C atom is linked to two other C atoms. (2.) The **isoparaffins**, those in which one C atom is linked to three others. (3.) The **neoparaffins**, those in which two C atoms are each linked to three others. (4.) The **mesoparaffins**, those in which one C atom is linked to four others. The constitution of these series is explained by the graphic formulæ :

(1.)



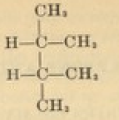
C_6H_{14}

(2.)



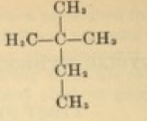
C_6H_{14}

(3.)



C_6H_{14}

(4.)



C_6H_{14}

The number of possible isomeres increases rapidly with an increasing number of carbon atoms. It has been calculated that the number of possible isomeres with increasing values of *n* are as follows:

$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$
1	1	1	2	3	5
$n=7$	$n=8$	$n=9$	$n=10$	$n=11$	$n=12$
9	18	35	75	159	357

Many of these hydrocarbons exist in nature, in petroleum, and in the gases accompanying it. They may be produced by the following **general reactions**:

1.) By the action of zinc, either alone, at elevated temperatures, or in the presence of H_2O, upon the corresponding iodids:

$$2C_2H_5I+Zn_2+2H_2O=Zn\,H_2O_2+ZnI_2+2C_2H_6$$

or

$$2C_2H_5I+Zn=ZnI_2+C_4H_{10}.$$

2.) By electrolysis of the corresponding fatty acid:

$$2C_2H_4O_2=2CO_2+C_2H_6+H_2.$$

3.) By the action of the organo-zincic derivative upon the iodid of the alcoholic radical, upon the corresponding olefin iodid, or upon the allylic iodid.

4.) By the action of highly concentrated hydriodic acid at 275°-300° (527°-572° F.) upon hydrocarbons of the ethene and ethine series, upon alcohols, amins, etc. This is a method of hydrogenation applicable in many other cases.

5.) By the destructive distillation of many organic substances.

General properties.—They are gaseous, liquid, or solid, and have sp. gr. and boiling points increasing with the number of C atoms (see table, p. 229). They are lighter than H_2O, neutral, insoluble in H_2O, soluble in alcohol, ether, and in liquid hydrocarbons. Their odor is faint and not unpleasant.

They are very stable and incapable of modification by addition. Chlorin and bromin decompose them, with formation of products of substitution. They are inflammable and burn with a luminous flame. Nitric acid forms nitro-derivatives with the higher terms.

Methyl hydrid—Methane—Marsh-gas—*Light carburetted hydrogen*—**Fire-damp—CH_4**—16—is given off in swamps as a product of decomposition of vegetable matter, in coal mines, and in the gases issuing from the earth in the vicinity of petroleum deposits. Coal-gas contains it in the proportion of 36–50 per cent. It may be prepared by strongly heating a mixture of sodium acetate with sodium hydroxid and quicklime.

It is a colorless, odorless, tasteless gas; very sparingly soluble in H_2O; sp. gr. 0.559A. At high temperature it is decomposed into C and H. It burns in air with a pale yellow flame. Mixed with air or O it explodes violently on contact with flame, producing water and carbon dioxid; the latter constituting the **after-damp** of miners. It is not affected by Cl in the dark, but, under the influence of diffuse daylight, one or more of the H atoms are displaced by an equivalent quantity of Cl. In direct sunlight the substitution is accompanied by an explosion.

Petroleum.—Crude petroleum differs in composition and in physical properties in the products of different wells, even in the same section of country. It varies in color from a faintly yellowish tinge to a dark brown, nearly black, with greenish reflections. The lighter-colored varieties are limpid, and the more highly colored of the consistency of thin syrup. The sp. gr. varies from 0.74 to 0.92. Crude petroleums contain all the hydrocarbons mentioned in the list on p. 229 (the lowest terms of the series being found in the gases accompanying petroleum and held in solution by the oil under the pressure it supports in natural pockets), besides hydrocarbons of the olefin, paraffene, and benzene series. They also contain varying quantities of sulfur compounds, which communicate a disgusting odor to some oils.

The crude oil is highly inflammable, usually highly colored, and is prepared for its multitudinous uses in the arts by the processes of distillation and refining. The products of lowest boiling point are usually consumed, but are sometimes condensed.

The principal products of petroleum are: **Petroleum ether I.**, or **Cymogene**, boils at 0° (32° F.), used in ice machines; **Petroleum ether II.**, or **Rhigolene**, a highly inflammable liquid, sp. gr. about 0.60, boils at about 20° (68° F.), used to produce cold by its rapid evaporation, and as a solvent. Its use in the vicinity of flame is attended with danger. **Gasolene** boils from 45° (113° F.)

to 76° (168°.8 F.); used as a fuel and for the manufacture of "**air gas.**" **Naphtha**, divided into three grades, C, B, and A, boils from 82°.2 (180° F.) to 148°.8 (300° F.); used as a solvent for fats, etc., and in the manufacture of "water gas." Sometimes called "safety oil." **Benzine**, or **benzolene**, boils from 148° (298° F.) to 160° (320° F); used as a solvent in making paints and varnishes. The most important product of petroleum is that portion which distils between 176° (349° F.) and 218° (424° F.) and which constitutes **kerosene** and other oils used for burning in lamps. An oil to be safely used for burning in lamps should not "flash," or give off inflammable vapor, below 37°.4 (100° F.), and should not burn at temperatures below 149° (300° F.).

From the residue remaining after the separation of the kerosene, many other products are obtained. **Lubricating oils**, of too high boiling-point for use in lamps. **Paraffin**, a white, crystalline solid, fusible at 45°–65° (113°–149° F.), which is used in the arts for a variety of purposes formerly served by wax, such as the manufacture of candles. In the laboratory it is very useful for coating the glass stoppers of bottles, and for other purposes, as it is not affected by acids or by alkalies. It is odorless, tasteless, insoluble in H_2O and in cold alcohol; soluble in boiling alcohol and in ether, fatty and volatile oils, and mineral oils. It is also obtained by the distillation of certain varieties of coal, and is found in nature in **fossil wax** or **ozocerite**.

The products known as **vaseline**, **petrolatum** (**U. S.**), **cosmoline**, etc., which are now so largely used in pharmacy and perfumery, are mixtures of paraffin and the heavier petroleum oils. Like petroleum itself, its various commercial derivatives are not definite compounds, but mixtures of the hydrocarbons of this series.

HALOID DERIVATIVES OF THE PARAFFINS.

By the action of Cl or Br upon the paraffins, or by the action of HCl, HBr or HI upon the corresponding hydrates, compounds are obtained in which one of the H atoms of the hydrocarbon has been replaced by an atom of Cl, Br or I: $C_2H_6+Br_2 = C_2H_5Br+HBr$, or $C_2H_5OH+HCl = C_2H_5Cl+H_2O$. These compounds may be considered as the chlorids, bromids or iodids of the alcoholic radicals; and are known as **haloid ethers**.

When Cl is allowed to act upon CH_4, it replaces a further number of H atoms until finally carbon tetrachlorid, CCl_4, is produced. Considering marsh gas as **methyl hydrid**, CH_3,H, the first product of substitution is **methyl chlorid**, CH_3,Cl; the second **monochlormethyl chlorid**, CH_2Cl,Cl; the third **dichlormethyl chlorid**, or chloroform, $CHCl_2Cl$; and the fourth **carbon tetrachlorid**, CCl_4.

Similar derivatives are formed with Br and I and with the other hydrocarbons of the series.

Methyl chlorid—**CH_3Cl**—50.5—is a colorless gas, slightly soluble in H_2O, and having a sweetish taste and odor. It is obtained by distilling together H_2SO_4, sodium chlorid and methyl alcohol. It may be condensed to a liquid which boils at −22° (−7°.6 F.). It burns with a greenish flame. Heated with potassium hydroxid it is converted into methyl alcohol.

Monochlormethyl chlorid—*Methene chlorid*—*Dichloromethane*—*Methylene chlorid*—*Chloromethyl*—**CH_2Cl,Cl**—85—is obtained by the action of Cl upon CH_3Cl; or by shaking an alcoholic solution of chloroform with powdered zinc and a little ammonium hydroxid. In either case the product must be purified.

It is a colorless, oily liquid, boils at 40°–42° (104°–107°.6 F.); sp. gr. 1.36; its odor is similar to that of chloroform; it is very slightly soluble in H_2O; and is not inflammable. Like most of the chlorinated derivatives of this series, it is possessed of anæsthetic powers. Its use as an anæsthetic is attended with the same (if not greater) danger as that of chloroform.

Dichlormethyl chlorid—*Methenyl chlorid*—*Formyl chlorid*—*Trichloromethane*—**Chloroform**—**Chloroformum (U. S., Br.)**—**$CHCl_2,Cl$**—120.5—is obtained by heating in a capacious still, 35–40 litres (9–11 gall.) of H_2O, adding 5 kilos (11 lbs.) of recently slacked lime and 10 kilos (22 lbs.) of chlorid of lime; 2.5 kilos (4 qts.) of alcohol are then added and the temperature quickly raised until the product begins to distil, when the fire is withdrawn, heat being again applied toward the end of the reaction. The crude chloroform so obtained is purified, first by agitation with H_2SO_4 then by mixing with alcohol and recently ignited potassium carbonate, and distilling the mixture.

Chloroform is now extensively manufactured by the action of bleaching powder upon acetone, the reaction being expressed by the equation: $2CO(CH_3)_2+6CaCl(OCl) = 2CHCl_3+2Ca(HO)_2+(CH_3,COO)_2Ca+3CaCl_2$.

It is a colorless, volatile liquid, having a strong, agreeable, ethereal odor, and a sweet taste; sp. gr. 1.497; very sparingly soluble in H_2O; miscible with alcohol and ether in all proportions; boils at 60°.8 (141°.4 F.). It is a good solvent for many substances insoluble in H_2O, such as phosphorus, iodin, fats, resins, caoutchouc, gutta-percha and the alkaloids.

It ignites with difficulty, but burns from a wick with a smoky, red flame, bordered with green. It is not acted on by H_2SO_4, except after long contact, when HCl is given off. In direct sunlight Cl converts it into CCl_4 and HCl. The alkalies in aqueous solution do not act upon it, but, when heated with them in alcoholic solution, it is decomposed with formation of chlorid and formiate of the alkaline metal. When perfectly pure it is not altered by exposure to light; but if it contain compounds of N, even in very minute quantity, it is gradually decomposed by solar action into HCl, Cl and other substances.

Impurities.—*Alcohol*, if present in large amount, lowers the sp. gr. of the chloroform, and causes it to fall through H_2O in opaque, pearly drops. If present in small amount it produces a green color with ferrous dinitrosulfid (obtained by acting on ferrous chlorid with a mixture of potassium nitrate and ammonium hydrosulfid). *Aldehyde* produces a brown color when $CHCl_3$ containing it is heated with liquor potassæ. *Hydrochloric acid* reddens blue litmus, and causes a white precipitate in an aqueous solution of silver nitrate shaken with chloroform. *Methyl and empyreumatic compounds* are the most dangerous of the impurities of chloroform. Their absence is recognized by the following characters: (1.) When the chloroform is shaken with an equal volume of colorless H_2SO_4, and allowed to stand 24 hours; the upper (chloroform) layer should be perfectly colorless, and the lower (acid) layer colorless or faintly yellow. (2.) When a small quantity is allowed to evaporate spontaneously, the last portions should have no pungent odor, and the remaining film of moisture should have no taste or odor other than those of chloroform.

Analytical Characters.—(1.) Add a little alcoholic solution of potash and 2-3 drops of anilin and warm; a disagreeable odor, resembling that of witch-hazel, is produced. (2.) Vapor of $CHCl_3$, when passed through a red-hot tube, is decomposed with formation of HCl and Cl, the former of which is recognized by the production of a white ppt., soluble in ammonium hydroxid, in an acid solution of silver nitrate. This test does not afford reliable results when the substance tested contains a free acid and chlorids. (3.) Dissolve about 0.01 gm. of β naphthol in a small quantity of KHO solution, warm, and add the suspected liquid; a blue color is produced. (4.) Add about 0.3 grm. resorcin in solution, and 3 gtts. NaHO solution and boil strongly. In the presence of $CHCl_3$ or of chloral a yellowish-red color is produced, and the liquid exhibits a beautiful yellow-green fluorescence.

Toxicology.—The action of chloroform varies as it is taken by the stomach or by inhalation. In the former case, owing to its insolubility, but little is absorbed, and the principal action is the local irritation of the mucous surfaces. Recovery has followed a dose of four ounces, and death has been caused by one drachm, taken into the stomach. Chloroform vapor acts much more energetically, and seems to owe its potency for evil to its paralyzing influence upon the respiratory nerve centres, and upon the cardiac ganglia. While persons suffering from heart disease are particularly susceptible to the paralyzing effect of chloroform vapor, there are many cases recorded of death from the inhalation of small quantities, properly diluted, in which no heart lesion was found upon a post-mortem examination. Chloroform is apparently not altered in the system, and is eliminated with the expired air.

No chemical antidote to chloroform is known. When it has been swallowed, the stomach-pump and emetics are indicated; when taken by inhalation, a free circulation of air should be established about the face: artificial respiration and the application of the induced current to the sides of the neck should be resorted to.

The nature of the poison is usually revealed at the autopsy by its peculiar odor, which is most noticeable on opening the cranial and thoracic cavities. In a toxicological analysis, chloroform is to be sought for especially in the lungs and blood. These are placed in a flask; if acid, neutralized with sodium carbonate; and subjected to distillation at the temperature of the water-bath. The vapors are passed through a tube of difficultly fusible glass; at first the tube is heated to redness for about an inch of its length, and test No. 2 applied to the issuing gas. The tube is then allowed to cool, and the distillate collected in a pointed tube, from the point of which any $CHCl_3$ is removed by a pipette and tested according to Nos. 1, 3, and 4 above.

Carbon tetrachlorid—*Chlorocarbon*—**CCl_4**—154—is formed by the prolonged action, in sunlight, of Cl upon CH_3Cl or $CHCl_3$; or more rapidly, by passing Cl, charged with vapor of carbon disulfid, through a red-hot tube, and purifying the product.

It is a colorless, oily liquid, insoluble in H_2O; soluble in alcohol and in ether; sp. gr. 1.56; boils at 78° (172°.4 F.). Its vapor is decomposed at a red heat into a mixture of the **dichlorid, C_2Cl_4**, **trichlorid, C_2Cl_6**, and free Cl.

Methyl bromid—**CH_3Br**—95.—A colorless liquid; sp. gr. 1.664; boils at 13° (55°.4 F.); formed by the combined action of P and Br on methyl hydrate.

Dibromomethyl bromid—*Methenyl bromid*—*Formyl bromid*—**Bromoform**—**$CHBr_2,Br$**—253—is prepared by gradually adding Br to a cold solution of potassium hydroxid in methyl alcohol until the liquid begins to be colored; and rectifying over calcium chlorid.

A colorless, aromatic, sweet liquid; sp. gr. 2.13; boils at 150°–152° (302°–306° F.); solidifies at −9° (15°.8 F.); sparingly soluble in H_2O; soluble in alcohol and ether. Boiled with alcoholic potash it is decomposed in the same way as is $CHCl_3$.

Its physiological action is similar to that of $CHCl_3$. It occurs as an impurity of commercial Br, accompanied by **carbon tetrabromid**, CBr_4.

Methyl iodid—$\mathbf{CH_3I}$—142—a colorless liquid, sp. gr. 2.237; boils at 45° (113° F.); burns with difficulty, producing violet vapor of iodin. It is prepared by a process similar to that for obtaining the bromid; and is used in the anilin industry.

Diiodomethyl iodid—*Methenyl iodid*—*Formyl iodid*—**Iodoform**—**Iodoformum, U. S.**—$\mathbf{CHI_2I}$—394.—Formed, like chloroform and bromoform, by the combined action of potash and the halogen upon alcohol; it is also produced by the action of I upon a great number of organic substances, and is usually prepared by heating a mixture of alkaline carbonate, H_2O, I and ethylic alcohol, and purifying the product by recrystallization from alcohol. It is also produced from acetone by making a solution containing 50 gm. KI, 6 gm. acetone, and 2 gm. NaHO in 2L. H_2O and gradually adding a dilute solution of $KClO_3$.

Iodoform is a solid, crystallizing in yellow, hexagonal plates, which melt at 115°-120° (239°-248° F.). It may be sublimed, a portion being decomposed. It is insoluble in water, acids, and alkaline solutions: soluble in alcohol, ether, carbon disulfid, and the fatty and essential oils: the solutions, when exposed to the light, undergo decomposition and assume a violet-red color. It has a sweet taste and a peculiar, penetrating odor, resembling, when the vapor is largely diluted with air, that of saffron. When heated with potash, a portion is decomposed into formiate and iodid, while another portion is carried off unaltered with the aqueous vapor. It contains 96.7% of its weight of iodin.

Ethyl chlorid—*Hydrochloric or muriatic ether*—$\mathbf{C_2H_5Cl}$—64.5.—A colorless, white, ethereal liquid; boils at 11° (51°.8 F.); obtained by passing gaseous HCl through ethylic alcohol to saturation, and distilling over the water-bath.

By the continued action of Cl in the sunshine upon ethyl chlorid, or upon ethene chlorid, $C_2H_4Cl_2$, a white, crystalline solid, **Hexachlorethane** or **carbon trichlorid,** $\mathbf{C_2Cl_6}$, is produced. It is insoluble in H_2O, soluble in alcöhol and in ether, has an aromatic odor, fuses at 160° (320° F.), and boils at 182° (359°.6 F.).

Ethyl bromid—*Hydrobromic ether*—$\mathbf{C_2H_5Br}$—109.—A colorless, ethereal liquid; boils at 40°.7 (105°.3 F.); obtained by the combined action of P and Br on ethylic alcohol.

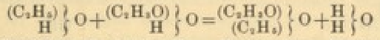
Ethyl iodid—*Hydriodic ether*—$\mathbf{C_2H_5I}$—156—is prepared by placing absolute alcohol and P in a vessel surrounded by a freezing mixture and gradually adding I; when the action has ceased, the liquid is decanted, distilled over the water-bath, and the distillate washed and rectified.

It is a colorless liquid; boils at 72°.2 (162° F.); has a powerful, ethereal odor; burns with difficulty. It is largely used in the anilin industry.

MONOATOMIC ALCOHOLS.

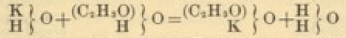
SERIES $C_nH_{2n+2}O$.

The name **alcohol,** formerly applied only to the substance now popularly so called, has gradually come to be used to designate a large class of important bodies, of which vinic alcohol is the representative. These substances are mainly characterized by their power of entering into double decomposition with acids, to form neutral compounds, called **compound ethers,** water being at the same time formed, at the expense of both alcohol and acid. **They are the hydroxids of hydrocarbon radicals, and as such resemble the metallic hydroxids, while the compound ethers are the counterparts of the metallic salts:**



$$\left.\begin{matrix}(C_2H_5)\\H\end{matrix}\right\}O+\left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}O=\left.\begin{matrix}(C_2H_3O)\\(C_2H_5)\end{matrix}\right\}O+\left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Ethyl hydroxid. Acetic acid. Ethyl acetate. Water.



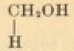
$$\left.\begin{matrix}K\\H\end{matrix}\right\}O+\left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}O=\left.\begin{matrix}(C_2H_3O)\\K\end{matrix}\right\}O+\left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Potassium hydroxid. Acetic acid. Potassium acetate. Water.

As the metallic hydroxids may be considered as formed by the union of one atom of the metallic element with a number of groups OH′, corresponding to its valence, so the alcohols are formed by union of an unoxidized radical with a number of groups OH′, equal to or less than the number of free valences of the radical. When the alcohol contains one OH, it is designated as **monoatomic**; when two, **diatomic**; when three, **triatomic**, etc.

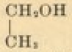
The simplest alcohols are those of this series derivable from the saturated hydrocarbons, and having the general formula $C_nH_{2n+2}O$, or $C_nH_{2n+1}OH$. They may be formed synthetically: (1.) By acting upon the corresponding iodid with potassium hydroxid: $C_2H_5I+KHO=KI+C_2H_5OH$. (2.) From the alcohol next below it in the series, by direct addition of CH_2, only, however, by a succession of five reactions. (3.) By the action of H_2SO_4 and H_2O upon the corresponding hydrocarbon of the series C_nH_{2n}.

The saturated monoatomic alcohols are, however, not limited to one corresponding to each alcoholic radical. There exist—corresponding to the higher alcohols—a number of substances having the same centesimal composition and the same alcoholic properties, but differing in their physical characters and in their products of decomposition and oxidation. These isomeres have been the subject of much careful study of late years. It has been found that the molecules of methyl, ethyl, and other higher alcohols are made up of the group $(CH_2OH)'$ united to H or to C_nH_{2n+1}, thus:



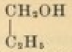
$$\begin{array}{c}CH_2OH\\ |\\ H\end{array}$$

Methyl alcohol.



$$\begin{array}{c}CH_2OH\\ |\\ CH_3\end{array}$$

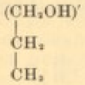
Ethyl alcohol.



$$\begin{array}{c}CH_2OH\\ |\\ C_2H_5\end{array}$$

Propyl alcohol.

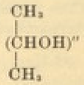
and all monoatomic alcohols containing this group, CH_2OH, have been designated as **primary alcohols.** Isomeric with these are other bodies, which, in place of the group $(CH_2OH)'$, contain the group $(CHOH)''$, and are distinguished as **secondary alcohols.** Thus we have:



$$\begin{array}{c}(CH_2OH)'\\ |\\ CH_2\\ |\\ CH_3\end{array}$$

C_3H_8O

Primary propyl alcohol.

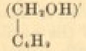


$$\begin{array}{c}CH_3\\ |\\ (CHOH)''\\ |\\ CH_3\end{array}$$

C_3H_8O

Secondary propyl alcohol.

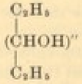
And further, other isomeric substances are known which contain the group $(COH)'''$, and which are called **tertiary alcohols,** thus:



$$\begin{array}{c}(CH_2OH)'\\ |\\ C_4H_9\end{array}$$

$C_5H_{12}O$

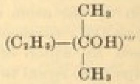
Primary amylic alcohol.



$$\begin{array}{c}C_2H_5\\ |\\ (CHOH)''\\ |\\ C_2H_5\end{array}$$

$C_5H_{12}O$

Secondary amylic alcohol.



$$\begin{array}{c}CH_3\\ |\\ (C_2H_5)-(COH)'''\\ |\\ CH_3\end{array}$$

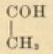
$C_5H_{12}O$

Tertiary amylic alcohol.

The alcohols of these three classes are distinguished from each other principally by their products of oxidation. The primary alcohols yield by oxidation, first an aldehyde and then an acid, each containing the same number of C atoms as the alcohol, and formed, the aldehyde by the removal of H_2 from the group (CH_2OH), and the acid by the substitution of O for H_2 in the same group, thus:

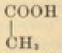
$$\begin{array}{c}CH_2OH\\ |\\ CH_3\end{array}$$

Ethyl alcohol.



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

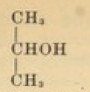
Ethyl aldehyde.



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

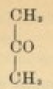
Acetic acid.

In the case of the secondary alcohols, the first product of oxidation is a **ketone,** containing the same number of C atoms as the alcohol, and formed by the substitution of O for HOH in the distinguishing group:



$$\begin{array}{l}CH_3\\ |\\ CHOH\\ |\\ CH_3\end{array}$$

Secondary propyl alcohol.



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

Propyl ketone or acetone.

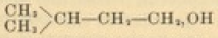
The tertiary alcohols yield by oxidation ketones or acids, whose molecules contain a less number of C atoms than the alcohol from which they are derived.

But the complication does not end here: isomeres exist corresponding to the higher alcohols, which are themselves primary alcohols, and contain the group $(CH_2OH)'$. Thus there exist no less than seven distinct substances, all having the centesimal composition of amyl alcohol, $C_5H_{12}O$, and the properties of alcohols; and theoretical considerations point to the probable existence of another. Of these eight substances, four are primary, three secondary alcohols, and the remaining one a tertiary alcohol. As each of these bodies contains the group of atoms characteristic of the class of alcohol to which it belongs, it is obvious that the differences observed in their properties are due to differences in the arrangement of the other atoms of the molecule. Experimental evidence, which it would require too much space to discuss in this place, has led chemists to ascribe the following formulæ of constitution to these isomeres:

Primary amylic alcohols:

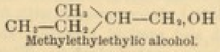
$$CH_3—CH_2—CH_2—CH_2—CH_2,OH$$

Normal amylic alcohol.



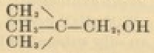
$$\left.\begin{array}{l}CH_3\\ CH_3\end{array}\right\rangle CH—CH_2—CH_2,OH$$

Amylic alcohol of fermentation.



$$\left.\begin{array}{r}CH_3\\ CH_3—CH_2\end{array}\right\rangle CH—CH_2,OH$$

Methylethylethylic alcohol.



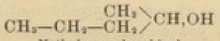
$$\begin{array}{l}CH_3\diagdown\\ CH_3—C—CH_2,OH\\ CH_3\diagup\end{array}$$

Unknown.

Secondary amylic alcohols:

$$\left.\begin{array}{l}CH_3—CH_2\\ CH_3—CH_2\end{array}\right\rangle CH,OH$$

Diethyl carbinol.



$$\left.\begin{array}{r}CH_3\\ CH_3—CH_2—CH_2\end{array}\right\rangle CH,OH$$

Methyl-propyl carbinol.

$$\begin{array}{l} CH_3 \diagdown \\ CH_3 \diagup \end{array} \overset{CH_3 \diagdown}{CH \diagup} CH,OH$$

Methyl-isopropyl carbinol.

Tertiary amylic alcohol:

$$\begin{array}{r} CH_3 \diagdown \\ CH_2{-}C,OH \\ CH_3{-}CH_2 \diagup \end{array}$$

Methyl hydroxid—Carbinol—Pyroxylic spirit—Methylic alcohol—Wood spirit—H,CH$_2$OH—32—may be formed from marsh-gas, CH$_3$H, by first converting it into the iodid, and acting upon this with potassium hydroxid: $CH_3I+KHO=KI+CH_3HO$. It is usually obtained by the destructive distillation of wood. The **crude wood vinegar** so produced is a mixture of acetic acid and methyl alcohol with a variety of other products. The crude vinegar, separated from tarry products, is redistilled; the first tenth of the distillate is treated with quicklime and again distilled; the distillate treated with dilute H_2SO_4; decanted and again distilled. The product, still quite impure, is the **wood alcohol, wood naphtha,** or **pyroxylic spirit** of commerce. The pure hydroxid can only be obtained by decomposing a crystalline compound, such as methyl oxalate, and rectifying the product until the boiling-point is constant at 66°.5 (151°.7 F.).

Pure methyl alcohol is a colorless liquid, having an ethereal and alcoholic odor, and a sharp, burning taste; sp. gr. 0.814 at 0°; boils at 66°.5 (151°.7 F.); burns with a pale flame, giving less heat than that of ethylic alcohol; mixes with water, alcohol, and ether in all proportions; is a good solvent of resinous substances, and also dissolves sulfur, phosphorus, potash, and soda.

Methyl hydroxid is not affected by exposure to air under ordinary circumstances, but in the presence of platinum-black it is oxidized, with formation of the corresponding aldehyde and acid, formic acid. Hot HNO_3 decomposes it with formation of nitrous fumes, formic acid and methyl nitrate. It is acted upon by H_2SO_4 in the same way as ethyl alcohol. The organic acids form methyl ethers with it. With HCl under the influence of a galvanic current, it forms an oily substance having the composition C_2H_3ClO.

Methylated spirit is ethyl alcohol containing sufficient wood spirit to render it unfit for the manufacture of ardent spirits, by reason of the disgusting odor and taste which crude wood alcohol owes to certain empyreumatic products which it contains. Spirits so treated are not subject to the heavy duties imposed upon ordinary alcohol, and are, therefore, largely used in the arts and for the preservation of anatomical preparations. It contains one-ninth of its bulk of wood naphtha.

Ethyl hydroxid—Ethylic alcohol—Methyl Carbinol—*Vinic alcohol*—**Alcohol—Spirits of wine—C_2H_5HO**—46.

Preparation.—Industrially alcohol and alcoholic liquids are obtained from substances rich in starch or glucose.

The manufacture of alcohol consists of three distinct processes: 1st, the conversion of starch into sugar; 2d, the fermentation of the saccharine liquid; 3d, the separation, by distillation, of the alcohol formed by fermentation.

The raw materials for the first process are **malt** and some substance (grain, potatoes, rice, corn, etc.) containing starch. Malt is barley which has been allowed to germinate, and, at the proper stage of germination, roasted. During this growth there is developed in the barley a peculiar nitrogenous principle called **diastase.** The starchy material is mixed with a suitable quantity of malt and water, and the mass maintained at a temperature of 65°–70° (149°–158° F.) for two to three hours, during which the diastase rapidly converts the starch into **dextrin,** and this in turn into **glucose.**

The saccharine fluid, or **wort,** obtained in the first process, is drawn off, cooled, and **yeast** is added. As a result of the growth of the yeast-plant, a complicated series of chemical changes take place, the principal one of which is the splitting up of the glucose into carbon dioxid and alcohol: $C_6H_{12}O_6=2C_2H_5OH+2CO_2$. There are formed at the same time small quantities of glycerin, succinic acid, and propyl, butyl, and amyl alcohols.

An aqueous fluid is thus obtained which contains 3–15 per cent. of alcohol. This is then separated by the third process, that of distillation and rectification. The apparatus used for this purpose has been so far perfected that by a single distillation an alcohol of 90–95 per cent. can be obtained.

In some cases alcohol is prepared from fluids rich in glucose, such as grape-juice, molasses, syrup, etc. In such cases the first process becomes unnecessary.

Commercial alcohol always contains H_2O, and when pure or *absolute* alcohol is required, the commercial product must be mixed with some hygroscopic solid substance, such as quicklime, from which it is distilled after having remained in contact twenty-four hours.

Fermentation.—This term (derived from *fervere*=to boil) was originally applied to alcoholic fermentation, by reason of the bubbling of the saccharine liquid caused by the escape of CO_2; subsequently it came to be applied to all decompositions similarly attended by the escape of gas.

At present it is used by many authors to apply to a number of heterogeneous processes; and some writers distinguish between "true" and "false" fermentation. It is best, we believe, to limit the application of the term to those decompositions designated as *true fermentations*.

Fermentation is a decomposition of an organic substance, produced by the processes of nutrition of a low form of animal or vegetable life.

The **true ferments** are therefore all organized beings, such as *torula cerevisiæ*, producing alcoholic fermentation; *penicillium glaucum*, producing lactic acid fermentation; and *mycoderma aceti*, producing acetic acid fermentation.

The false fermentations are not produced by an organized body, but by a soluble, unorganized, nitrogenous substance, whose method of action is as yet imperfectly understood. They may be, therefore, designated by the term **cryptolysis.** Diastase, pepsin and trypsin are **cryptolytes.**

Properties.—Alcohol is a thin, colorless, transparent liquid, having a spirituous odor, and a sharp, burning taste; sp. gr. 0.8095 at 0°, 0.7939 at 15° (59° F.); it boils at 78°.5 (173°.3 F.), and has not been solidified. At temperatures below −90° (−130° F.) it is viscous. It mixes with water in all proportions, the union being attended by elevation in temperature and contraction in volume (after cooling to the original temperature). It also attracts moisture from the air to such a degree that absolute alcohol only remains such for a very short time after its preparation. It is to this power of attracting H_2O that alcohol owes its preservative power for animal substances. It is a very useful solvent, dissolving a number of gases, most of the mineral and organic acids and alkalies, most of the chlorids and carbonates, some of the nitrates, all the sulfates, essences, and resins. Alcoholic solutions of fixed medicinal substances are called **tinctures** ; those of volatile principles, **spirits.**

The action of oxygen upon alcohol varies according to the conditions. Under the influence of energetic oxidants, such as chromic acid, or, when alcohol is burned in the air, the oxidation is rapid and complete, and is attended by the extrication of much heat, and the formation of carbon dioxid and water: $C_2H_6O+3O_2=2CO_2+3H_2O$. Mixtures of air and vapor of alcohol explode upon contact with flame. If a less active oxidant be used, such as platinum-black, or by the action of atmospheric oxygen at low temperatures, a simple oxidation of the alcoholic radical takes place, with formation of *acetic acid* $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O+O_2=\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O+H_2O$, a reaction which is utilized in the manufacture of acetic acid and vinegar. If the oxidation be still further limited, *aldehyde* is formed: $2C_2H_6O+O_2=2C_2H_4O+2H_2O$. If vapor of alcohol be passed through a tube filled with platinum sponge and heated to redness, or if a coil of heated platinum wire be introduced into an atmosphere of alcohol vapor, the products of oxidation are quite numerous: among them are water, ethylene, aldehyde, acetylene, carbon monoxid, and acetal. Heated platinum wire introduced into vapor of alcohol continues to glow by the heat resulting from the oxidation, a fact which has been utilized in the thermocautery.

Chlorin and bromin act energetically upon alcohol, producing a number of chlorinated and brominated derivatives, the final products being *chloral* and *bromal* (q. v.). If the action of Cl be moderated, aldehyde and HCl are first produced. Iodin acts quite slowly in the cold, but old solutions of I in alcohol (tr. iodin) are found to contain HI, ethyl iodid, and other imperfectly studied products. In the presence of an alkali, I acts upon alcohol to produce iodoform. Potassium and sodium dissolve in alcohol with evolution of H; upon cooling, a white solid crystallizes, which is the double oxid of ethyl and the alkali metal, and is known as potassium or sodium ethylate. Nitric acid, aided by a gentle heat, acts violently upon alcohol, producing nitrous ether, brown fumes, and products of oxidation. (For the action of other acids upon alcohol see the corresponding ethers.) The hydroxids of the alkali metals dissolve in alcohol, but react upon it slowly; the solution turns brown and contains an acetate. If alcohol be gently heated with HNO_3 and nitrate of silver or of mercury, a gray precipitate falls, which is silver or mercury fulminate.

Varieties.—It occurs in different degrees of concentration: **absolute alcohol** is pure alcohol, C_2H_6O. It is not purchasable, and must be made as required. The so-called absolute alcohol of the shops is rarely stronger than 98 per cent. **Alcohol** (**U. S.**), sp. gr. 0.820, contains 94 per cent. by volume, and **spiritus rectificatus** (**Br.**), sp. gr. 0.838, contains 84 per cent. This is the ordinary rectified spirit used in the arts. **Alcohol dilutum** (**U. S.**)=**Spiritus tenuior** (**Br.**), sp. gr. 0.920, used in the preparation of tinctures, contains 53 per cent. It is of about the same strength as the **proof spirit** of commerce.

Analytical Characters.—(1.) Heated with a small quantity of solution of potassium dichromate and H_2SO_4, the liquid assumes an emerald-green color, and, if the quantity of C_2H_6O be not very small, the peculiar fruity odor of aldehyde is developed. (2.) Warmed and treated with a few drops of potash solution and a small quantity of iodin, an alcoholic liquid deposits a yellow, crystalline ppt. of iodoform, either immediately or after a time. (3.) If HNO_3 be added to a liquid containing C_2H_6O, nitrous ether, recognizable by its odor, is given off. If a solution of mercurous nitrate with excess of HNO_3 be then added, and the mixture heated, a further evolution of nitrous ether occurs, and a yellow-gray deposit of fulminating mercury is formed, which may be collected, washed, dried and exploded. (4.) If an alcoholic liquid be heated for a few moments with H_2SO_4 diluted with H_2O and distilled, the distillate, on treatment with H_2SO_4 and potassium permanganate, and afterward with sodium hyposulfite, yields aldehyde, which may be recognized by the production of a violet color with a dilute solution of fuchsin.

None of the above reactions, *taken singly*, is characteristic of alcohol.

Action on the Economy.—In a concentrated form alcohol exerts a dehydrating action upon animal tissues with which it comes in contact; causing coagulation of the albuminoid constituents. When diluted, ethylic alcohol may be a food, a medicine, or a poison, according to the dose and the condition of the person taking it. When taken in excessive doses, or in large doses for a long time, it produces symptoms and lesions characteristic of pure alcoholism, acute or chronic, modified or aggravated by those produced by other substances, such as amyl alcohol, which accompany it in the alcoholic fluids used as beverages. Taken in moderate quantities, with food, it aids digestion and produces a sense of comfort and exhilaration. As a medicine it is a valuable stimulant.

Much has been written concerning the value of alcohol as a food. If it have any value as such, it is as a producer of heat and force by its oxidation in the body. Experiments have failed to show that more than a small percentage (16 per cent. in 24 hrs.) of medium doses of alcohol ingested are eliminated by all channels; the remainder, therefore, disappears in the body, as the idea that it can there "accumulate" is entirely untenable. That some part should be eliminated unchanged is to be expected from the rapid diffusion and the high volatility of alcohol.

On the other hand, if alcohol be oxidized in the body, we should expect, in the absence of violent muscular exercise, an increase in temperature, and the appearance in the excreta of some product of oxidation of alcohol: aldehyde, acetic acid, carbon dioxid, or water, while the elimination of nitrogenous excreta, urea, etc., would remain unaltered or be diminished. While there is no doubt that excessive doses of alcohol produce a diminution of body temperature, the experimental evidence concerning the action in this direction of moderate doses is conflicting and incomplete. Of the products of oxidation, aldehyde has not been detected in the excreta, and acetic acid only in the intestinal canal. The elimination of carbonic acid, as such, does not seem to be increased, although positive information upon this point is wanting. If acetic acid be produced, this would form an acetate, which in turn would be oxidized to a carbonate, and eliminated as such by the urine. The elimination of water under the influence of large doses of alcohol is greater than at other times: but whether this water is produced by the oxidation of the hydrogen of the alcohol, or is removed from the tissues by its dehydrating action, is an open question.

While physiological experiment yields only uncertain evidence, the experience of arctic travellers and others shows that the use of alcohol tends to diminish rather than increase the capacity to withstand cold. The experience of athletes and of military commanders is that intense and prolonged muscular exertion can be best performed without the use of alcohol. The experience of most literary men is that long-continued mental activity is more difficult with than without alcohol.

In cases of acute poisoning by alcohol, the stomach-pump and catheter should be used as early as possible. A plentiful supply of air, the cold douche, and strong coffee are indicated.

Alcoholic Beverages.—The variety of beverages in whose preparation alcoholic fermentation plays an important part is very great, and the products differ from each other materially in their composition and in their physiological action. They may be divided into four classes, the classification being based upon the sources from which they are obtained and upon the method of their preparation.

I.—Those prepared by the fermentation of malted grain—**beers, ales, and porters.**

II.—Those prepared by the fermentation of grape juice—**wines**

III.—Those prepared by the fermentation of the juices of fruits other than the grape—**cider, fruit-wines.**

IV.—Those prepared by the distillation of some fermented saccharine liquid—**ardent spirits.**

Beer, ale, and porter are aqueous infusions or decoctions of malted grain, fermented and flavored with hops. They contain, therefore, the soluble constituents of the grain employed; dextrin and glucose, produced during the malting; alcohol and carbon dioxid, produced during the fermentation; and the soluble constituents of the flavoring material. The alcoholic strength of malt liquors varies from 1.5 to 9 per cent. Weiss beer contains 1.5–1.9 per cent.; lager, 4.1–4.5 per cent.; bock beer, 3.88–5.23 per cent.; London porter, 5.4–6.9 per cent.; Burton ale, 5.9 per cent.; Scotch ale, 8.5–9 per cent. Malt liquors all contain a considerable quantity of nitrogenous material (0.4–1 per cent. N), and succinic, lactic, and acetic acids. The amount of inorganic material, in which the phosphates of potassium, sodium, and magnesium predominate largely, varies from 0.2 to 0.3 per cent. The sp. gr. is from 1.014 to 1.033.

The adulterations of malt liquors are numerous and varied.

Sodium carbonate is added with the double purpose of neutralizing an excess of acetic acid and increasing the foam. The most serious adulteration consists in the introduction of bitter principles other than hops, and notably of strychnin, cocculus indicus (picrotoxin), and picric acid.

Wines are produced by the fermentation of grape-juice. In the case of red wines the **marc,** or mass of skins, seed and stems, is allowed to remain in contact with the **must,** or fermenting juice, until, by production of alcohol, the liquid dissolves a portion of the coloring matter of the skins. A certain proportion of tannin is also dissolved, whose presence is necessary to prevent *stringiness.* Sweet wines are produced from must rich in glucose, and by arresting the fermentation before that sugar has been completely decomposed. Dry wines are obtained by more complete fermentation of must less rich in glucose. Tartaric acid is the predominating acid in grape-juice, and as the proportion of alcohol increases during fermentation the acid potassium tartrate is deposited.

Most wines of good quality improve in flavor with age, and this improvement is greatly hastened by the process of **pasteuring,** which consists in warming the wine to a temperature of 60° C. (140° F.), without contact of air.

Light wines are those whose percentage of alcohol is less than 12 per cent. In this class are included the clarets, Sauternes, Rhine, and Moselle wines; champagnes, Burgundies, the American wines (except some varieties of California wine), Australian, Greek, Hungarian, and Italian wines.

The champagnes and some Moselle wines are sparkling, a quality which is communicated to them by bottling them before the fermentation is completed, thus retaining the carbon dioxid, which is dissolved by virtue of the pressure which it exerts. When properly prepared they are agreeable to the palate, and assist the digestion; when new, however, they are liable to communicate their fermentation to the contents of the stomach and thus seriously disturb digestion.

Of the still wines, the most widely used are the *clarets,* **Vinum rubrum (U. S.)**, or red Bordeaux wines, and the *hocks,* **Vinum album (U. S.)**, or white Rhine, Moselle and American wines. The former are of low alcoholic strength, mildly astringent, and contain but a small quantity of nitrogenous material, qualities which render them particularly adapted to table use and as mild stimulants. The Rhine wines are thinner and more acid, and generally of lower alcoholic strength than the clarets. The Burgundy and Rhone wines are celebrated for their high flavor and body; they are not strongly alcoholic, but contain a large quantity of nitrogenous material, to which they are indebted for their notoriety as developers of gout. Our native American wines, particularly those of the Ohio Valley and of California, are yearly improving in flavor and quality; they more closely resemble the Rhine wines and Sauternes than other European wines.

Heavy wines are those whose alcoholic strength is greater than 12 per cent., usually 14 to 17 per cent.; they include the sherries, ports, Madeiras, Marsala, and some California wines, and are all the products of warm climates. Sherry is an amber-colored wine, grown in the south of Spain, **Vinum Xericum** (**Br.**). Marsala closely resembles sherry in appearance, and is frequently substituted for it. Port is a rich, dark red wine, grown in Portugal.

The adulteration of wine by the addition of *foreign* substances is confined almost entirely to their artificial coloration, which is produced by the most various substances, indigo, logwood, fuchsin, etc. The addition of natural constituents of wines, obtained from other sources, and the mixing of different grades of wine are, however, extensively practised. Water and alcohol are the chief substances so added; an excess of the former may be detected by the taste, and the low sp. gr. after expulsion of the alcohol. Most wines intended for export are **fortified** by the addition of alcohol. When the alcoholic spirit used is free from amyl alcohol, and is added in moderate quantities, there can be no serious objection to the practice, especially when applied to certain wines which, without such treatment, do not bear transportation. The mixing of fine grades of wine with those of a poorer quality is extensively practised, particularly with sherries, champagnes, clarets, and Burgundies, and is perfectly legitimate. The same cannot be said, however, of the manufacture of factitious wine, either entirely from materials not produced from the grape, or by converting white into red wines, or by mixing wines with coloring matters, alcohol, etc., to produce imitations of wines of a different class, an industry which flourishes extensively in Normandy, at Bingen on the Rhine, and at Hamburg. The wines so produced are usually heavy wines, port and sherry so called.

Cider is the fermented juice of the apple, prepared very much in the same way as wine is from grape-juice, and containing 3.5 to 7.5 per cent. of alcohol. It is very prone to acetous fermentation, which renders it sour and not only unpalatable, but liable to produce colic and diarrhœa with those not hardened to its use.

Spirits are alcoholic beverages, prepared by fermentation and distillation. They differ from beers and wines in containing a greater proportion of alcohol, and in not containing any of the non-volatile constituents of the grains or fruits from which they are prepared. Besides alcohol and water they contain acetic, butyric, valerianic, and œnanthic ethers, to which they owe their flavor; sometimes tannin and coloring matter derived from the cask; amylic alcohol remaining after imperfect purification; **sugar** intentionally added; and caramel. It is to the last-named substance that all dark spirits owe their color: although, after long keeping in wood a naturally colorless spirit assumes a straw color.

The varieties of spirituous beverages in common use are: **Brandy, spiritus vini gallici (U. S., Br.)**, obtained by the distillation of wine, and manufactured in France and in California and Ohio. It is of sp. gr. 0.929 to 0.934, is dark or light in color, according to the quantity of burnt sugar added, and contains about 1.2 per cent. of solid matter. **American whiskey, spiritus frumenti (U. S.)**, prepared from wheat, rye, barley, or Indian corn; has a sp. gr. of 0.922 to 0.937 and contains 0.1 to 0.3 per cent. of solids. *Scotch and Irish whiskies*, colorless spirits distilled from fermented grains; sp. gr. 0.915 to 0.920, having a peculiar smoky flavor produced by drying the malted grain by a peat fire. *Gin*, also distilled from malted grain, sp. gr. 0.930 to 0.944, flavored with juniper, and sometimes fraudulently with turpentine. *Rum*, a spirit distilled from molasses, and varying in color and flavor from the dark *Jamaica rum* to the colorless *St. Croix rum*. The former is of sp. gr. 0.914 to 0.926, and contains one per cent. of solid matter.

Liqueurs or **cordials** are spirits sweetened and flavored with vegetable aromatics, and frequently colored; *anisette* is flavored with aniseed; *absinthe*, with wormwood; *curaçoa*, with orange-peel; *kirschwasser*, with cherries, the stones being cracked and the spirits distilled from the bruised fermented fruit; *kümmel*, with cummin and caraway seeds; *maraschino*, with cherries; *noyeau*, with peach and apricot kernels.

Propyl hydroxid—Ethyl carbinol—Primary propyl alcohol— $\mathbf{CH_3.CH_2.CH_2OH}$—60—is produced, along with ethylic alcohol, during fermentation, and obtained by fractional distillation of marc brandy, from *cognac oil*, *huile de marc* (not to be confounded with oil of wine), an oily matter, possessing the flavor of inferior brandy, which separates from marc brandy, distilled at high temperatures; and from the residues of manufacture of alcohol from beet-root, grain, molasses, etc. It is a colorless liquid, has a hot alcoholic taste, and a fruity odor; boils at 96°.7 (206°.1 F.); and is miscible with water. It has not been put to any use in the arts. Its intoxicating and poisonous actions are greater than those of ethyl alcohol. It exists in small quantity in cider.

Butyl alcohols—$\mathbf{C_4H_9OH}$—74.—The four butyl alcohols theoretically possible are known to exist:

Propyl carbinol—Primary normal butyl alcohol—*Butyl alcohol of fermentation*—$\mathbf{CH_3—CH_2—CH_2—CH_2OH}$—is formed in small quantities during alcoholic fermentation, and may be obtained by repeated fractional distillation from the oily liquid left in the rectification of vinic alcohol. It is a colorless liquid; boils at 114°.7 (238°.5 F.). It is more actively poisonous than ethyl or methyl alcohol.

Isopropyl carbinol—Isobutyl alcohol—$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH—CH_2OH$—occurs in the fusel oil obtained in the products of fermentation and distillation of beet-root molasses. It is a colorless liquid, sp. gr. 0.8032; boils at 110° (230° F.).

Ethyl-methyl carbinol; secondary butyl alcohol—
$\begin{matrix}CH_3—CH_2\\CH_3\end{matrix}\!\!>CHOH$—a liquid which boils at 99° (210°.2 F.).

Trimethyl carbinol; tertiary butyl alcohol, $\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!\!—COH$—a crystalline solid, which fuses at 20°–25° (68°–77° F.), and boils at 82° (179°.6 F.).

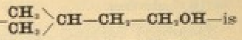
Amylic alcohols—$C_5H_{11}OH$—88.—Of the eight amyl alcohols theoretically possible (see p. 239) seven have been obtained. The substance usually known as **amylic alcohol, potato spirit, fusel oil, alcohol amylicum** (**Br.**), is the primary alcohol $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH—CH_2—CH_2OH$—with lesser quantities of other alcohols, differing in nature and amount with the grain used, and the conditions of the fermentation and distillation. Each kind of "spirit" furnishing and containing a peculiar fusel.

In the process of manufacture of ardent spirits the fusel oil accumulates in great part in the still, but much of it distils over, and is more or less completely removed from the product by the process of **defuselation.**

Spirits properly freed of fusel oil give off no irritating or foul fumes, when hot. They are not colored red when mixed with three parts C_2H_6O and one part strong H_2SO_4. They are not colored red or black by ammoniacal silver nitrate solution. When 150 parts of the spirit, mixed with 1 part potash, dissolved in a little H_2O, are evaporated down to 15 parts, and mixed with an equal volume of dilute H_2SO_4, no offensive odor should be given off.

While young spirits owe their rough taste and, in great measure, their intoxicating qualities to the presence of fusel oil, it is a popular error that a spirit would be improved by complete removal of all products except ethyl alcohol. The improvement of a spirit by age is due to chemical changes in the small amount of fusel retained in a properly manufactured product, and, were this absent, the spirit would deteriorate rather than improve by age.

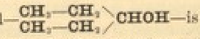
The individual amylic alcohols have the following characters: **Butyl carbinol; normal amylic alcohol,** $CH_3—CH_2—CH_2—CH_2—CH_2OH$—is a colorless liquid, boils at 135° (275° F.). Obtained from normal butyl alcohol. It yields normal valerianic acid on oxidation.



Isobutyl carbinol—Amyl alcohol—$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH-CH_2-CH_2OH$—is the principal constituent of the fusel oil from grain and potatoes. It is obtained from the last milky products of rectification of alcoholic liquids. These are shaken with H_2O to remove ethyl alcohol, the supernatant oily fluid is decanted, dried by contact with fused calcium chlorid, and distilled; that portion which passes over between 128° and 132° (262°.4–269°.6 F.) being collected.

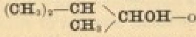
It is a colorless, oily liquid, has an acrid taste and a peculiar odor, at first not unpleasant, afterward nauseating and provocative of severe headache. It boils at 132° (269°.6 F.) and crystallizes at −20° (4° F.); sp. gr. 0.8184 at 15° (5° F.). It mixes with alcohol and ether, but not with water. It burns difficultly with a pale blue flame.

When exposed to air it oxidizes very slowly; quite rapidly, however, in contact with platinum-black, forming valerianic acid. The same acid, along with other substances, is produced by the action of the more powerful oxidants upon amyl alcohol. Chlorin attacks it energetically, forming amyl chlorid, HCl, and other chlorinated derivatives. Sulfuric acid dissolves in amyl alcohol, with formation of amyl-sulfuric acid, $SO_4(C_5H_{11})H$, corresponding to ethyl-sulfuric acid. It also forms similar acids with phosphoric, oxalic, citric, and tartaric acids. Its ethers, when dissolved in ethyl alcohol, have the taste and odor of various fruits, and are used in the preparation of artificial fruit-essences. Amyl alcohol is also used in analysis as a solvent, particularly for certain alkaloids, and in pharmacy for the artificial production of valerianic acid and the valerianates.



Diethyl carbinol—$\left.\begin{matrix}CH_2-CH_3\\CH_2-CH_3\end{matrix}\right\rangle CHOH$—is produced by the action of a mixture of zinc and ethyl iodid on ethyl formiate, with the subsequent addition of H_2O. It is a liquid which boils at 116°.5 (241°.7 F.).

Methyl-propyl-carbinol — $\left.\begin{matrix}CH_3\\CH_3-CH_2-CH_2\end{matrix}\right\rangle CHOH$—a liquid, boiling at 118°.5 (245°.3 F.), obtained by the hydrogenation of methylpropylic acetone.



Methyl-isopropyl-carbinol—Amylene hydrate—$\left.\begin{matrix}(CH_3)_2-CH\\CH_3\end{matrix}\right\rangle CHOH$—obtained by the hydrogenation of methyl-isopropylic acetone; or by the action of hydriodic acid upon amylene, and the action of moist silver oxid upon the product so obtained. It is a colorless liquid, sp. gr. 0.829 at 0° (32° F.), having a pungent, ethereal odor; boils at 108° (226°.4 F.); soluble in H_2O and in alcohol. Has been used as a hypnotic.

Ethyl-dimethyl-carbinol—*Tertiary amylic alcohol*—

$$\begin{matrix} & \mathbf{CH_3}\diagdown & \\ \mathbf{CH_3{-}} & \mathbf{CH_2{-}} & \mathbf{COH} \\ & \mathbf{CH_3}\diagup & \end{matrix}$$

—is a liquid which solidifies at −12° (10°.4 F.) and boils at 102°.5 (216°.5 F.); formed by the action of zinc methyl upon propionyl chlorid, or by decomposition of tertiary sulfamylic acid by boiling H_2O. It is a colorless liquid; sp. gr. 0.828 at 0° (32° F.), crystallizes at −30° (−22° F.), boils at about 100° (212° F.). The nitrite of this alcohol has been used as a substitute for amyl nitrite.

Cetyl hydrate—*Cetylic alcohol*—*Ethal*—$\mathbf{C_{16}H_{33}OH}$—242—is obtained by the saponification of **spermaceti** (its palmitic ether). It is a white, crystalline solid; fusible at 49° (120°.2 F.); insoluble in H_2O; soluble in alcohol and ether; tasteless and odorless.

Ceryl hydrate—$\mathbf{C_{27}H_{55}OH}$—396—and **Myricyl hydrate**—$\mathbf{C_{30}H_{61}OH}$—438—are obtained as white, crystalline solids: the former from China wax; the latter from beeswax, by saponification.

SIMPLE ETHERS.

OXIDS OF ALCOHOLIC RADICALS OF THE SERIES C_nH_{2n+1}.

The term **ether** was originally applied to any volatile liquid obtained by the action of an acid upon an alcohol.

The simple ethers are the oxids of the alcoholic radicals. They bear the same relation to the alcohols that the oxids of the basylous elements bear to their hydroxids:

$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$	$\left.\begin{matrix}K\\K\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	$\left.\begin{matrix}K\\H\end{matrix}\right\}O$
Ethyl oxid (ethylic ether).	Potassium oxid.	Ethyl hydroxid (alcohol).	Potassium hydroxid.

When the two alcoholic radicals are the same, as in the above instance, the ether is designated as **simple**; when the radicals are different, as in methyl-ethyl oxid, $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O$, they are called **mixed ethers.**

Methyl oxid—$\left.\begin{matrix}\mathbf{CH_3}\\\mathbf{CH_3}\end{matrix}\right\}\mathbf{O}$—46—isomeric with ethyl alcohol, is obtained by the action of H_2SO_4 and boric acid upon methyl alcohol, or by the action of silver oxid on methyl iodid. It is a colorless gas; has an ethereal odor; burns with a pale flame; liquefies at −36° (−32°.8 F.); and boils at −21° (−5°.8 F.); is soluble in H_2O, H_2SO_4 and ethyl alcohol.

Ethyl oxid — Ethylic ether — Ether—Sulfuric ether — Æther fortior (U. S.)—Æther purus (Br.)—$\left.\begin{matrix}\mathbf{C_2H_5}\\\mathbf{C_2H_5}\end{matrix}\right\}\mathbf{O}$—74.

Preparation.—A mixture is made of 5 pts. of alcohol, 90%, and 9 pts. of concentrated H_2SO_4, in a vessel surrounded by cold H_2O. This mixture is introduced into a retort, over which is a vessel from which a slow stream of alcohol is made to enter the retort. Heat is applied, and the addition of alcohol and the heat are so regulated that the temperature does not rise above 140° (284° F.). The retort is connected with a well-cooled condenser, and the process continued until the temperature in the retort rises above the point indicated. It is important that the tube by which the alcohol is introduced be drawn out to a small opening, and dip well down below the surface of the liquid. The distillate thus obtained contains ether, alcohol, water, and gases resulting from the decomposition of the alcohol and H_2SO_4, notably SO_2. It is subjected to a first purification by shaking with H_2O containing potash or lime, decanting the supernatant ether and redistilling. The product of this process is "washed ether," or **æther (U. S.)**. It is still contaminated with water and alcohol, and when desired pure, as for producing anæsthesia and for processes of analysis, it is subjected to a second purification. It is again shaken with H_2O, decanted after separation, shaken with recently fused calcium chlorid and newly burnt lime, with which it is left in contact 24 hours, and from which it is then distilled.

It was known at an early day that a small quantity of H_2SO_4 is capable of converting a large quantity of alcohol into ether, and that at the end of the process the H_2SO_4 remains in the retort unaltered, except by secondary reactions. A metaphysical explanation of the process was found in the assertion that the acid acted by its mere presence, by **catalysis**, as it was said. In other words, it acts because it acts, a very ready but a very feminine method of explaining what is not understood, which is still invoked by some authors as a covering for our ignorance of the rationale of certain chemico-physiological phenomena. It was only in 1850 that Alex. Williamson, by a series of ingenious experiments, determined the true nature of the process. In the conversion of alcohol into ether, an intermediate substance, sulfovinic acid, is alternately formed at the expense of the alcohol, and destroyed with formation of ether and regeneration of H_2SO_4. At first H_2SO_4 and alcohol act upon each other, molecule for molecule, to form H_2O and sulfovinic acid: $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O+\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2 = \left.\begin{matrix}H\\H\end{matrix}\right\}O+\left.\begin{matrix}SO_2\\C_2H_5\\H\end{matrix}\right\}O_2$. The new acid as soon as formed reacts with a second molecule of alcohol, with regeneration of H_2SO_4 and formation of ether: $\left.\begin{matrix}SO_2\\C_2H_5\\H\end{matrix}\right\}O_2+\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O=\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2+\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$.

Theoretically, therefore, a given quantity of H_2SO_4 could convert an unlimited amount of alcohol into ether. Such would also be the case in practice, were it not that the acid gradually becomes too dilute, by admixture with the H_2O formed during the reaction, and at the same time is decomposed by secondary reactions, into which it enters with impurities in the alcohol; causes which in practice limit the amount of ether produced to about four to five times the bulk of acid used.

Ether is a colorless, limpid, mobile, highly refracting liquid; it has a sharp, burning taste, and a peculiar, tenacious odor, characterized as ethereal. Sp. gr. 0.723 at 12°.5 (54°.5 F.); it boils at 34°.5 (94°.1 F.), and crystallizes at −31° (−23°.8 F.). Its tension of vapor is very great, especially at high temperatures; it should, therefore, be stored in strong bottles, and should be kept in situations protected from elevations of temperature. It is exceedingly volatile, and, when allowed to evaporate freely, absorbs a great amount of heat, of which property advantage is taken to produce local anæsthesia, the part being benumbed by the cold produced by the rapid evaporation of ether sprayed upon the surface. Water dissolves one-ninth its weight of ether. Ethylic and methylic alcohols are miscible with it in all proportions. Ether is an excellent solvent of many substances not soluble in water and alcohol, while, on the other hand, it does not dissolve many substances soluble in those fluids The resins and fats are readily soluble in ether; the salts of the alkaloids and many vegetable coloring matters are soluble in alcohol and water, but insoluble in ether, while the free alkaloids are for the most part soluble in ether, but insoluble, or very sparingly soluble, in water.

Ether, whether in the form of vapor or of liquid, is highly inflammable; and burns with a luminous flame. The vapor forms with air a violently explosive mixture. It is denser than air, through which it falls and diffuses itself to a great distance; great caution is therefore required in handling ether in a locality in which there is a light or fire, especially if the fire be near the floor.

Pure ether is neutral in reaction, but, on exposure to air or O, especially in the light, it becomes acid from the formation of a small quantity of acetic acid. H_2SO_4 mixes with ether, with elevation of temperature, and formation of sulfovinic acid. Sulfuric anhydrid forms ethyl sulfate. HNO_3, aided by heat, oxidizes ether to carbon dioxid and acetic and oxalic acids. Ether, saturated with HCl and distilled, yields ethyl chlorid. Cl, in the presence of H_2O, oxidizes ether, with formation of aldehyde, acetic acid, and chloral. In the absence of H_2O, however, a series of products of substitution are produced, in which 2, 4 and 10 atoms of H are replaced by a corresponding number of atoms of Cl. These substances in turn, by substitution of alcoholic radicals, or of atoms of elements, for atoms of Cl, give rise to other derivatives.

Action on the Economy.—Ether is largely used in medicine for producing anæsthesia, either locally by diminution of temperature due to its rapid evaporation, or generally by inhalation. When taken in overdose it causes death, although it is by no means as liable to give rise to fatal accidents as is chloroform. Patients suffering from an overdose may, in the vast majority of cases, be resuscitated by artificial respiration and the induced current, one pole to be applied to the nape of the neck, and the other carried across the body just below the anterior attachments of the diaphragm.

In cases of death from ether the odor is generally well marked in the clothing and surroundings, and especially on opening the thoracic cavity. In the analysis it is sought for in the blood and lungs at the same time as chloroform (q.v.).

MONOBASIC ACIDS.

SERIES $C_nH_{2n}O_2$.

As the higher terms of this series are obtained from the fats, and the lower terms are volatile liquids, these acids are sometimes designated as the **volatile fatty acids.**

Although formed in a variety of ways, these acids may be considered as being derived from the primary monoatomic alcohols, by the substitution of O for H_2 in the group CH_2OH:

$$CH_3—CH_2—CH_2—CH_2—CH_2,OH$$

Normal amylic alcohol.

$$CH_3—CH_2—CH_2—CH_2—CO,OH$$

Normal valerianic acid.

Considered typically, the substitution of O for H_2 occurs in the radical: $\left.\begin{matrix}C_5H_{11}\\H\end{matrix}\right\}O—\left.\begin{matrix}C_5H_9O\\H\end{matrix}\right\}O$, and communicates to the radical electro-negative or acid qualities.

Formic acid—HCO,OH—46—occurs in the acid secretion of red ants, in the stinging hairs of certain insects, in the blood, urine, bile, perspiration, and muscular fluid of man, in the stinging-nettle, and in the leaves of trees of the pine family. It is produced in a number of reactions; by the oxidation of many organic substances: sugar, starch, fibrin, gelatin, albumin, etc.; by the action of potash upon chloroform and kindred bodies; by the action of mineral acids in hydrocyanic acid; during the fermentation of diabetic urine; by the direct union of carbon monoxid and water; by the decomposition of oxalic acid under the influence of glycerin at about 100° (212° F.).

It is a colorless liquid, having an acid taste and a penetrating odor; it acts as a vesicant; it boils at 100° (212° F.), and, when pure, crystallizes at 0° (32° F.). It is miscible with H_2O in all proportions.

The mineral acids decompose it into H_2O and carbon monoxid. Oxidizing agents convert it into H_2O and carbon dioxid. Alkaline hydroxids decompose it with formation of a carbonate and liberation of H. It acts as a reducing agent with the salts of the noble metals.

Acetic acid—*Acetyl hydrate—Hydrogen acetate—Pyroligneous acid*—**Acidum aceticum** (**U. S.**; **Br.**)—**$CH_3,COOH$**—60.

It is formed—(1.) By the oxidation of alcohol:

$$CH_3,CH_2OH+O_2=CH_3,COOH+H_2O.$$

(2.) By the dry distillation of wood.

(3.) By the decomposition of natural acetates by mineral acids.

(4.) By the action of potash in fusion on sugar, starch, oxalic, tartaric, citric acids, etc.

(5.) By the decomposition of gelatin, fibrin, casein, etc., by H_2SO_4 and manganese dioxid.

(6.) By the action of carbon dioxid upon sodium methyl: $CO_2+NaCH_3=C_2H_3O_2Na$; and decomposition of the sodium acetate so produced.

The acetic acid used in the arts and in pharmacy is prepared by the destructive distillation of wood. The products of the distillation, which vary with the nature of the wood used, are numerous. Charcoal remains in the retort, while the distilled product consists of an acid, watery liquid; a tarry material; and gaseous products. The gases are carbon dioxid, carbon monoxid, and hydrocarbons. The tar is a mixture of empyreumatic oils, hydrocarbons, phenol, oxyphenol, acetic acid, ammonium acetate, etc.

The acid water is very complex, and contains, besides acetic acid, formic, propionic, butyric, valerianic, and oxyphenic acids, acetone, naphthalene, benzene, toluene, cumene, creasote, methyl alcohol, and methyl acetate, etc. Partially freed from tar by decantation, it still contains about 20 per cent. of tarry and oily material, and about 4 per cent. of acetic acid; this is the **crude pyroligneous acid** of commerce.

The crude product is subjected to a first purification by distillation; the first portions are collected separately and yield methyl alcohol (q.v.); the remainder of the distillate is the *distilled pyroligneous acid*, used to a limited extent as an antiseptic, but principally for the manufacture of acetic acid and the acetates.

It can only be freed from the impurities which it still contains by chemical means. To this end slacked lime and chalk are added, at a gentle heat, to neutralization; the liquid is boiled and allowed to settle twenty-four hours; the clear liquid, which is a solution of calcium acetate, is decanted and evaporated; the calcium salt is converted into sodium acetate, which is then purified by calcination at a temperature below 330° (626° F.), dissolved, filtered, and recrystallized; the salt is then decomposed by a proper quantity of H_2SO_4, and the liberated acetic acid separated by distillation.

The product so obtained is a solution of acetic acid in water, containing 36 per cent. of true acetic acid, and being of sp. gr. 1.047, U. S. (the acid of the Br. Ph. is weaker—33 per cent. $C_2H_4O_2$, and sp. gr. 1.044).

Pure acetic acid, known as **glacial acetic acid, acidum aceticum glaciale** (**U. S.**), is obtained by decomposition of a pure dry acetate by heat.

Acetic acid is a colorless liquid. Below 17° (62°.6 F.), when pure, it is a crystalline solid. It boils at 119° (246°.2 F.); sp. gr. 1.0801 at 0° (32° F.); its odor is penetrating and acid; in contact with the skin it destroys the epidermis and causes vesication; it mixes with H_2O in all proportions, the mixtures being less in volume than the sum of the volumes of the constituents. The sp. gr. of the mixtures gradually increase up to that containing 23 per cent. of H_2O, after which they again diminish, and all the mixtures containing more than 43 per cent. of acid are of higher sp. gr. than the acid itself.

Vapor of acetic acid burns with a pale blue flame; and is decomposed at a red heat. It only decomposes calcic carbonate in the presence of H_2O. Hot H_2SO_4 decomposes and blackens it, SO_2 and CO_2 being given off. Under ordinary circumstances Cl acts upon it slowly, more actively under the influence of sunlight, to produce **monochloracetic acid, CH_2ClCO,OH**; **dichloracetic acid, $CHCl_2CO,OH$**; and **trichloracetic acid, CCl_3CO,OH**. The last named is an odorless, acid, strongly vesicant, crystalline solid; fuses at 46° (114°.8 F.) and boils at 195°–200° (383°–392° F.).

Analytical Characters.—(1.) Warmed with H_2SO_4 it blackens. (2.) With silver nitrate a white crystalline ppt., partly dissolved by heat; no reduction of Ag on boiling. (3.) Heated with H_2SO_4 and C_2H_6O, acetic ether, recognizable by its odor, is given off. (4.) When an acetate is calcined with a small quantity of As_2O_3 the foul odor of cacodyl oxid is developed. (5.) Neutral solution of ferric chlorid produces in neutral solutions of acetates a deep red color, which turns yellow on addition of free acid.

Vinegar is an acid liquid owing its acidity to acetic acid, and holding certain fixed and volatile substances in solution. It is obtained from some liquid containing 10 per cent. or less of alcohol, which is converted into acetic acid by the transferring of atmospheric oxygen to the alcohol during the process of nutrition of a peculiar vegetable ferment, known as *mycoderma aceti*, or, popularly, as *mother of vinegar*. Vinegar is now manufactured principally by one of two processes—the German method, and that of Pasteur. In the former, the alcoholic fluid, which must also contain albuminous matter, is allowed to trickle slowly through barrels containing beech-wood shavings, supported by a perforated false bottom. By a suitable arrangement of holes and tubes, an ascending current of air is made to pass through the barrel. The acetic ferment clings to the shavings, and under its influence acetification takes place rapidly, owing to the large surface exposed to the air. In Pasteur's process, the ferment is sown upon the surface of the alcoholic liquid, contained in large, shallow, covered vats, from which the vinegar is drawn off after acetification has been completed; the mother is collected, washed, and used in a subsequent operation.

The liquids from which vinegar is made are wine, cider, and beer, to which dilute alcohol is frequently added; the most esteemed being that obtained from white wine. *Wine vinegar* has a pleasant, acid taste and odor; it consists of water, acetic acid (about 5 per cent.), potassium bitartrate, alcohol, acetic ether, glucose, malic acid, mineral salts present in wine, a fermentescible, nitrogenized substance, coloring matter, etc. Sp. gr. 1.020 to 1.025. When evaporated, it yields from 1.7 to 2.4 per cent. of solid residue.

Vinegars made from alcoholic liquids other than wine contain no potassium bitartrate, contain less acetic acid, and have not the aromatic odor of wine vinegar. *Cider vinegar* is of sp. gr. 1.020; is yellowish, has an odor of apples, and yields 1.5 per cent. of extract on evaporation. *Beer vinegar* is of sp. gr. 1.032; has a bitterish flavor, and an odor of sour beer; it leaves 6 per cent. of extract on evaporation.

The principal *adulterations* of vinegar are: *Sulfuric acid*, which produces a black or brown color when a few drops of the vinegar and some fragments of cane-sugar are evaporated over the water-bath to dryness. *Water*, an excess of which is indicated by a low power of saturation of the vinegar, in the absence of mineral acids. Two parts of good wine vinegar neutralize 10 parts of sodium carbonate; the same quantity of cider vinegar, 3.5 parts; and of beer vinegar, 2.5 parts of carbonate. *Pyroligneous acid* may be detected by the creasote-like odor and taste. *Pepper*, *capsicum*, and other acrid substances, are often added to communicate fictitious strength. In vinegar so adulterated an acrid odor is perceptible after neutralization of the acid with sodium carbonate. *Copper, zinc, lead, and tin* frequently occur in vinegar which has been in contact with those elements, either during the process of manufacture or subsequently.

Distilled vinegar is prepared by distilling vinegar in glass vessels; it contains none of the fixed ingredients of vinegar, but its volatile constituents (acetic acid, water, alcohol, acetic ether, odorous principles, etc.), and a small quantity of aldehyde.

When dry acetate of copper is distilled, a blue, strongly acid liquid passes over; this, upon rectification, yields a colorless, mobile liquid, which boils at 56° (132°.8 F.), has a peculiar odor, and is a mixture of acetic acid, water, and acetone, known as **radical vinegar.**

Toxicology.—When taken internally, acetic acid and vinegar (the latter in doses of 4–5 fl. ℥) act as irritants and corrosives, causing in some instances perforation of the stomach, and death in 6–15 hours. Milk of magnesia should be given as an antidote, with the view to neutralizing the acid.

Propionic acid—$CH_3,CH_2—COOH$—is formed by the action of caustic potassa upon sugar, starch, gum, and ethyl cyanid; during fermentation, vinous or acetic; in the distillation of wood; during the putrefaction of peas, beans, etc.; by the oxidation of normal propylic alcohol, etc. It is best prepared by heating ethyl cyanid with potash until the odor of the ether has disappeared; the acid is then liberated from its potassium compound by H_2SO_4 and purified.

It is a colorless liquid, sp. gr. 0.996, does not solidify at −21° (−5°.8 F.), boils at 140° (284° F.), mixes with water and alcohol in all proportions, resembles acetic acid in odor and taste. Its salts are soluble and crystallizable.

Butyric acid—Propyl-formic acid—$CH_3—CH_2—CH_2—COOH$—has been found in the milk, perspiration, muscular fluid, the juices of the spleen and of other glands, the urine, contents of the stomach and large intestine, fæces, and guano; in certain fruits, in yeast, in the products of decomposition of many vegetable substances; and in natural waters; in fresh butter in small quantity, more abundantly in that which is rancid.

It is formed by the action of H_2SO_4 and manganese dioxid, aided by heat, upon cheese, starch, gelatin, etc.; during the combustion of tobacco (as ammonium butyrate); by the action of HNO_3 upon oleic acid; during the putrefaction of fibrin and other albuminoids; during a peculiar fermentation of glucose and starchy material in the presence of casein or gluten. This fermentation, known as the butyric, takes place in two stages; at first the glucose is converted into lactic acid: $C_6H_{12}O_6=2(C_3H_6O_3)$; and this in turn is decomposed into butyric acid, carbon dioxid, and hydrogen: $2C_3H_6O_3=C_4H_8O_2+2CO_2+2H_2$.

Butyric acid is obtained from the animal charcoal which has been used in the purification of glycerol, in which it exists as calcium butyrate. It is also formed by subjecting to fermentation a mixture composed of glucose, water, chalk, and cheese or gluten. The calcium butyrate is decomposed by H_2SO_4, and the butyric acid separated by distillation.

Butyric acid is a colorless, mobile liquid, having a disagreeable, persistent odor of rancid butter, and a sharp, acid taste; soluble in water, alcohol, ether, and methyl alcohol; boils at 164° (327°.2 F.), distilling unchanged; solidifies in a mixture of solid carbon dioxid and ether; sp. gr. 0.974 at 15° (59° F.); a good solvent of fats.

It is not acted upon by H_2SO_4 in the cold, and only slightly under the influence of heat. Nitric acid dissolves it unaltered in the cold, but on the application of heat, oxidizes it to succinic acid. Dry Cl under the influence of sunlight, and Br under the influence of heat and pressure, form products of substitution with butyric acid. It readily forms ethers and salts.

Butyric acid is formed in the intestine, by the process of fermentation mentioned above, at the expense of those portions of the carbohydrate elements of food which escape absorption, and is discharged with the fæces as ammonium butyrate.

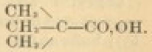
Isobutyric acid—Isopropyl-formic acid—$\left.\begin{array}{l}\mathbf{CH_3}\\\mathbf{CH_3}\end{array}\right\rangle\mathbf{CH—COOH}$—boils at 152° (305°.6 F.), has been found in human fæces. It corresponds to isobutyl alcohol, from which it is produced by oxidation.

Valerianic acids—$\mathbf{C_4H_9CO,OH}$—102.—Corresponding to the four primary amylic alcohols, there are four possible amylic or valerianic acids, of which three, I., II., and IV., are known.

I. $CH_3—CH_2—CH_2—CH_2—CO,OH.$

II. 
$\left.\begin{array}{l}CH_3\\CH_3\end{array}\right\rangle CH—CH_2—CO,OH.$

III. 
$\left.\begin{array}{r}CH_3—CH_2\\CH_3\end{array}\right\rangle CH—CO,OH.$

IV. 
$\left.\begin{array}{l}CH_3\\CH_3\\CH_3\end{array}\right\rangle C—CO,OH.$

I. **Normal valerianic acid—Butylformic acid**—*Propylacetic acid*—is obtained by the oxidation of normal amylic alcohol. It is an oily liquid, boils at 185° (365° F.), and has an odor resembling that of butyric acid.

II. **Ordinary valerianic acid**—*Delphinic acid—Phocenic acid*—**Isovaleric acid**—*Isopropyl acetic acid*—**Isobutylformic acid—Acidum valerianicum (Br.).**—This acid exists in the oil of the porpoise, and in valerian root and in angelica root. It is formed during putrid fermentation or oxidation of albuminoid substances. It occurs in the urine and fæces in typhus, variola, and acute atrophy of the liver. It is also formed in a variety of chemical reactions, and notably by the oxidation of amylic alcohol.

It is prepared either by distilling water from valerian root, or, more economically, by mixing rectified amylic alcohol with H_2SO_4, adding when cold, a solution of potassium dichromate, and distilling after the reaction has become moderated; the distillate is neutralized with sodium carbonate; and the acid is obtained from the sodium valerianate so produced, by decomposition by H_2SO_4 and rectification.

The ordinary valerianic acid is an oily, colorless liquid, having a penetrating odor, and a sharp, acrid taste. It solidifies at –16° (3°.2 F.); boils at 173°–175° (343°.4–347° F.); sp. gr. 0.9343–0.9465 at 20° (68° F.); burns with a white, smoky flame. It dissolves in 30 parts of water, and in alcohol and ether in all proportions. It dissolves phosphorus, camphor, and certain resins.

IV. **Trimethyl acetic acid**—*Pivalic acid*—is a crystalline solid, which fuses at 35°.5 (96° F.) and boils at 163°.7 (326°.7 F.); sparingly soluble in H_2O; obtained by the action of cyanid of mercury upon tertiary butyl iodid.

Caproic acids—*Hexylic acids*—**C_5H_{11},COOH**—116.—There probably exist quite a number of isomeres having the composition indicated above, some of which have been prepared from butter, cocoa-oil, and cheese, and by decomposition of amyl cyanid, or of hexyl alcohol.

The acid obtained from butter, in which it exists as a glyceric ether, is a colorless, oily liquid, boils at 205° (401° F.); sp. gr. 0.931 at 15° (59° F.); has an odor of perspiration and a sharp, acid taste; is very sparingly soluble in water, but soluble in alcohol.

Œnanthylic acid—*Heptylic acid*—**C_6H_{13},COOH**—130—exists in spirits distilled from rice and maize, and is formed by the action of HNO_3 on fatty substances, especially castor-oil. It is a colorless oil; sp. gr. 0.9167; boils at 212° (413°.6 F.).

Caprylic acid—*Octylic acid*—**C_7H_{15},COOH**—144—accompanies caproic acid in butter, cocoa-oil, etc. It is a solid; fuses at 15° (59° F.); boils at 236° (457° F.); almost insoluble in H_2O.

Pelargonic acid—*Nonylic acid*—**C_8H_{17},COOH**—158.—A colorless oil, solid below 10° (50° F.); boils at 260° (500° F.); exists in oil of geranium, and is formed by the action of HNO_3 on oil of rue.

Capric acid—*Decylic acid*—**C_9H_{19},COOH**—172—exists in butter, cocoa-oil, etc., associated with caproic and caprylic acids in their glyceric ethers, and in the residues of distillation of Scotch whiskey, as amyl caprate. It is a white, crystalline solid; melts at 27°.5 (81°.5 F.); boils at 273° (523°.4 F.).

Lauric acid—*Laurostearic acid*—**$C_{11}H_{23}$,COOH**—200—is a solid, fusible at 43°.5 (110°.3 F.), obtained from laurel berries, cocoa-butter, and other vegetable fats.

Myristic acid—**$C_{13}H_{27},COOH$**—228.—A crystalline solid, fusible at 54° (129°.2 F.); existing in many vegetable oils, cow's butter, and spermaceti.

Palmitic acid—*Ethalic acid*—**$C_{15}H_{31},COOH$**—256—exists in palm-oil, in combination when the oil is fresh, and free when the oil is old; it also enters into the composition of nearly all animal and vegetable fats. It is obtained from the fats, palm-oil, etc., by saponification with caustic potassa and subsequent decomposition of the soap by a strong acid. It is also formed by the action of caustic potash in fusion upon cetyl alcohol (ethal), and by the action of the same reagent upon oleic acid.

Palmitic acid is a white, crystalline solid; odorless, tasteless; lighter than H_2O, in which it is insoluble; quite soluble in alcohol and in ether; fuses at 62° (143°.6 F.); distils unchanged with vapor of water.

Margaric acid—**$C_{16}H_{33},COOH$**—270—formerly supposed to exist as a glycerid in all fats, solid and liquid. What had been taken for margaric acid was a mixture of 90 per cent. of palmitic and 10 per cent. of stearic acid. It is obtained by the action of potassium hydroxid upon cetyl cyanid, as a white, crystalline body; fusible at 59°.9 (140° F.).

Stearic acid—**$C_{17}H_{35},COOH$**—284—exists as a glycerid in all solid fats, and in many oils, and also free to a limited extent.

To obtain it pure, the fat is saponified with an alkali, and the soap decomposed by HCl; the mixture of fatty acids is dissolved in a large quantity of alcohol, and the boiling solution *partly* precipitated by the addition of a concentrated solution of barium acetate. The precipitate is collected, washed, and decomposed by HCl; the stearic acid which separates is washed and recrystallized from alcohol. The process is repeated until the product fuses at 70° (158° F.). Stearic acid is formed from oleic acid (q.v.) by the action of iodin under pressure at 270°-280° (518°-536° F.).

Pure stearic acid is a colorless, odorless, tasteless solid; fusible at 70° (158° F.); unctuous to the touch; insoluble in H_2O; very soluble in alcohol and in ether. The alkaline stearates are soluble in H_2O; those of Ca, Ba, and Pb are insoluble.

Stearic and palmitic acids exist free in the intestine during the digestion of fats, a portion of which is decomposed by the action of the pancreatic secretion into fatty acids and glycerol. The same decomposition also occurs in the presence of putrefying albuminoid substances.

Arachic acid—**$C_{19}H_{39},COOH$**—312—exists as a glycerid in peanut-oil (now largely used as a substitute for olive-oil), in oil of ben, and in small quantity in butter. It is a crystalline solid, which melts at 75° (167° F.).

ANHYDRIDS, CHLORIDS, ETC., CORRESPONDING TO THE MONOBASIC ACIDS.

The **anhydrids** of the acid radicals bear the same relation to the acids themselves that the simple ethers bear to the alcohols:

$CH_3{-}COOH$ Acetic acid.	$CH_3{-}CH_2OH$ Ethylic alcohol.
$\left.\begin{matrix}CH_3{-}CO\\CH_3{-}CO\end{matrix}\right\rangle O$ Acetic anhydrid.	$\left.\begin{matrix}CH_2CH_3\\CH_2CH_3\end{matrix}\right\rangle O$ Ethylic ether.

Acetic anhydrid—$(CH_3CO)_2O$—is produced by the action of carbon disulfid upon lead acetate:

$$2\left.\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\right\rangle Pb + CS_2 = 2\left.\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\right\rangle O + CO_2 + 2\ PbS.$$

The acid radicals also unite with the halogens to form compounds corresponding to the chlorids, bromids, and iodids of the alcoholic radicals.

Acetyl chlorid—CH_3COCl—78.5—obtained by the action of phosphorus trichlorid upon glacial acetic acid, is used in synthetic investigations for the introduction of the group CH_3CO into other molecules.

Acetyl-acetic acid—$CH_3{-}CO{-}CH_2{-}COOH$ is produced as the ethylic ether of a sodium derivative by the action of metallic Na upon ethyl acetate. The acid itself may be obtained as a very unstable, acid liquid, soluble in water in all proportions. It is the type of a great number of similarly constituted acids, containing other radicals and their derivatives, and is extensively used in the preparation of synthetic products of great variety, as, for instance, in the manufacture of antipyrin (q. v.).

COMPOUND ETHERS.

As the alcohols resemble the mineral bases, and the organic acids resemble those of mineral origin, so the compound ethers are similar in constitution to the salts, being *formed by the double decomposition of an alcohol with an acid, mineral or organic*, as a salt is formed by double decomposition of an acid and a mineral base, the radical playing the part of an atom of corresponding valence:

$$\underset{\text{Potassium hydroxid.}}{\left.\begin{matrix}K'\\H\end{matrix}\right\}O} + \underset{\text{Nitric acid.}}{\left.\begin{matrix}(NO_2)'\\H\end{matrix}\right\}O} = \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} + \underset{\text{Potassium nitrate.}}{\left.\begin{matrix}(NO_2)'\\K'\end{matrix}\right\}O}$$

$$\underset{\text{Ethyl hydroxid (alcohol).}}{\left.\begin{matrix}(C_2H_5)'\\H\end{matrix}\right\}O} + \underset{\text{Nitric acid.}}{\left.\begin{matrix}(NO_2)'\\H\end{matrix}\right\}O} = \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} + \underset{\text{Ethyl nitrate (nitric ether).}}{\left.\begin{matrix}(NO_2)'\\(C_2H_5)'\end{matrix}\right\}O}$$

Therefore **the compound ethers are acids whose hydrogen has been partially or completely displaced by a hydrocarbon radical or radicals.**

Some of the compound ethers still contain a portion of the acid hydrogen which, being replaceable by another radical or by a metal, communicates acid qualities to the substance, which is at the same time a compound ether and a true acid.

The compound ethers are produced:

1.) By the action of the acid upon the alcohol:

$$\underset{\text{Sulfuric acid.}}{H_2SO_4} + \underset{\text{Ethyl hydroxid.}}{C_2H_5,OH} = \underset{\text{Ethylsulfuric acid.}}{C_2H_5,HSO_4} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\text{Sulfuric acid.}}{H_2SO_4} + \underset{\text{Ethyl hydroxid.}}{2C_2H_5,OH} = \underset{\text{Ethyl sulfate.}}{(C_2H_5)_2,SO_4} + \underset{\text{Water.}}{2H_2O}$$

2.) By the action of the corresponding haloid ethers upon the silver salt of the acid:

$$\underset{\text{Silver nitrate.}}{AgNO_3} + \underset{\text{Ethyl iodid.}}{C_2H_5I} = \underset{\text{Silver iodid.}}{AgI} + \underset{\text{Ethyl nitrate.}}{C_2H_5,NO_3}$$

3.) By the action of the chlorids of the acid radicals upon the sodium derivatives of the alcohols, and in some instances upon the alcohols themselves:

$$\underset{\text{Acetyl chlorid.}}{C_2H_3O_2Cl} + \underset{\text{Sodium ethylate.}}{C_2H_5Na} = \underset{\text{Sodium chlorid.}}{NaCl} + \underset{\text{Ethyl acetate.}}{(C_2H_5)C_2H_3O_2}.$$

All compound ethers are decomposed into acid and alcohol by the action of water at high temperatures, or of caustic potash or soda:

$$\underset{\text{Ethyl nitrate.}}{(C_2H_5)NO_3} + \underset{\text{Potassium hydroxid.}}{KHO} = \underset{\text{Potassium nitrate.}}{KNO_3} + \underset{\text{Ethyl hydroxid.}}{C_2H_5HO}$$

As this decomposition is analogous to that utilized in the manufacture of soap (q. v.), it is known as **saponification**, and whenever an ether is so decomposed it is said to be **saponified.**

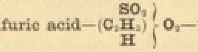
Ethyl nitrate—*Nitric ether*—$\left.\begin{matrix}NO_2\\C_2H_5\end{matrix}\right\}O$—91.—A colorless liquid; has a sweet taste and bitter after-taste; sp. gr. 1.112 at 17° (62°.6 F.); boils at 85° (185° F.); gives off explosive vapors. Prepared by distilling a mixture of HNO_3 and C_2H_6O in the presence of urea.

Ethyl nitrite—*Nitrous ether*—$\left.\begin{matrix}NO\\C_2H_5\end{matrix}\right\}O$—75—is best prepared by directing the nitrous fumes, produced by the action of starch on HNO_3 under the influence of heat, into alcohol, contained in a retort connected with a well-cooled receiver.

It is a yellowish liquid; has an apple-like odor, and a sharp, sweetish taste; sp. gr. 0.947; boils at 18° (64°.4 F.); gives off inflammable vapor; very sparingly soluble in H_2O; readily soluble in alcohol and ether.

It is decomposed by warm H_2O, by alkalies, by H_2SO_4, H_2S, and the alkaline sulfids, and is liable to spontaneous decomposition especially in the presence of H_2O. Its vapor produces anæsthesia, and it exists in alcoholic solution in **Spiritus ætheris nitrosi** (**U. S., Br.**), which also contains aldehyde, which latter substance by its oxidation frequently renders the spirit acid and unfit for use. (See Nitro-paraffins.)

Ethyl sulfates.—These are two in number: $(C_2H_5)HSO_4$ = **Ethyl-sulfuric** or **sulfovinic acid** and $(C_2H_5)_2SO_4$—**Ethyl sulfate—Sulfuric ether.**



Ethyl-sulfuric acid—$\left.\begin{matrix}SO_2\\(C_2H_5)\\H\end{matrix}\right\}O_2$—126—is formed as an intermediate product in the manufacture of ethylic ether (q. v.). It is a colorless, syrupy, highly acid liquid; sp. gr. 1.316; soluble in water and alcohol in all proportions, insoluble in ether.

It decomposes slowly at ordinary temperatures, more rapidly when heated. When heated alone or with alcohol, it yields ether and H_2SO_4. When heated with H_2O, it yields alcohol and H_2SO_4. It forms crystalline salts, known as **sulfovinates**, one of which, **sodium sulfovinate** $(C_2H_5)NaSO_4$, has been used in medicine. It is a white, deliquescent solid; soluble in H_2O.

Ethyl sulfate—$(C_2H_5)_2SO_4$—154—the true sulfuric ether, is obtained by passing vapor of SO_3 into *pure* ethylic ether, thoroughly cooled.

It is a colorless, oily liquid; has a sharp, burning taste, and the odor of peppermint; sp. gr. 1.120; it cannot be distilled without decomposition; in contact with H_2O it is decomposed with formation of sulfovinic acid.

By the action of an excess of H_2SO_4 upon alcohol; by the dry distillation of the sulfovinates; and in the last stages of manufacture of ether, a yellowish, oily liquid, having a penetrating odor, and a sharp, bitter taste, is formed. This is **sweet** or **heavy oil of wine**, and its ethereal solution is **Oleum æthereum** (**U. S.**). It seems to be a mixture of ethyl sulfate with hydrocarbons of the series C_nH_{2n}. On contact with H_2O or an alkaline solution, it is decomposed, sulfovinic acid is formed, and there separates a colorless oil, of sp. gr. 0.917, boiling at 280° (536° F.), which is **light oil of wine**. This oil is polymeric with ethylene, and is probably cetine, $C_{16}H_{32}$. It is sometimes called **etherin** or **etherol.**

Sulfurous and Hyposulfurous Ethers.—These compounds have recently assumed medical interest from their relationship to mercaptan, sulfonal and a number of aromatic derivatives used as medicines.

There exist two isomeric sulfurous acids (see p. 97), both of which yield neutral ethers, but only one of which, the unsymmetrical, $\begin{matrix}O\\O\end{matrix}\!\!>S<\!\!\begin{matrix}H\\OH\end{matrix}$, forms acid ethers. These acid ethers are known as **sulfonic acids.** (See Aromatic sulfonic acids, mercaptan, sulfones, sulfonal.)

Diethyl sulfite—$(C_2H_5)_2SO_3$—is produced by the action of thionyl chlorid on absolute alcohol: $SOCl_2 + 2C_2H_5HO = SO_3\ (C_2H_5) + 2HCl$. It is a colorless liquid, having a powerful odor: sp. gr. 1.085, boils at 161° (321°.8 F.). H_2O decomposes it into alcohol and sulfurous acid.

Ethyl sulfonic acid—$SO_2<\!\!\begin{matrix}C_2H_5\\OH\end{matrix}$—is formed by the action of ethyl iodid on potassium sulfite: $C_2H_5I+SO_3K_2=C_2H_5,\ SO_2OK + KI$. It forms salts and ethers.

Sulfinic acids—are the acid ethers of hyposulfurous acid $SO<\!\!\begin{matrix}H\\OH\end{matrix}$, and are analogous to the sulfonic acids.

Ethyl acetate—Acetic ether—Æther aceticus (U. S.)—$\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O$—88—is obtained by distilling a mixture of sodium acetate, alcohol and H_2SO_4; or by passing carbon dioxid through an alcoholic solution of potassium acetate.

It is a colorless liquid, has an agreeable, ethereal odor; boils at 74° (165°.2 F.); sp. gr. 0.89 at 15° (59° F.); soluble in 6 pts. water, and in all proportions in methyl and ethyl alcohols and in ether; a good solvent of essences, resins, cantharidin, morphin, gun-cotton, and in general, of substances soluble in ether; burns with a yellowish-white flame. Chlorin acts energetically upon it, producing products of substitution, varying according to the intensity of the light from $C_4H_6Cl_2O_2$ to $C_4Cl_8O_2$.

Amyl nitrate—$\left.\begin{matrix}NO_2\\C_5H_{11}\end{matrix}\right\}O$—133—obtained by distilling a mixture of HNO_3 and amylic alcohol in the presence of a small quantity of urea. It is a colorless, oily liquid; sp. gr. 0.994 at 10° (50° F.); boils at 148° (298°.4 F.) with partial decomposition.

Amyl nitrite—Amyl nitris (U. S.)—$\left.\begin{matrix}NO\\C_5H_{11}\end{matrix}\right\}O$—117—prepared by directing the nitrous fumes, evolved by the action of HNO_3 upon starch, into amyl alcohol contained in a retort heated over a water-bath; purifying the distillate by washing with an alkaline solution and rectifying.

It is a slightly yellowish liquid; sp. gr. 0.877; boils at 95° (203° F.); its vapor explodes when heated to 260° (500° F.); insoluble in water; soluble in alcohol in all proportions; vapor orange-colored. Alcoholic solution of potash decomposes it slowly, with formation of potassium nitrite and oxids of ethyl and amyl. When dropped upon fused potash, it ignites and yields potassium valerianate.

Amyl nitrite is frequently impure; its boiling-point should not vary more than two or three degrees from that given above.

Cetyl palmitate—**Cetin**—$\left.\begin{matrix}C_{16}H_{31}O\\C_{16}H_{33}\end{matrix}\right\}O$—480—is the chief constituent of **spermaceti**=**cetaceum** (**U. S., Br.**), which, besides cetin, contains ethers of palmitic, stearic, myristic, and laurostearic acids; and of the alcohols: **lethal,** $C_{12}H_{26}O$; **methal,** $C_{14}H_{30}O$; **ethal,** $C_{16}H_{34}O$; and **stethal,** $C_{18}H_{38}O$.

Melissyl palmitate—*Melissin*—$\left.\begin{matrix}C_{16}H_{31}O\\C_{30}H_{61}\end{matrix}\right\}O$—676.—Beeswax consists mainly of two substances; **cerotic acid,** $C_{27}H_{53}O,OH$, which is soluble in boiling alcohol, and **melissyl palmitate**, insoluble in that liquid, united with minute quantities of substances which communicate to the wax its color and odor. Yellow wax melts at 62°–63° (143°.6–145°.4 F.); after bleaching, which is brought about by exposure to light, air, and moisture, it does not fuse below 66° (150°.8 F.). **China wax**, a white substance resembling spermaceti, is a vegetable product, consisting chiefly of **ceryl cerotate,** $C_{27}H_{53}O_2(C_{27}H_{55})$.

ALDEHYDES.

SERIES $C_nH_{2n}O$.

It will be remembered that the monobasic acids are obtained from the alcohols by oxidation of the radical:

$$\left.\begin{matrix}(C_2H_5)\\H\end{matrix}\right\}O \qquad\qquad \left.\begin{matrix}(C_2H_3O)'\\H\end{matrix}\right\}O$$

Ethyl alcohol. Acetic acid.

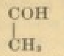
These oxidized radicals are capable of forming compounds similar in constitution to those of the non-oxidized radicals. There are chlorids, bromids, and iodids; their hydrates are the **acids,** $\left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}O$ = acetic acid; their oxids are known as **anhydrids,** $\left.\begin{matrix}(C_2H_3O)\\(C_2H_3O)\end{matrix}\right\}O$=acetic anhydrid; and their hydrids are the **aldehydes** $\left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}$= acetic aldehyde. The name aldehyde is a corruption of **alcohol dehydrogenatum,** from the method of their formation, by the removal of hydrogen from alcohol.

The aldehydes all contain the group of atoms $(COH)'$, and their constitution may be thus graphically indicated:

$$\begin{array}{c}COH\\|\\CH_3\end{array} \qquad\qquad \begin{array}{c}COH\\|\\CH_2\\|\\CH_3\end{array}$$

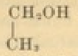
Acetic aldehyde. Propionic aldehyde.

They are capable, by fixing H_2, of regenerating the alcohol; and, by fixing O, of forming the corresponding acid:



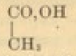
$$\begin{matrix}COH\\|\\CH_3\end{matrix}$$

Acetic aldehyde.



$$\begin{matrix}CH_2OH\\|\\CH_3\end{matrix}$$

Ethylic alcohol.



$$\begin{matrix}CO,OH\\|\\CH_3\end{matrix}$$

Acetic acid.

The aldehydes combine with the acid sulfites of the alkali metals to form crystalline compounds. They combine with ammonia to form **aldehyde-ammonias**: $CH_3CHO+NH_3 = CH_3CH\left\langle\begin{matrix}OH\\NH_2\end{matrix}\right.$. They are converted by Cl and Br into the chlorids or bromids of the acid radicals.

The aldehydes are formed:

1.) By the limited oxidation of the corresponding alcohol: $CH_3CH_2OH+O = CH_3COH+H_2O$.

2.) By the action of nascent H upon the chlorids or anhydrids of the corresponding acids: $CH_3COCl+H_2 = CH_3,COH+HCl$ or $(CH_3CO)_2O+2H_2 = 2CH_3COH+H_2O$.

3.) By the distillation of a mixture of calcium formiate and the Ca salt of the corresponding acid: $(HCOO)_2Ca+(CH_3COO)_2Ca = 2CO_3Ca+2CH_3,COH$.

Formaldehyde—*Formyl hydrid*—**H,COH**—30—is formed when air charged with vapor of methylic alcohol is passed over an incandescent platinum wire. It is also produced by the dry distillation of calcium formiate: $(HCOO)_2Ca = CaCO_3+HCOH$. It has not been obtained pure, but is known in solution in methyl alcohol.

Corresponding to this aldehyde is a product of condensation.

Paraformaldehyde, or **Trioxymethane** **(H,COH)**$_3$, which is obtained, as a crystalline substance, fusing at 152° (305°.6 F.), insoluble in H_2O, alcohol and ether, by distilling glycollic acid with H_2SO_4, or by the action of silver oxalate or oxid on methene iodid: $3CH_2I_2+3COOAg_2 = (HCOH)_3+6AgI+3CO$.

Acetaldehyde—**Acetic aldehyde**—*Acetyl hydrid*—**CH$_3$COH**—44—is formed in all reactions in which alcohol is deprived of H without introduction of O. It is prepared by distilling from a capacious retort, connected with a well-cooled condenser, a mixture of H_2SO_4, 6 pts.; H_2O, 4 pts.; alcohol, 4 pts.; and powdered manganese dioxid, 6 pts. The product is redistilled from calcium chlorid below 50° (122° F.). The second distillate is mixed with two volumes of ether, cooled by a freezing mixture, and saturated with dry NH_3; there separate crystals of **ammonium acetylid**, **C$_2$H$_3$O, NH$_4$**, which are washed with ether, dried, and decomposed in a distilling apparatus, over the water-bath, with the proper quantity of dilute H_2SO_4; the distillate is finally dried over calcium chlorid and rectified below 35° (95° F.).

Aldehyde is a colorless, mobile liquid ; has a strong, suffocating odor ; sp. gr. 0.790 at 18° (64°.4 F.) ; boils at 21° (69°.8 F.) ; soluble in all proportions in water, alcohol and ether. If perfectly pure, it may be kept unchanged ; but if an excess of acid have been used in its preparation, it gradually decomposes. When heated to 100° (212° F.), it is decomposed into water and crotonic aldehyde.

In the presence of nascent H, aldehyde takes up H_2 and regenerates alcohol. Cl converts it into acetyl chlorid, C_2H_3O, Cl, and other products. Oxidizing agents quickly convert it into acetic acid. At the ordinary temperature H_2SO_4 ; HCl ; and SO_2 convert it into a solid substance called **paraldehyde, $C_6H_{12}O_3$** (?), which fuses at 10°.5 (50°.9 F.) ; boils at 124° (255°.2 F.), and is more soluble in cold than in warm water. When heated with potassium hydroxid, aldehyde becomes brown, a brown resin separates, and the solution contains potassium formiate and acetate. If a watery solution of aldehyde be treated, first with NH_3 and then with H_2S, a solid, crystalline base, **thialdin, $C_6H_{13}NS_2$**, separates. It also forms crystalline compounds with the alkaline bisulfites. It decomposes solutions of silver nitrate, separating the silver in the metallic form, and under conditions which cause it to adhere strongly to glass.

Vapor of aldehyde, when inhaled in a concentrated form, produces asphyxia, even in comparatively small quantity ; when diluted with air it is said to act as an anæsthetic. When taken internally it causes sudden and deep intoxication, and it is to its presence that the first products of the distillation of spirits of inferior quality owe in a great measure their rapid, deleterious action.

Trichloraldehyde — *Trichloracetyl hydrid*—**Chloral**—**CCl_3COH** —147.5—is one of the final products of the action of Cl upon alcohol, and is obtained by passing dry Cl through absolute alcohol to saturation ; applying heat toward the end of the reaction, which requires several hours for its completion. The liquid separates into two layers ; the lower is removed and shaken with an equal volume of concentrated H_2SO_4 and again allowed to separate into two layers ; the upper is decanted ; again mixed with H_2SO_4, from which it is distilled ; the distillate is treated with quicklime, from which it is again distilled, that portion which passes over between 94° and 99° (201°.2–210°.2 F.) being collected. It sometimes happens that chloral in contact with H_2SO_4 is converted into a modification, insoluble in H_2O, known as **metachloral** ; when this occurs it is washed with H_2O, dried and heated to 180° (356° F.), when it is converted into the soluble variety, which distils over.

Chloral is a colorless liquid, unctuous to the touch ; has a penetrating odor and an acrid, caustic taste; sp. gr. 1.502 at 18° (64°.4 F.); boils at 94°.4 (201°.9 F.); very soluble in water, alcohol, and ether; dissolves Cl, Br, I, S and P. Its vapor is highly irritating. It distils without alteration.

Although chloral has not been obtained by the direct substitution of Cl for H in aldehyde, its reactions show it to be an aldehyde. It forms crystalline compounds with the bisulfites; it reduces solutions of silver nitrate in the presence of NH_3; NH_3 and H_2S form with it a compound similar to thialdin; with nascent H it regenerates aldehyde; oxidizing agents convert it into trichloracetic acid. Alkaline solutions decompose it with formation of chloroform and a formiate.

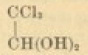
With a small quantity of H_2O chloral forms a solid, crystalline hydrate, heat being at the same time liberated. This hydrate has the composition C_2HCl_3O,H_2O, and its constitution, as well as that of chloral itself, is indicated by the formulæ:

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

Aldehyde.

$$\begin{array}{c} CCl_3 \\ | \\ CHO \end{array}$$

Trichloraldehyde (chloral).

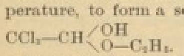


$$\begin{array}{l} CCl_3 \\ | \\ CH(OH)_2 \end{array}$$

Chloral hydrate.

Chloral hydrate—Chloral (U. S.)—is a white, crystalline solid; fuses at 57° (134°.6 F.); boils at 98° (208°.4 F.), at which temperature it suffers partial decomposition into chloral and H_2O; volatilizes slowly at ordinary temperatures; is very soluble in H_2O; neutral in reaction; has an ethereal odor, and a sharp, pungent taste. Concentrated H_2SO_4 decomposes it with formation of chloral and **chloralid**. HNO_3 converts it into trichloracetic acid. When pure it gives no precipitate with silver nitrate solution, and is not browned by contact with concentrated H_2SO_4. Under the influence of sunlight it is violently decomposed by potassium chlorate. Chlorin, phosgene gas, carbon dioxid, and chloroform are given off, and after a time, crystals of potassium trichloracetate separate from the cooled mixture.

Chloral also combines with alcohol, with elevation of temperature, to form a solid, crystalline body—**chloral alcoholate**:



$$CCl_3—CH\begin{cases} OH \\ O—C_2H_5. \end{cases}$$

Action of Chloral Hydrate upon the Economy.—Although it was the ready decomposition of chloral into a formiate and chloroform which first suggested its use as a hypnotic to Liebreich, and although this decomposition was at one time believed to occur in the body under the influence of the alkaline reaction of the blood, more recent investigations have shown that the formation of chloroform from chloral in the blood is, to say the least, highly improbable, and the chloral has, in common with many other chlorinated derivatives of this series, the property of acting directly upon the nerve-centres.

Neither the urine nor the expired air contains chloroform when chloral is taken internally; when taken in large doses, chloral appears in the urine. The fact that the action of chloral is prolonged for a longer period than that of the other chlorinated derivatives of the fatty series is probably due, in a great measure, to its less volatility and less rapid elimination.

When taken in overdose, chloral acts as a poison, and its use as such is rapidly increasing as acquaintance with its powers becomes more widely disseminated.

No chemical antidote is known. The treatment should be directed to the removal of any chloral remaining in the stomach by the stomach-pump, and to the maintenance or restoration of respiration.

In fatal cases of poisoning by chloral that substance may be detected in the blood, urine, and contents of the stomach by the following method: the liquid is rendered strongly alkaline with potassium hydroxid; placed in a flask, which is warmed to 50°–60° (122°–140° F.), and through which a slow current of air, heated to the same temperature, is made to pass; the air, after bubbling through the liquid, is tested for chloroform by the methods described on p. 234. If affirmative results are obtained in this testing, it remains to determine whether the chloroform detected existed in the fluid tested in its own form, or resulted from the decomposition of chloral; to this end a fresh portion of the suspected liquid is *rendered acid* and tested as before. A negative result is obtained in the second testing when chloral is present.

Bromal—**CBr_3,COH**—281.—A colorless, oily, pungent liquid; sp. gr. 3.34; boils at 172° (341°.6 F.); neutral; soluble in H_2O, alcohol, and ether. It combines with H_2O to form **bromal hydrate**, **$CBr_3,CH(OH)_2$**; large transparent crystals; soluble in H_2O; decomposed by alkalies into bromoform and a formiate. Produces anæsthesia without sleep; very poisonous.

Thioaldehydes.—By the action of H_2S on aldehyde in the presence of HCl two products are obtained, having the composition $(CH_3CSH)_3$, known as α and β **Trithioaldehyde**. The former is in large prismatic crystals, fusible at 101° (213°.8 F.), the latter in long needles, fusible at 125°–126° (257°–258°.8 F.).

Propaldehyde—**Propionic aldehyde**—**CH_3,CH_2,COH**—58—obtained by the general reaction from propylic alcohol, is a colorless liquid, resembling acetic aldehyde; boils at 40° (120°.2 F.).

Normal Butaldehyde—**Butyric aldehyde**—**CH_3,CH_2,CH_2,COH**—72—is an oily liquid, boiling at 73° (163°.4 F.). Its trichlorinated derivative, **Trichlorbutaldehyde**, or **Butyric chloral**, **CCl_3,CH_2,COH**—is the substance whose hydrate is used as a medicine under the name **croton chloral hydrate.** It is a colorless liquid, boiling at 160° (320° F.), obtained by the action of Cl on acetaldehyde.

ACETALS.

These substances may be considered as derived from the aldehydes by the substitution of two groups OR (R = an alcoholic radical C_nH_{2n+1}) for the O of an aldehyde.

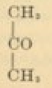
Methylal — Formal—$\mathbf{CH_2}\Big\langle\begin{matrix}\mathbf{OCH_3}\\ \mathbf{OCH_3}\end{matrix}$—76—is formed by distilling a mixture of MnO_2, methyl alcohol, H_2SO_4 and H_2O. It is a colorless liquid; sp. gr. 0.8551 at 17° (62°.6 F.), boiling at 42° (107°.6 F.); soluble in H_2O, alcohol, and oils. It has a burning, aromatic taste and an odor resembling those of chloroform and acetic acid. It has been used as a hypnotic.

Acetal—$\mathbf{CH_2}\Big\langle\begin{matrix}\mathbf{OC_2H_5}\\ \mathbf{OC_2H_5}\end{matrix}$—104—a colorless liquid, boils at 104° (219°.2 F.), sp. gr. 0.8314; sparingly soluble in H_2O, readily in alcohol; obtained by heating a mixture of aldehyde, alcohol and glacial acetic acid, or in the same manner as formal, using ethylic in place of methylic alcohol.

KETONES OR ACETONES.

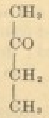
SERIES $C_nH_{2n}O$.

These substances all contain the group of atoms $(CO)''$, and their constitution may be represented graphically thus:



$$\begin{matrix}CH_3\\ |\\ CO\\ |\\ CH_3\end{matrix}$$

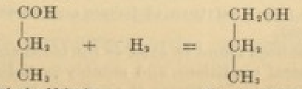
Dimethyl ketone (acetone).



$$\begin{matrix}CH_3\\ |\\ CO\\ |\\ CH_2\\ |\\ CH_3\end{matrix}$$

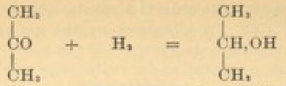
Methyl-ethyl ketone.

the first being a **symmetrical ketone** and the latter an **unsymmetrical.** The ketones are isomeric with the aldehydes, from which they are distinguished: 1st, by the action of H, which produces a primary alcohol with an aldehyde, and a secondary alcohol with a ketone:



$$\begin{matrix}COH\\ |\\ CH_2\\ |\\ CH_3\end{matrix} \quad + \quad H_2 \quad = \quad \begin{matrix}CH_2OH\\ |\\ CH_2\\ |\\ CH_3\end{matrix}$$

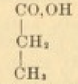
Propionic aldehyde. Propyl alcohol.



$$\begin{array}{c} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} + H_2 = \begin{array}{c} CH_3 \\ | \\ CH,OH \\ | \\ CH_3 \end{array}$$

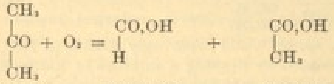
Acetone. Isopropyl alcohol.

2d, by the action of O, which unites directly with an aldehyde to produce the corresponding acid, while it causes the disruption of the molecule of the ketone, with formation of two acids:



$$\begin{array}{c} COH \\ | \\ CH_2 \\ | \\ CH_3 \end{array} + O = \begin{array}{c} CO,OH \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

Propionic aldehyde. Propionic acid.



$$\begin{array}{c} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} + O_2 = \begin{array}{c} CO,OH \\ | \\ H \end{array} + \begin{array}{c} CO,OH \\ | \\ CH_3 \end{array}$$

Acetone. Formic acid. Acetic acid.

Dimethyl ketone—**Acetone**—*Acetylmethylid*—*Pyroacetic ether* or *spirit*—$\mathbf{CO}\begin{cases}\mathbf{CH_3} \\ \mathbf{CH_3}\end{cases}$—58—is formed as one of the products of the dry distillation of the acetates; by the decomposition of the vapor of acetic acid at a red heat; by the dry distillation of sugar, tartaric acid, etc.; and in a number of other reactions. It is obtained by distilling dry calcium acetate in an earthenware retort at a dull red heat; the distillate, collected in a well-cooled receiver, is freed from H_2O by digestion with fused calcium chlorid, and rectified; those portions being collected which pass over at 60° (140° F.). It is also formed in large quantity in the preparation of anilin.

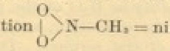
It is a limpid, colorless liquid; sp. gr. 0.7921 at 18° (64°.4 F.); boils at 56° (132°.8 F.); soluble in H_2O, alcohol, and ether; has a peculiar, ethereal odor, and a burning taste; is a good solvent of resins, fats, camphor, gun-cotton; readily inflammable. It forms crystalline compounds with the alkaline bisulfites. Cl and Br, in the presence of alkalies, convert it into chloroform or bromoform; Cl alone produces with acetone a number of chlorinated products of substitution. Certain oxidizing agents transform it into a mixture of formic and acetic acids; others into oxalic acid.

Acetone has been found to exist in the blood and urine in certain pathological conditions, and notably in diabetes; the peculiar odor exhaled by diabetics is produced by this substance, which has also been considered as being the cause of the respiratory derangements and coma which frequently occur in the last stages of the disease.

That acetone exists in the blood in such cases is certain; it is not certain, however, that its presence produces the condition designated as **acetonæmia.** It can hardly be doubted that the acetone thus existing in the blood is indirectly formed from diabetic sugar, and it is probable also that a complex acid, known as **ethyldiacetic, $C_6H_9O_3H$,** is formed as an intermediate product.

See aromatic ketones.

NITROPARAFFINS.

There exist two distinct isomeric series having the composition $C_nH_{2n+1}NO_2$. One contains the true nitrous ethers (see compound ethers), formed by the substitution of the hydrocarbon radical for the hydrogen of nitrous acid, and having the constitution $O=N-O, CH_3$ = methyl nitrite. The other contains substances in which the hydrocarbon radical is directly attached to the N atom, which may be considered as paraffins in which the group (NO_2) has taken the place of an atom of hydrogen, and have the constitution  $\left.\begin{matrix} O \\ | \\ O \end{matrix}\right\rangle N-CH_3$ = nitromethane.

These bodies are formed by the action of the monoiodic derivatives of the paraffins upon silver nitrite:

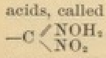
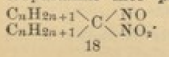
$$\underset{\text{Methyl iodid.}}{CH_3I} + AgNO_2 = AgI + \underset{\text{Nitromethane.}}{O_2NCH_3}$$

They are converted by nascent hydrogen into amidoparaffins or monamins:

$$\underset{\text{Nitromethane.}}{O_2NCH_3} + 3H_2 = \underset{\text{Methylamin.}}{H_2NCH_3} + 2H_2O$$

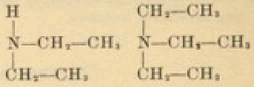
They are decomposed by H_2SO_4 or HCl into hydroxylammonium salts, and acids $C_nH_{2n}O_2$, containing all the C:

$$\underset{\text{Nitroethane.}}{O_2NC_2H_5} + H_2O = \underset{\text{Hydroxylammonium acetate.}}{CH_3,COO(NH_4O)}$$

Nitrous acid converts the primary nitroparaffins into powerful acids, called **nitrolic acids,** having the general formula:  $C_nH_{2n+1}-C\left\langle\begin{matrix} NOH_2 \\ NO_2 \end{matrix}\right.$. But the same agent converts the secondary nitroparaffins into **pseudonitrols,** having the general formula:  $\begin{matrix} C_nH_{2n+1} \\ C_nH_{2n+1} \end{matrix}\Big\rangle C\Big\langle\begin{matrix} NO \\ NO_2 \end{matrix}$.

MONAMINS—AMIDOPARAFFINS.

The **monamins** are substances which may be considered as being derived from one molecule of NH_3 by the substitution of one, two, or three alcoholic radicals for one, two, or three H atoms. They are designated as **primary, secondary,** and **tertiary,** according as they contain one, two, or three alcoholic radicals:



$$\underset{\text{Ammonia.}}{NH_3} \qquad \underset{\substack{\text{Ethylamin}\\\text{(primary).}}}{(C_2H_5)H_2N} \qquad \underset{\substack{\text{Diethylamin}\\\text{(secondary).}}}{(C_2H_5)_2HN} \qquad \underset{\substack{\text{Triethylamin}\\\text{(tertiary).}}}{(C_2H_5)_3N}$$

They are also known as **compound ammonias,** and resemble ammonia in their chemical properties; uniting with acids, without elimination of H_2O, to form salts resembling those of ammonium. They also combine with H_2O to form **quaternary ammonium hydroxids,** similar in constitution to ammonium hydroxid. The alkalinity and solubility in H_2O of the primary monamins are greater than those of the secondary, and those of the secondary greater than those of the tertiary. Their chlorids form sparingly soluble compounds with platinic chlorid.

The **primary monamins** are formed by the action of potassium hydroxid upon the corresponding cyanic ether:

$$\underset{\text{Ethyl cyanate.}}{CNOC_2H_5} + \underset{\text{Potash.}}{2KHO} = \underset{\text{Ethylamin.}}{NH_2C_2H_5} + \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{CO_3K_2}$$

or by heating together an alcoholic solution of ammonia and an ether:

$$\underset{\substack{\text{Ethyl}\\\text{iodid.}}}{C_2H_5I} + \underset{\text{Ammonia.}}{NH_3} = \underset{\substack{\text{Hydriodic}\\\text{acid.}}}{HI} + \underset{\text{Ethylamin.}}{NH_2C_2H_5}$$

or by the action of nascent H upon the cyanids of the alcoholic radicals:

$$\underset{\text{Methyl cyanid.}}{CNCH_3} + \underset{\text{Hydrogen.}}{2H_2} = \underset{\text{Ethylamin.}}{NH_2C_2H_5}$$

The **secondary monamins** are formed by the action of the iodids or bromids of the alcoholic radicals upon the primary monamins:

$$\underset{\text{Ethylamin.}}{NH_2C_2H_5} + \underset{\text{Ethyl iodid.}}{C_2H_5I} = \underset{\text{Diethylamin.}}{NH(C_2H_5)_2} + HI$$

The **tertiary monamins** are produced by the distillation of the hydroxids or iodids of the quaternary ammoniums, or by the action of the iodids of the alcoholic radicals upon the secondary monamins.

It is obvious from the above-described properties of these substances that they are true alkaloids, among which also belong the diamins and triamins.

Methylamin—*Methylia*—$\left.\begin{matrix}\mathbf{CH_3}\\ \mathbf{H_2}\end{matrix}\right\}\mathbf{N}$—31—is a colorless gas; has a fishy, ammoniacal odor; inflammable; is the most soluble gas known, one volume of H_2O dissolving 1,154 volumes of methylia at 12°.5 (54°.5 F.).

The aqueous solution possesses the odor of the gas, and is highly caustic and alkaline. It neutralizes the acids with formation of methylammonium salts (*e.g.*, $CH_3H_3NNO_3$ = methylammonium nitrate), which are for the most part crystallizable and very soluble in H_2O. Its chloraurate crystallizes in beautiful golden-yellow needles, soluble in water, alcohol, and ether. Its chloroplatinate crystallizes in golden-yellow scales, soluble in water, insoluble in alcohol.

See trimethylamin, below.

Dimethylamin—*Dimethylia*—$\left.\begin{matrix}\mathbf{(CH_3)_2}\\ \mathrm{H}\end{matrix}\right\}\mathbf{N}$—45—is a liquid below 8° (46°.4 F.); has an ammoniacal odor, and is quite soluble in H_2O. It constitutes about 50 per cent. of the commercial trimethylamin, which also contains 5 to 10 per cent. of trimethylamin, the remainder being a mixture of monomethylamin, isobutylamin, and propylamin. Its chloroplatinate forms long needles.

See trimethylamin, below.

Trimethylamin—*Trimethylia*—$\mathbf{(CH_3)_3N}$—59—is formed by the action of methyl iodid upon NH_3, and as a product of decomposition of many organic substances, it being one of the products of the action of potash on many vegetable substances, alkaloids, etc. It also occurs naturally in cod liver oil, ergot, chenopodium, yeast, guano, human urine, the blood of the calf, and many flowers.

It is an oily liquid, having a disagreeable odor of fish; boils at 8° (48°.2 F.); alkaline; soluble in H_2O, alcohol, and ether; inflammable. It combines with acids to form salts of trimethylammonium, which are crystallizable.

Trimethylamin has long been known to exist in the pickle in which herrings have been preserved. More recently it has been found to be an important product of putrefactive changes in fish, starch-paste, brain-tissue, muscular tissue, and other albuminoid substances, being accompanied by lesser quantities of monomethylamin, dimethylamin, ethylamin, and diethylamin, as well as by other peculiar alkaloidal bodies. It has also been observed accompanying more active alkaloids in blood-serum, etc., which have served for the culture of various bacilli. See cholin and neurin, below, and ptomains.

Its chloroplatinate crystallizes in octahedra, insoluble in alcohol.

The commercial trimethylamin, obtained by the dry distillation of distillery-waste, contains but $\frac{5}{10}$ per cent. of the substance whose name it bears. (See dimethylamin, above.) It has frequently been mistaken by writers upon materia medica for its isomere *propylamin*, $\left.\begin{matrix}(C_3H_7)\\H_2\end{matrix}\right\}N$, which differs from it in odor, and in boiling at 50° (122° F.). Its chlorid, under the names **chlorid of propylamia, of secalia, of secalin,** has been used in the treatment of gout and of rheumatism.

Tetramethyl Ammonium Hydroxid—$\mathbf{(CH_3)_4NOH}$—91.—This substance, whose constitution is similar to that of ammonium hydroxid, is obtained by decomposing the corresponding iodid $(CH_3)_4NI$, formed by the action of methyl iodid upon trimethylamin. It is a crystalline solid; deliquescent; very soluble in H_2O; caustic; not volatile without decomposition. It attracts carbon dioxid from the air, and combines with acids to form crystallizable salts.

The iodid is said to exert an action upon the economy similar to that of curare.

Cholin—*Trimethyloxethylammonium hydrate*—$\left.\begin{matrix}\mathbf{(CH_3)_3}\\\mathbf{(CH_2,CH_2-OH)}\end{matrix}\right\}\mathbf{N,OH}=C_5H_{15}NO_2$—121—is a quaternary monammonium hydroxid, containing three methyl groups and one ethylene hydroxid (oxethyl) group. It occurs in hops, in fungi, in certain seeds, in the human placenta, in bile and in the yolks of eggs. It is a constituent of an important class of substances, the lecithins (q. v.).

It is produced during the first twenty-four to forty-eight hours of putrefaction of animal tissues, from the decomposition of the lecithins, and diminishes from the third day, when other ptomains (neuridin, putrescin, cadaverin) increase in amount. It has been obtained synthetically by the action of trimethylamin upon ethylene oxid, or upon ethylene chlorhydrin. When heated, it splits up into glycol and trimethylamin. Nitric acid converts it into muscarin.

It appears as a thick syrup, soluble in H_2O and in alcohol, and strongly alkaline in reaction. Even in dilute aqueous solution it prevents the coagulation of albumin and redissolves coagulated albumin and fibrin. It is a strong base; attracts carbon dioxid from the air; forms with HCl a salt, soluble in alcohol, which crystallizes in plates and needles, very much resembling in appearance those of cholesterin. Its chloroplatinate is purified with difficulty; its chloraurate readily. Solutions of its chlorid differ in their behavior with alkaloidal reagents from those of neurin in forming no precipitate with tannic acid, and in forming a voluminous white precipitate with phosphomolybdic acid, which becomes crystalline on standing.

It is poisonous only in large doses, in which respect it differs from neurin (see below).

Amanitin—*Trimethyloxethylideneammonium hydroxid*—$\left.\begin{matrix}(\mathbf{CH_3})_3\\ (\mathbf{CH_3—CHOH})\end{matrix}\right\}$ **N,OH** $= C_5H_{15}NO_2$—121—is an isomere of cholin existing along with muscarin (see below) in *Agaricus muscarius*. By oxidation with HNO_3 it yields muscarin.

Muscarin—$\left.\begin{matrix}(\mathbf{CH_3})_3\\ (\mathbf{C_2H_3O_2})\end{matrix}\right\}$ **N,OH** $= C_5H_{15}NO_3$—is a substituted tetramethylammonium hydroxid related to cholin, neurin and amanitin, from which it may be obtained by oxidation.

It occurs in nature in *Agaricus muscarius*, and is produced during putrefactive decomposition of albuminoid substances.

The free alkaloid occurs in very deliquescent, irregular crystals, or, if not perfectly dry, a colorless, odorless, and tasteless, but strongly alkaline syrup; readily soluble in all proportions in water and in alcohol; very sparingly soluble in chloroform; insoluble in ether. It is a more powerful base than ammonium hydroxid, forming an alkaline carbonate and neutral salts with other acids. When decomposed it yields trimethylamin. Its chloroplatinate crystallizes in octahedra. Its chlorid forms colorless, brilliant, deliquescent needles.

When administered to animals, muscarin causes increased secretion of saliva and tears; vomiting; evacuation of fæces, at first solid, later liquid; contraction of the pupils, almost to the extent of closure; diminution of the rapidity of the pulse; interference with respiration and locomotion; gradual sinking of the heart's action and respiration; and death. Atropin prevents the action of muscarin, and diminishes its intensity when already established.

Neurin—*Trimethylvinylammonium hydroxid*—$\left.\begin{matrix}(\mathbf{CH_3})_3\\ (\mathbf{C_2H_3})\end{matrix}\right\}$ **NOH** = $\mathbf{C_5H_{13}NO}$—is a substance nearly related to cholin, and long confounded with it, supposed by Liebreich to exist in the brain. The same body is one of the alkaloids produced by the putrefaction of muscular tissues, and is endowed with poisonous qualities, resembling, but less intense than, those of muscarin.

Another cadaveric alkaloid, related to neurin and produced under similar conditions, is a diamin: **neuridin**, $\mathbf{C_5H_{14}N_2}$ (see p. 333).

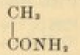
MONAMIDS.

These bodies differ from the amins in containing *oxygenated*, or *acid* radicals, in place of alcoholic radicals. Like the amins, they are divisible into **primary, secondary,** and **tertiary**. They are the nitrids of the acid radicals, as the amins are the nitrids of the alcoholic radicals.

The monamids may also be regarded as the acids in which the OH of the group COOH has been replaced by (NH_2):

$$\begin{matrix}CH_3\\|\\COOH\end{matrix}$$

Acetic acid.



$$\begin{matrix}CH_3\\|\\CONH_2\end{matrix}$$

Acetamid.

The **primary monamids**, containing radicals of the acids of the acetic series, are formed : (1.) By the action of heat upon an ammoniacal salt :

$$\underset{\text{Ammonium acetate.}}{\left.\begin{matrix}(C_2H_3O)'\\NH_4\end{matrix}\right\}O}=\underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O}+\underset{\text{Acetamid.}}{\left.\begin{matrix}(C_2H_3O)'\\H_2\end{matrix}\right\}N}$$

(2.) By the action of a compound ether upon ammonia :

$$\underset{\text{Ethyl acetate.}}{\left.\begin{matrix}(C_2H_3O)'\\(C_2H_5)'\end{matrix}\right\}O}+\underset{\text{Ammonia.}}{\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N}=\underset{\text{Acetamid.}}{\left.\begin{matrix}(C_2H_3O)'\\H_2\end{matrix}\right\}N}+\underset{\text{Alcohol.}}{\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O}$$

(3.) By the action of the chlorid of an acid radical upon dry NH_3 :

$$\underset{\text{Acetyl chlorid.}}{\left.\begin{matrix}(C_2H_3O)'\\Cl\end{matrix}\right\}}+2\underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)}=\underset{\text{Ammonium chlorid.}}{\left.\begin{matrix}NH_4\\Cl\end{matrix}\right\}}+\underset{\text{Acetamid.}}{\left.\begin{matrix}(C_2H_3O)'\\H_2\end{matrix}\right\}N}$$

The **secondary monamids** of the same class are obtained : (1.) By the action of the chlorids of acid radicals upon the primary amids :

$$\underset{\text{Acetamid.}}{\left.\begin{matrix}(C_2H_3O)'\\H_2\end{matrix}\right\}N}+\underset{\text{Acetyl chlorid.}}{\left.\begin{matrix}(C_2H_3O)'\\Cl\end{matrix}\right\}}=\underset{\text{Diacetamid.}}{\left.\begin{matrix}(C_2H_3O)_2\\H\end{matrix}\right\}N}+\underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}$$

(2.) By the action of HCl upon the primary monamids at high temperatures :

$$2\underset{\text{Acetamid.}}{\left(\left.\begin{matrix}(C_2H_3O)'\\H_2\end{matrix}\right\}N\right)}+\underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}=\underset{\text{Diacetamid.}}{\left.\begin{matrix}(C_2H_3O)_2\\H\end{matrix}\right\}N}+\underset{\text{Ammonium chlorid.}}{\left.\begin{matrix}NH_4\\Cl\end{matrix}\right\}}$$

The **tertiary monamids** of this series of radicals have been but imperfectly studied; some of them have been obtained by the action of the chlorids of acid radicals upon metallic derivatives of the secondary amids.

The **primary monamids** containing radicals of the fatty acids are solid, crystallizable, neutral in reaction, volatile without decomposition, mostly soluble in alcohol and ether, and mostly capable of uniting with acids to form compounds similar in constitution to the ammoniacal salts. They are capable of uniting with H_2O to form the ammoniacal salt of the corresponding acid, and with the alkaline hydroxids to form the metallic salt of the corresponding acid and ammonia. The **secondary monamids**, containing two radicals of the fatty series, are acid in reaction, and their remaining atom of extra-radical H may be replaced by an electro-positive atom.

Formamid—$\mathbf{CHO,H_2N}$—45—is a colorless liquid, soluble in H_2O and in alcohol, boils at 192°–195° (377°.6—383° F.), suffering partial decomposition, obtained by heating ethyl formiate with an alcoholic solution of ammonia, or by the dry distillation of ammonium formiate. It is decomposed by dehydrating agents, with formation of hydrocyanic acid. **Mercury formamid** is obtained in solution by gently heating freshly precipitated mercuric oxid with H_2O and formamid.

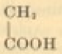
Under the name **chloralamid** a compound, formed by the union of chloral and formamid, and having the constitution, $\mathbf{CCl_3CH\left\langle\begin{matrix}OH\\NHCHO\end{matrix}\right.}$, has been recently used as a hypnotic. It forms colorless, odorless, faintly bitter crystals, fusible at 115° (239° F.), sparingly soluble in water. It is decomposed by alkalies, chloroform and ammonia being among the products of the decomposition. It is not affected by acids.

Chloralimid—$\mathbf{CCl_3,C\left\langle\begin{matrix}N—H\\H\end{matrix}\right.}$—is another related derivative, formed by the action of ammonium acetate upon chloral hydrate, or by the action of heat upon chloral ammonia. It is a crystalline solid, sparingly soluble in water, readily soluble in ether and in alcohol. When heated to 180° (356° F.) it is decomposed into chloroform and formamid.

Acetamid—$\mathbf{\left.\begin{matrix}(C_2H_3O)'\\H_2\end{matrix}\right\}N}$—59—is obtained by heating, under pressure, a mixture of ethyl acetate and aqua ammoniæ, and purifying by distillation. It is a solid, crystalline substance, very soluble in H_2O, alcohol, and ether; fuses at 78° (172°.4 F.); boils at 221° (429°.8 F.); has a sweetish, cooling taste, and an odor of mice. Boiling potassium hydroxid solution decomposes it into potassium acetate and ammonia. Phosphoric anhydrid deprives it of H_2O, and forms with it **acetonitril** or **methyl cyanid.**

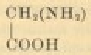
AMIDO-ACIDS OF THE FATTY SERIES.

These compounds, also known as **glycocols**, are of mixed function, acid and basic, obtained by the substitution of the univalent group $(NH_2)'$ for an atom of radical H of an acid :



$$\begin{array}{l} CH_3 \\ | \\ COOH \end{array}$$

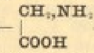
Acetic acid.



$$\begin{array}{l} CH_2(NH_2) \\ | \\ COOH \end{array}$$

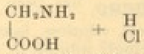
Amido-acetic acid (glycocol).

Some of them, and many of their derivatives, exist in animal bodies. Corresponding to them are many isomeres belonging to other series.



Amido-acetic acid—**Glycocol**—*Sugar of gelatin*—*Glycolamic acid*—*Glycin*—$\begin{array}{l} \mathbf{CH_2,NH_2} \\ | \\ \mathbf{COOH} \end{array}$—75—was first obtained by the action of H_2SO_4 upon gelatin. It is best prepared by acting upon glue with caustic potassa, NH_3 being liberated: H_2SO_4 is then added, and the crystals of potassium sulfate separated; the liquid is evaporated, the residue dissolved in alcohol, from which solution the glycocol is allowed to crystallize.

It may also be obtained synthetically by a method which indicates its constitution—by the action of ammonia upon chloracetic acid :



$$\begin{array}{l} CH_2Cl \\ | \\ COOH \end{array} + \begin{array}{l} H\diagdown \\ H{-}N \\ H\diagup \end{array} = \begin{array}{l} CH_2NH_2 \\ | \\ COOH \end{array} + \begin{array}{l} H \\ Cl \end{array}$$

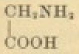
Chloracetic acid. Ammonia. Amido-acetic acid. Hydrochloric acid.

It may be obtained from ox-bile, in which it exists as the salt of a conjugate acid ; from uric acid by the action of hydriodic acid ; and by the union of formic aldehyde, hydrocyanic acid and water. It is isomeric with **glycolamid**—$\left.\begin{array}{r} CH_2OH,CO \\ H_2 \end{array}\right\} N$.

It has been found to exist free in animal nature only in the muscle of the scallop, and, when taken internally, its constituents are eliminated as urea. In combination it exists in the gelatinoids, and with cholic acid as sodium glycocholate (*q. v.*) in the bile. It is one of the products of decomposition of glycocholic acid, hyoglycocholic acid, and hippuric acid by dilute acids and by alkalies, and of the decomposition of tissues containing gelatinoids.

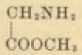
It appears as large, colorless, transparent crystals ; has a sweet taste ; melts at 170° (338° F.) ; decomposes at higher temperatures ; sparingly soluble in cold H_2O ; much more soluble in warm H_2O ; insoluble in absolute alcohol and in ether ; acid in reaction.

It combines with acids to form crystalline compounds, which are decomposed at the temperature of boiling water; hot H_2SO_4 carbonizes it; HNO_2 converts it into glycolic acid (*q. v.*); with HCl it forms a chlorid; heated under pressure with benzoic acid it forms hippuric acid. Its acid function is more marked; it expels carbonic and acetic acids from calcium carbonate and plumbic acetate. The presence of a small quantity of glycocol prevents the precipitation of cupric hydroxid from cupric sulfate solution by potassium hydroxid; the solution becomes dark blue, does not yield cuprous hydroxid on boiling, and precipitates crystalline needles of copper glycolamate on the addition of alcohol to the cold solution. With ferric chlorid it gives an intense red solution, whose color is discharged by acids, and reappears on neutralization. With phenol and sodium hypochlorite it gives a blue color, as does ammonia. By oxidation with potassium permanganate in alkaline solution it yields carbon dioxid, oxalic, carbonic, and oxamic acids, and water. It also forms crystalline compounds with many salts and ethers. Methyl amido-acetate is isomeric with sarcosin.



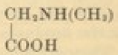
$$\begin{array}{l} CH_2NH_2 \\ | \\ COOH \end{array}$$

Glycocol (amido-acetic acid).



$$\begin{array}{l} CH_2NH_2 \\ | \\ COOCH_3 \end{array}$$

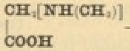
Methyl amido-acetate.



$$\begin{array}{l} CH_2NH(CH_3) \\ | \\ COOH \end{array}$$

Sarcosin (methyl-glycocol).

Methyl-glycocol—Sarcosin—



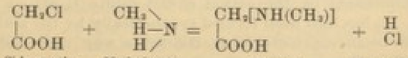
$$\begin{array}{l} CH_2[NH(CH_3)] \\ | \\ COOH \end{array}$$

—89—isomeric with alanin and with lactamid (*q. v.*), does not exist as such in animal nature, but has been obtained from creatin (*q. v.*) by the action of barium hydroxid:

$$\underset{\text{Creatin.}}{C_4H_9N_3O_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sarcosin.}}{C_3H_7NO_2} + \underset{\text{Urea.}}{CON_2H_4}$$

urea being formed at the same time, and decomposed by the further action of the barium hydroxid into NH_3 and barium carbonate.

Its constitution is indicated by its synthetic formation from chloracetic acid and methylamin:



$$\underset{\text{Chloracetic acid.}}{\begin{array}{l} CH_2Cl \\ | \\ COOH \end{array}} + \underset{\text{Methylamin.}}{\begin{array}{l} CH_3 \diagdown \\ \;\; H—N \\ H \diagup \end{array}} = \underset{\text{Sarcosin.}}{\begin{array}{l} CH_2[NH(CH_3)] \\ | \\ COOH \end{array}} + \underset{\text{Hydrochloric acid.}}{\begin{array}{l} H \\ Cl \end{array}}$$

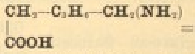
It crystallizes in colorless, transparent prisms; very soluble in water; sparingly soluble in alcohol and ether. Its aqueous solution is not acid, and has a sweetish taste; it unites with acids to form crystalline salts, but does not form metallic salts. It is capable of combining with cyanamid to form creatin.

Amido-propionic acids — Alanins — $C_3H_7NO_2$ — 89.— Two are known, isomeric with sarcosin and with lactamid. One, α **Alanin, $CH_3-CH(NH_2)-COOH$,** is formed by the reduction of α nitroso-propionic acid by Sn+HCl. The other, β **Alanin, $CH_2NH_2-CH_2-COOH$,** whose constitution is similar to that of glycocol, is formed either by the reduction of β nitrosopropionic acid, or by the action of β iodopropionic acid on ammonia. Neither exists, so far as known at present, in nature.

Both are crystalline solids, sparingly soluble in alcohol, insoluble in ether, and very soluble in water, forming neutral, sweet solutions. They differ in the solubility of their Cu compounds, and in that on treatment with CH_3I the α compound yields trimethylalanin, while the β compound forms trimethylamin.

The α compound acts as a cerebro-spinal depressant in frogs, and causes spinal paralysis, diminution of temperature, and death in pigeons in doses of one gram.

Amidobutyric acids—*Butalanins*—**$C_4H_9NO_2$**—and **Amidovalerianic acids—$C_5H_{11}NO_2$**—are only of theoretic interest at present. The latter has been found in the tissue of the pancreas and among the products of the action of pancreatic juice upon albumin. They are among the products of the decomposition of albumin by caustic baryta.

Amidocaproic Acid—Leucin— 

$$\begin{array}{l} CH_3-C_3H_6-CH_2(NH_2) \\ | \\ COOH \end{array} = C_6H_{13}NO_2$$

—131—has been obtained from the normal spleen, pancreas, salivary, lymphatic, thymus, and thyroid glands, lungs, and liver. Pathologically, its quantity in the liver is much increased in diseases of that organ, and in typhus and variola; in the bile in typhus; in the blood in leucocythæmia, and in yellow atrophy of the liver; in the urine in yellow atrophy of the liver, in typhus, and in variola; in choleraic discharges from the intestine; in pus; in the fluids of dropsy; and of atheromatous cysts. In these situations it is usually accompanied by tyrosin (*q. v.*).

It is formed along with tyrosin by the decomposition of nitrogenized animal and vegetable substances, by heating with strong alkalies or dilute acids; and is one of the products of putrefaction. It is best obtained by the action of hot dilute H_2SO_4 on bone shavings. It has also been formed synthetically by the action of NH_3 upon bromocaproic acid, in the same way that alanin is formed from iodopropionic acid (see above).

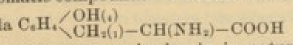
Leucin crystallines from alcohol in soft, pearly plates, lighter than H_2O, and somewhat resembling cholesterin; sometimes in round masses composed of closely grouped needles radiating from a centre. It is sparingly soluble in cold H_2O; readily in warm

H_2O ; almost insoluble in cold alcohol and ether ; soluble in boiling alcohol ; it is odorless and tasteless, and its solutions are neutral. It sublimes at 170° (338° F.) without decomposition ; if suddenly heated above 180° (356° F.), it is decomposed into amylamin and carbon dioxid.

When heated to 140° (284° F.), with hydriodic acid under pressure, it is decomposed into caproic acid and ammonia. Nitrous acid converts it into leucic acid, $\mathbf{C_6H_{12}O_3}$, H_2O and N. It unites with acids to form soluble, crystalline salts. It also dissolves readily in solutions of alkaline hydroxids, forming crystalline compounds with the metallic elements.

The formation of leucin in the body is one of the steps of the transformation of at least some part of the albuminoids into urea. When leucin and tyrosin appear in the urine, that fluid is poor in urea and usually contains biliary coloring matters ; the substitution of leucin for urea may be so extensive that the urine contains no urea, and contains leucin in such quantity that it crystallizes out spontaneously.

The presence of leucin and tyrosin in the urine may be detected as follows : the freshly collected urine is treated with basic lead acetate, filtered, the filtrate treated with H_2S, filtered from the precipitated lead sulfid, and the filtrate evaporated over the water-bath ; leucin and tyrosin crystallize ; they may be separated by extraction of the residue with hot alcohol, which dissolves the leucin and leaves the tyrosin. The leucin left by evaporation of the alcoholic solution may be recognized by its crystalline form and by the following characters : (1) a small portion is moistened on platinum foil with HNO_3, which is then cautiously evaporated ; a colorless residue remains, which, when warmed with caustic soda solution, turns yellow or brown, and by further concentration is converted into oily drops, which do not adhere to the platinum (Scherer's test) ; (2) a portion of the residue is heated in a dry test-tube ; it melts into oily drops, and the odor of amylamin (odor of ammonia combined with that of fusel oil) is observed ; (3) if a boiling mixture of leucin and solution of neutral lead acetate be carefully neutralized with ammonia, brilliant crystals of a compound of leucin and lead oxid separate ; (4) leucin carefully heated in a glass tube, open at both ends, to 170° (338° F.), sublimes without fusing, and condenses in flocculent shreds. If heated beyond 180° (356° F.), the decomposition mentioned in (2) occurs.



Tyrosin—$\mathbf{C_9H_{11}NO_3}$—145—is an amido-acid belonging among the aromatic compounds. Its constitution is represented by the formula $C_6H_4{<}\begin{matrix}OH_{(4)}\\ CH_{2(1)}-CH(NH_2)-COOH\end{matrix}$ (see pp. 397–399), but as it always accompanies leucin in nature, it is best considered here.

The methods of its formation are given under leucin. It crystallizes from its watery and ammoniacal solutions in silky needles, arranged in stellate bundles; very sparingly soluble in cold H_2O; almost insoluble in alcohol; more soluble in hot H_2O. When heated, it turns brown and yields an oily matter having the odor of phenol; when heated in small quantities to 270° (518° F.), it is decomposed into carbon dioxid and a white solid, having the composition $C_8H_{11}NO$, which sublimes. It combines with both acids and bases.

When taken into the stomach it is not altered in the economy, but is eliminated in the urine and fæces.

When moistened with HNO_3 and carefully evaporated, a deep yellow residue remains, which turns darker with NaHO. With concentrated H_2SO_4 and slightly warmed, it dissolves with a transient red color—the solution, filtered and neutralized with $CaCO_3$, gives a violet color with Fe_2Cl_6 solution.

Biliary Acids.—The bile of most animals contains the sodium salts of two amido-acids of complex constitution. These acids may be decomposed into a non-nitrogenized acid (cholic acid), and either an amido-acid (glycocol), or an amido-sulfurous acid (taurin). The following biliary acids have been described:

Glycocholic acid—$C_{26}H_{43}NO_6$—465—exists as its sodium salt in the bile of the herbivora, and in much smaller proportion in that of the carnivora; it exists in small quantity in human blood and urine in icterus.

It is best obtained from fresh ox-bile; this is mixed with ether and 5 volume per cent of the bile of concentrated HCl added. The liquid becomes turbid and soon forms a crystalline mass upon which floats colored ether. The ether, which contains coloring matters, cholesterin and fats, is decanted off. The solid mass is agitated with H_2O and washed so long as the washings remain green. The residue, dissolved in boiling water, yields pure glycocholic acid. The green-wash waters contain taurocholic acid and other biliary principles.

Glycocholic acid forms brilliant, colorless, transparent needles, which are sparingly soluble in cold H_2O, readily soluble in warm H_2O and in alcohol, almost insoluble in ether. The watery solution is acid in reaction, and tastes at first sweet, afterward intensely bitter. Its alcoholic solution exerts a right-handed polarization $[\alpha]_D = +29°$.

When heated with potash, baryta, or dilute H_2SO_4 or HCl, it is decomposed into **cholic acid** and glycocol:

$$\underset{\text{Glycocholic acid.}}{C_{26}H_{43}NO_6} + \underset{\text{Water.}}{H_2O} = \underset{\text{Cholic acid.}}{C_{24}H_{40}O_5} + \underset{\text{Glycocol.}}{C_2H_5NO_2}.$$

Glycocholic acid dissolves unchanged in cold concentrated H_2SO_4, and is precipitated on dilution of the solution with H_2O. If the mixture be warmed the bile acid is decomposed, and there separate oily drops of **cholonic acid, $C_{26}H_{41}NO_5$**, differing from glycocholic acid by $-H_2O$. When allowed to remain long in contact with concentrated H_2SO_4, glycocholic acid is converted into a colorless, resinous mass, which slowly forms a saffron-yellow solution with the mineral acid, which turns flame-red when warmed, and which, on dilution, deposits a flocculent material which is colorless, greenish, or brownish, according to the temperature at which it is formed. Glycocholic acid, altered by contact with concentrated H_2SO_4, absorbs O when exposed to the air, and turns red, then blue, and finally brown after a few days.

Sodium Glycocholate, $C_{26}H_{42}NO_6Na$, exists in the bile; it crystallizes in stellate needles, very soluble in H_2O, less so in absolute alcohol, and insoluble in ether; its alcoholic solution exerts right-handed polarization $[\alpha]_D = +25°.7$.

Lead Glycocholate, $(C_{26}H_{42}NO_6)_2$ Pb (?), is formed as a white, flocculent precipitate, when solution of lead subacetate is added to a solution of a glycocholate or of glycocholic acid; with the *neutral* acetate the precipitation does not occur in the presence of an excess of acetic acid. It is soluble in alcohol, and in an excess of lead acetate solution.

The glycocholates of the alkaline earths are soluble in H_2O. Glycocholic acid and the glycocholates react with Pettenkofer's test (see below).

Glycocholic acid forms compounds with the alkaloids, some of which are crystalline, others amorphous; they are for the most part very sparingly soluble in H_2O, but readily soluble in solutions of the biliary salts and in bile.

Taurocholic acid—$C_{26}H_{45}NO_7S$—515—exists as its sodium salt in the bile of man and of the carnivora, and in much less abundance in that of the herbivora. In the bile of the dog it seems to be unaccompanied by any other biliary acid. It may be obtained from dog's bile by evaporating with animal charcoal, extraction with absolute alcohol and precipitation with ether. The precipitated taurocholate is then dissolved in H_2O and precipitated with slightly ammoniacal $(C_2H_3O_2)_2$ Pb solution. The lead salt is dissolved in boiling absolute alcohol and decomposed by H_2S. Finally the filtered alcoholic solution of free taurocholic acid is precipitated with ether in slight excess.

It forms silky, crystalline needles, which, when exposed to the air, deliquesce rapidly, and which, even under absolute ether, are gradually converted into a transparent, amorphous, resinous mass. It is soluble in H_2O and alcohol; insoluble in ether; its aqueous solution is very bitter; in alcoholic solution it deviates the plane of polarization to the left, $[\alpha]_D = -24°.5$; its solutions are acid in reaction.

Taurocholic acid is decomposed by heating with barium hydrate, with dilute acids, and even by evaporation of its solution, into cholic acid and **taurin**:

$$\underset{\text{Taurocholic acid.}}{C_{26}H_{45}NO_7S} + \underset{\text{Water.}}{H_2O} = \underset{\text{Cholic acid.}}{C_{24}H_{40}O_5} + \underset{\text{Taurin.}}{C_2H_7NO_3S}$$

The same decomposition occurs in the presence of putrefying material, and in the intestine. Taurocholic acid has not been found to accompany glycocholic in the urine of icteric patients.

The taurocholates are neutral in reaction; those of the alkaline metals are soluble in alcohol and in water; and by long contact with ether they assume the crystalline form. They may be separated from the glycocholates in watery solution, either: (1) by dilute H_2SO_4 in the presence of a small quantity of ether, which precipitates glycocholic acid alone; or (2) by adding *neutral* lead acetate to the solution of the mixed salts (which must be neutral in reaction) lead glycocholate is precipitated and separated by filtration. To the mother liquor basic lead acetate and ammonia are added, when lead taurocholate is precipitated. The acids are obtained from the hot alcoholic solutions of the Pb salts by decomposition with H_2S, filtration, concentration, and precipitation by ether.

Solutions of the taurocholates, like those of the glycocholates, have the power of dissolving cholesterin and of emulsifying the fats. They also form with the salts of the alkaloids compounds which are insoluble in H_2O, but soluble in an excess of the biliary salt. The taurocholate of morphin is crystallizable. They react with Pettenkofer's test.

Hyoglycocholic acid, $C_{27}H_{43}NO_5$, and **Hyotaurocholic acid,** $C_{27}H_{45}NO_6S$ (?), are conjugate acids of **hyocholic acid,** $C_{25}H_{40}O_4$, and glycocol and taurin, which exist in the bile of the pig. **Chenotaurocholic acid,** a conjugate acid of taurin and **chenocholic acid,** $C_{27}H_{44}O_4$, is obtained from the bile of the goose.

Cholic acid—$C_{24}H_{40}O_5$—408—is a product of decomposition of glyco- and taurocholic acids, obtained as indicated above. It also occurs, as the result of a similar decomposition, in the intestines and fæces of both herbivora and carnivora. It forms large, clear, deliquescent crystals; sparingly soluble in H_2O, readily soluble in alcohol and ether; intensely bitter in taste, with a sweetish after-taste. In alcoholic solution it is dextrogyrous $[\alpha]_D = +35°$. The alkaline cholates are crystallizable and readily soluble in H_2O, the others difficultly soluble. Cholic acid and the cholates respond to Pettenkofer's test.

By boiling with acids or by continued heating to 200° (392° F.), cholic acid loses the elements of H_2O, and is transformed into **dyslysin,** $C_{24}H_{36}O_3$, a neutral, resinous material, insoluble in H_2O and alcohol, sparingly soluble in ether.

Dehydrocholic acid—$C_{24}H_{34}O_5$—is produced from cholic acid by careful oxidation with chromic and glacial acetic acids. It forms crystalline needles sparingly soluble in water, readily soluble in hot alcohol. It is monobasic, dextrogyrous, and bitter. It does not respond to the Pettenkofer reaction. Further oxidation converts it into

Bilianic acid—$C_{24}H_{34}O_8$(?)—which is also produced, along with **isobilianic acid,** by the action of chromic and sulfuric acids upon cholic acid. It is a crystalline solid, sparingly soluble in cold H_2O, readily soluble in hot H_2O and in alcohol. It is dextrogyrous, not bitter, and does not respond to the Pettenkofer reaction.

Deoxycholic acid—$C_{24}H_{40}O_4$—has been obtained from bile which had become putrid and from which cholic acid had completely disappeared. It is a monobasic acid, produced by the reduction of cholic acid.

Choleic acid—$C_{25}H_{42}O_4$—is formed, along with cholic acid, by the saponification of ox-bile by alkalies. On oxidation it yields **dehydrocholeic acid**—$C_{25}H_{36}O_4$—and **cholanic acid**—$C_{25}H_{36}O_7$, the former monobasic, the latter tribasic, as well as **isocholanic acid. Fellic acid**—$C_{23}H_{40}O_4$—is said to exist in and to be peculiar to human bile.

The Pettenkofer Reaction.—Glycocholic, taurocholic, cholic and choleic acids and their salts have the property of forming a yellow solution with concentrated H_2SO_4, the color of which rapidly increases in intensity, and which exhibits a green fluorescence. Their watery solutions also, when treated with a small quantity of cane-sugar and with concentrated H_2SO_4, so added that the mixture acquires a temperature of 70° (158° F.) but does not become heated much beyond that point, develop a beautiful cherry-red color, which gradually changes to dark reddish-purple. Although this reaction is observed in the presence of very small quantities of the biliary acids, it loses its value, unless applied as directed below, from the fact that many other substances give the same reaction, either with H_2SO_4 alone, or in the presence of cane-sugar. Among these substances are many which exist naturally in animal fluids, or which may be introduced with the food or as medicines; such are cholesterin, the albuminoids, lecithin, oleic acid, cerebrin, phenol, turpentine, tannic acid, salicylic acid, morphin, codein, many oils and fats, cod-liver oil, etc.

The following method of applying Pettenkofer's test to the urine and other fluids removes, we believe, every source of error. The urine, etc., is first evaporated to dryness at the temperature of the water-bath, a small quantity of coarse animal charcoal having been added; the residue is extracted with absolute alcohol, the alcoholic liquid filtered, partially evaporated, and treated with ten times its bulk of absolute ether; after standing an hour or two, any precipitate which may have formed is collected upon a small filter, washed with ether, and dissolved in a small quantity of H_2O; this aqueous solution is placed in a test-tube, a drop or two of a strong aqueous solution of cane-sugar (sugar, 1; water, 4), and then pure concentrated H_2SO_4 are added; the addition of the acid being so regulated, and the test-tube dipped from time to time in cold water, that the temperature shall be from 60°–75° (140°–167° F.). In the presence of biliary acids the mixture usually becomes turbid at first, and then turns cherry-red and finally purple, the intensity of the color varying with the amount of biliary acid present.

Physiological Chemistry of the Biliary Acids.—These substances are formed in the liver, and they are not reabsorbed from the intestine unchanged. Solutions of the biliary salts, injected into the circulation in small quantity, cause a diminution in the frequency of the pulse and of the respiratory movements, a lowering of the temperature and arterial tension, and disintegration of the blood-corpuscles. In large doses (2–4 grams [30–60 grains] for a dog) they produce the same effects to a more marked degree; epileptiform convulsions, black and bloody urine, and death more or less rapidly. These effects do not follow the injection of the products of decomposition of the biliary acids, except cholic acid, and in that case the symptoms are much less marked. Nor are the biliary acids discharged unaltered with the fæces; they are decomposed in the intestine. The extract, suitably purified, of the contents of the upper part of the small intestine, gives a well-marked reaction with Pettenkofer's test; while similar extracts of the contents of the lower part of the large intestine, or of the fæces, fail to give the reaction, and consequently are free from glyco- or taurocholic, cholic acid, or dyslysin; the fæces, moreover, do not contain either taurin or glycocol. During the processes which take place in the intestine, the bile-acids are decomposed into cholic acid and taurin or glycocol, which are subsequently reabsorbed, either as such, or after having been subjected to further decomposition; and as a consequence of their decomposition they probably have some influence upon intestinal digestion.

Taurocholic acid added to a solution of peptone causes a slight precipitate which has been shown to consist entirely of the acid itself; but albumen and syntonin are precipitated in coarse flocks from their solutions by and along with taurocholic acid, and that so completely that the filtered liquid fails to react with the most delicate tests for albumen. This acid is therefore an excellent reagent for the quantitative separation of the albuminoids from the peptones.

A saturated aqueous solution of glycocholic acid is not precipitated either by peptone or propeptone; but if a peptone followed by an acid is added to a concentrated solution of sodium glycocholate, a precipitate of glycocholic acid, without peptone, is formed. A mixture of the human biliary acids acts in the same manner as taurocholic acid.

Taurocholic acid when present in the proportion of 0.2 to 0.5 per cent prevents the putrefaction of a mixture of muscular tissue and pancreas, as well as lactic and alcoholic fermentations. Glycocholic acid is much less active. This antiseptic power is possessed only by the free acids, not by their salts, hence bile putrefies readily, if neutral or alkaline. But the acidity of the chyme in the intestine, which persists for quite a distance from the pylorus, by liberating the acids, permits of their exerting their antiseptic action and thus retarding pancreatic putrefaction.

The proportion of biliary salts in human bile varies considerably, as shown by the following analyses:

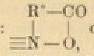
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Mucin.	2.66	2.98	2.91	1.45	....	2.48	1.29	.....	1.29
Cholesterin ...	0.16	0.26	4.73	3.09	0.25	0.25	0.34	.....	0.35
Fats	0.32	0.92			0.04	0.05	0.36	.....	0.73
Biliary salts...	7.22	9.14	10.79	5.65	.... 4.48	0.75 2.09	1.93 0.44	1.57 4.90	0.87 3.03
Soaps.	.....	...	....	.....	0.64	0.82	1.63	1.46	1.39
Mineral salts..	0.65	0.77	1.08	0.63	3.86	0.46?	1.46?	.....	....
Water.........	86.00	85.92	82.27	89.81	....	90.88	91.08	.....	....
Total solids ...	14.00	14.08	17.73	10.19	....	9.12	8.92	.....	....

I. Frerichs: Bile from man, æt. 18, killed by a fall. II. Frerichs: Male, æt. 22, died of a wound. III. Gorup-Besanez: Male, æt. 49, decapitated. IV. Gorup-Besanez: Female, æt. 29, decapitated. V. Jacobsen: Male, biliary fistula. VI., VII. Trifanowski: Males. VIII. Socolof: Mean of six analyses of human bile. IX. Hoppe-Seyler: Mean of five analyses of bile from subjects with healthy livers.

Pathologically, the biliary acids may be detected in the blood and urine in icterus and acute atrophy of the liver; although by no means as frequently as the biliary coloring matters.

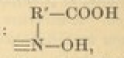
BETAÏNS.

The **Betaïns** are the anhydrids:



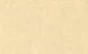
$$\begin{array}{ll} R''{-}CO & \\ \vert & \vert \\ \equiv N - & O, \end{array}$$

corresponding to substances of mixed function, partly acid and derived from the amido-acids, and partly quaternary ammonium:



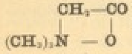
$$\begin{array}{l} R''{-}COOH \\ \vert \\ \equiv N{-}OH, \end{array}$$

in which R″ may be either methylene, ethylene, etc., or a bivalent, closed chain residue such as C_6H_4; and the remaining ≡N valences satisfied either by three univalent radicals, such as CH_3, or by a single trivalent radical, such as $(C_5H_5)'''$, as in pyridin-betaïn; or the trivalent radical may take the place of R as in nicotic-methyl betaïn:



$$\begin{array}{lcl} & C_5H_4{-} & CO \\ & \vert\vert\vert & \vert \\ CH_3{-} & N\ - & O. \end{array}$$

Betaïn—*Trimethyl-acetic betaïn—Oxyneurin—Oxycholin*—



$$\begin{array}{lcl} & CH_2{-} & CO \\ & \vert & \vert \\ (CH_3)_3 & N\ - & O \end{array}$$

$= \mathbf{C_5H_{11}NO_2}$—117—was first obtained from the juice of the sugar-beet; afterward it was obtained by oxidation of neurin; and is also produced synthetically, either by acting upon trimethylamin with monochloracetic acid, as gycocol is obtained by the action of the same acid upon ordinary ammonia; or by acting upon glycocol itself with methyl iodid.

Betaïn crystallizes in large, brilliant crystals, containing one molecule of water of crystallization. At the ordinary temperature they are deliquescent, but effloresce at 100° (212° F.). It is very soluble in water and in alcohol. It is decomposed by heat, with evolution of trimethylamin. It forms crystalline salts. Its chloraurate is crystalline, and very sparingly soluble in cold water.

AMIDINS—ACETONAMINS—ALDEHYDINS—HYDRAZINS.

The **amidins** are basic substances formed by the substitution of $(NH)''$ for the oxygen of the amids. They therefore have the general formula $R{-}C\begin{smallmatrix}\diagup NH \\ \diagdown NH_2\end{smallmatrix}$, derived from that of the monamids: $R{-}C\begin{smallmatrix}\diagup O \\ \diagdown NH_2\end{smallmatrix}$ in which R represents a hydrocarbon radical. They form mono-, di- and trisubstituted derivatives by the replacement of the H in the groups NH and NH_2 by atoms or radicals.

The **acetonamins** are basic substances formed by the action of ammonia or of the monamins upon acetone.

The **aldehydins** are substances produced by the action of ammonia or of the monamins upon aldehyde. The most important of the class belong to the aromatic series. By the action of alcohol on butyric aldehyde, **dibutyraldin**, $C_8H_{17}NO$ is produced;

which, by dehydration, is converted into **paraconiin, $C_8H_{15}N$,** a base which is isomeric with **conicein**, a derivative of coniin, but not with the latter alkaloid, which is a pyridin base (see p. 425).

The **hydrazins** are derivable from the group H_2N-NH_2 (see p. 105) by the substitution of radicals for one or more of the hydrogen atoms. Although the most important of the class, belonging among the aromatic compounds (see p. 421), some are derivatives of the fatty series, such as ethylhydrazin: C_2H_5, $HN-NH_2$.

AZOPARAFFINS—NITRILS—CYANOGEN COMPOUNDS.

These substances may be considered either as compounds of the univalent radical **cyanogen**, $(\mathbf{C}^{iv}\,\mathbf{N}''')'$; or as paraffins, C_nH_{2n+2}, in which three atoms of hydrogen have been replaced by a trivalent N''' atom, hence **azoparaffins**; or as **nitrils**, compounds of N with the trivalent radicals C_nH_{2n-1}.

Dicyanogen—$(\mathbf{CN})_2$—52—is prepared by heating mercuric cyanid. It is a colorless gas; has a pronounced odor of bitter almonds; sp. gr. 1.8064 A.; burns in air with a purple flame, giving off N and CO_2. It is quite soluble in H_2O, the solution turning brown in air.

It has a very deleterious action upon both animal and vegetable life, even when largely diluted with air.

Hydrogen cyanid—*Cyanogen hydrid*—**Hydrocyanic acid—Prussic acid**—$\left.\begin{matrix}\mathbf{CN}\\ \mathbf{H}\end{matrix}\right\}$—27—exists ready formed in the juice of *cassava*, and is formed by the action of H_2O upon bitter almonds, cherry-laurel leaves, etc. It is also formed in a great number of reactions: by the passage of the electric discharge through a mixture of acetylene and N; by the action of chloroform on NH_3; by the distillation of, or the action of HNO_3 upon many organic substances; by the decomposition of cyanids.

It is always prepared by the decomposition of a cyanid or a ferrocyanid. Usually by acting upon potassium ferrocyanid with dilute sulfuric acid, and distilling. Its preparation in the pure form is an operation attended with the most serious danger, and should only be attempted by those well trained in chemical manipulation. For medical uses a very dilute acid is required; the **acid hydrocyanicum dil.** (**U. S., Br.**) contains, if freshly and properly prepared, two per cent. of anhydrous acid. That of the French Codex is much stronger—ten per cent.

The pure acid is a colorless, mobile liquid, has a penetrating and characteristic odor; sp. gr. 9.7058 at 7° (44°.6 F.); crystallizes at −15° (5° F.); boils at 26°.5 (79°.7 F.); is rapidly decomposed by exposure to light. The dilute acid of the U. S. P. is a colorless liquid, having the odor of the acid; faintly acid, the reddened litmus returning to blue on exposure to air; sp. gr. 0.997; 10 grams of the acid should be accurately neutralized by 1.27 gram of silver nitrate. The dilute acid deteriorates on exposure to light, although more slowly than the concentrated; a trace of phosphoric acid added to the solution retards the decomposition.

Most strong acids decompose HCN. The alkalies enter into double decomposition with it to form **cyanids.** It is decomposed by Cl and Br, with formation of cyanogen chlorid or bromid. Nascent H converts it into methylamin.

Analytical Characters.—(1.) With silver nitrate a dense, white ppt.; which is not dissolved on addition of HNO_3 to the liquid, but dissolves when separated and heated with concentrated HNO_3; soluble in solutions of alkaline cyanids or hyposulfites. (2.) Treated with NH_4HS, evaporated to dryness, and ferric chlorid added to the residue; a blood-red color. (3.) With potash and then a mixture of ferrous and ferric sulfates; a greenish ppt., which is partly dissolved with a deep blue color by HCl. (4.) Heated with a dilute solution of picric acid and then cooled; a deep red color. (5.) Moisten a piece of filter paper with a freshly prepared alcoholic solution of guaiac; dip the paper into a very dilute solution of $CuSO_4$, and, after drying, into the liquid to be tested. In the presence of HCN it assumes a deep blue color.

Toxicology.—Hydrocyanic acid is a violent poison, whether it be inhaled as vapor, or swallowed, either in the form of dilute acid, of soluble cyanid, or of the pharmaceutical preparations containing it, such as oil of bitter almonds and cherry-laurel water; its action being more rapid when taken by inhalation or in aqueous solution than in other forms. When the medicinal acid is taken in poisonous dose, its lethal effect may seem to be produced instantaneously; nevertheless, several respiratory efforts usually are made after the victim seems to be dead, and instances are not wanting in which there was time for considerable voluntary motion between the time of the ingestion of the poison and unconsciousness. In the great majority of cases the patient is either dead or fully under the influence of the poison on the arrival of the physician, who should, however, not neglect to apply the proper remedies if the faintest spark of life remain. Chemical antidotes are, owing to the rapidity of action of the poison, of no avail, although possibly chlorin, recommended as an antidote by many, may have a chemical action on that portion of the acid already absorbed. The treatment indicated is directed to the maintenance of respiration; cold douche, galvanism, artificial respiration, until elimination has removed the poison. If the patient survive an hour after taking the poison, the prognosis becomes very favorable; in the first stages it is exceedingly unfavorable, unless the quantity taken has been very small.

In cases of death from hydrocyanic acid a marked odor of the poison is almost always observed in the apartment and upon opening the body, even several days after death. In cases of suicide or accident, the vessel from which the poison has been taken will usually be found in close proximity to the body, although the absence of such vessel is not proof that the case is necessarily one of homicide.

Notwithstanding the volatility and instability of the poison, its presence has been detected two months after death, although the chances of separating it are certainly the better the sooner after death the analysis is made. The search for hydrocyanic acid is combined with that for phosphorus; the part of the distillate containing the more volatile products is examined by the tests given above. It is best, when the presence of free hydrocyanic acid is suspected, to distil at first without acidulating. In cases of suspected homicide by hydrocyanic acid the stomach should never be opened until immediately before the analysis.

Cyanids.—The most important of the metallic cyanids are those of K and Ag (see pp. 190, 193).

The **hydrocyanic ethers** of the univalent alcoholic radicals are called **nitrils**, and are frequently the starting-points from which other organic products are obtained.

They are produced:

1.) By distilling a mixture of potassium cyanid and the potassium salt of the corresponding monosulfate of the alcoholic radical:

$$\underset{\text{Potassium cyanid.}}{KCN} + \underset{\text{Potassium ethylsulfate.}}{\left.\begin{matrix}C_2H_5\\SO_2K\end{matrix}\right\}O_2} = \underset{\text{Ethyl cyanid.}}{C_2H_5,CN} + \underset{\text{Dipotassic sulfate.}}{K_2SO_4}$$

2.) By complete dehydration, by the action of P_2O_5, of the ammoniacal salt of the corresponding acid, or of its amid:

$$\underset{\text{Ammonium acetate.}}{CH_3,COO(NH_4)} = \underset{\text{Methyl cyanid.}}{CH_3,CN} + 2H_2O$$

$$\underset{\text{Acetamid.}}{CH_3,CO,NH_2} = \underset{\text{Acetonitril.}}{CH_3,CN} + H_2O$$

3.) By the action of the chlorids of the acid radicals upon silver cyanate:

$$\underset{\text{Silver cyanate.}}{CNOAg} + \underset{\text{Acetyl chlorid.}}{CH_3COCl} = AgCl + \underset{\text{Methyl cyanid.}}{CH_3CN} + CO_2$$

The nitrils combine with nascent hydrogen to form the corresponding amins:

$$\underset{\text{Acetonitril.}}{CH_3,CN} + 2H_2 = \underset{\text{Ethylamin.}}{C_2H_5,H_2N}$$

Hydrating agents convert the nitrils into ammonia and the corresponding acid:

$$\underset{\text{Propionitril.}}{C_2H_5,CN} + 2H_2O = NH_3 + \underset{\text{Propionic acid.}}{C_2H_5,COOH}$$

Sulfuric acid, or sulfur trioxid, converts the nitrils into sulfo-acids and monoammonic sulfate:

$$\underset{\text{Ethylcyanid.}}{C_2H_5,CN} + H_2O + 2H_2SO_4 = NH_4H(SO_4) + \underset{\text{Sulfopropionic acid.}}{SO_3,C_2H_4,COOH}$$

Isomeric with the nitrils are substances known as **isocyanids, carbylamins** or **carbamins**, which are formed:

1.) By the action of a primary monamin on chloroform in the presence of caustic potash:

$$\underset{\text{Methylamin.}}{CH_3,H_2N} + CHCl_3 = 3HCl + \underset{\text{Methyl isocyanid.}}{CN,CH_3}$$

2.) By the action of the iodoparaffins on silver cyanid:

$$\underset{\text{Methyl iodid.}}{CH_3I} + AgCN = AgI + \underset{\text{Methyl carbylamin.}}{CN,CH_3}$$

The difference in the constitution of the two classes of bodies is due to the N being trivalent in the nitril, and quinquivalent in the carbylamin:

$$\underset{\text{Methyl cyanid.}}{N\equiv C-CH_3} \qquad \underset{\text{Methyl isocyanid.}}{C\equiv N-CH_3}$$

The isocyanids do not yield ammonia and an acid by the action of hydrating agents, but are converted into formic acid and a primary amin:

$$\underset{\text{Ethyl isocyanid.}}{NC,C_2H_5} + 2H_2O = \underset{\text{Ethylamin.}}{NH_2,C_2H_5} + \underset{\text{Formic acid.}}{H,COOH}$$

The nitrils and carbamins combine with the hydracids to form crystalline salts, decomposable by water. The latter much more energetically than the former. They are all volatile liquids; the nitrils having ethereal odors when pure, the isocyanids odors which are very powerful and disagreeable.

Cyanogen chlorids. — Two polymeric chlorids are known. **Gaseous cyanogen chlorid**—**$CNCl$**—is formed by the action of Cl upon anhydrous hydrocyanic acid or upon mercuric cyanid in the dark. It is a colorless gas, intensely irritating and poisonous. **Solid cyanogen chlorid**—**$C_3N_3Cl_3$**—is formed, as a crystalline solid, when anhydrous hydrocyanic acid is acted upon by Cl in sunlight. It fuses at 140° C. (284° F.).

Cyanic acid—*Cyanogen hydrate*—$\left.\begin{matrix}\mathbf{CN}\\ \mathbf{H}\end{matrix}\right\rangle\mathbf{O}$—43—does not exist in nature. It is obtained by calcining the cyanids in presence of an oxidizing agent; or by the action of dicyanogen upon solutions of the alkalies or alkaline carbonates; or by the distillation of cyanuric acid.

It is a colorless liquid; has a strong odor, resembling that of formic acid; its vapor is irritating to the eyes, and it produces vesication when applied to the skin. It is soluble in water. When free it is readily changed by exposure to air into an isomere, **cyamelid.**

The acid forms salts and ethers which constitute two isomeric series, indicating the existence of two acids, the **normal,** having the constitution $N{\equiv}C{-}OH$, and the **iso**, having the constitution $O = C = N{-}H$.

Ammonium isocyanate $O = C = N{-}NH_4$ is converted into urea by heat.

Cyanuric acid—$\mathbf{C_3N_3H_3O_3}$—is a polymere of cyanic acid, formed by the action of heat or of Cl upon urea. It forms colorless crystals, sparingly soluble in H_2O, the solutions odorless, almost tasteless, and feebly acid. It is a tribasic acid. It is very stable and may be dissolved in strong H_2SO_4 or HNO_3 without suffering decomposition.

Fulminic acid—$\mathbf{C_2N_2H_2O_2}$—is a bibasic acid whose Ag and Hg salts are formed by the action of nitrous acid upon alcohol in the presence of the salts of Ag and Hg. These are the **fulminating powders** used in the manufacture of percussion caps.

Fulminuric acid—$\mathbf{C_3N_3H_3O_3}$—metameric with cyanuric acid, is a bibasic acid, formed by the action of a metallic chlorid upon a solution of mercuric fulminate.

Thiocyanic acid—**Sulfocyanic acid**—*Cyanogen sulfhydrate*—$\left.\begin{matrix}\mathbf{CN}\\ \mathbf{H}\end{matrix}\right\rangle\mathbf{S}$—59—bears the same relation to cyanic acid that CS_2 does to CO_2. It is obtained by the decomposition of its salts, which are obtained by boiling a solution of the cyanid with S; by the action of dicyanogen upon the metallic sulfid; and in several other ways.

The free acid is a colorless liquid; crystallizes at −12°.5 (9°.5 F.); boils at 102°.5 (216°.5 F.); acid in reaction. The prominent reaction of the acid and of its salts is the production of a deep red color with the ferric salts; the color being discharged by solution of mercuric chlorid, but not by HCl.

Sulfocyanic acid exists in human saliva in combination, probably with sodium. The free acid is actively poisonous and its salts were formerly supposed to be so also. It is probable, however, that much of the deleterious action of the potassium salt—that usually experimented with—is due as much to the metal as to the acid.

Cyanamid—**CN,NH_2**—is produced by the action of gaseous cyanogen chlorid upon ammonia: $CNCl+2NH_3=NH_4Cl+CN,NH_2$. It forms colorless crystals, soluble in water, alcohol or ether. Corresponding to it are substituted cyanamids, which may be formed by substituting a primary amin for ammonia in the above-mentioned method of preparation: $CNCl+2NH_2CH_3=NH_2,CH_3,Cl+CN,NHCH_3$.

Metallocyanids.—The radical cyanogen, besides combining with metallic elements to form true cyanids, in which the radical (CN) enters as a univalent atom, is capable of combining with certain metals (notably those of the iron and platinum groups) to form complex radicals. These combining with H, form acids, and with basic elements form salts in which the analytical reactions of the metallic element entering into the radical are completely masked. Of these **metallocyanids** the best known are those in which iron enters into the radical. As iron is capable of forming two series of compounds, in one of which the single atom Fe'' enters in its bivalent capacity, and in the other of which the hexavalent double atom $(Fe_2)^{vi}$ is contained; so uniting with cyanogen, iron forms two ferrocyanogen radicals: $[(CN)'_6Fe'']^{iv}$, **ferrocyanogen,** and $[(CN)'_{12}(Fe_2)^{vi}]^{vi}$ **ferricyanogen**; each of which unites with hydrogen to form an acid, corresponding to which are numerous salts: $(C_6N_6Fe)H_4$, **hydroferrocyanic acid,** tetrabasic; and $(C_{12}N_{12}Fe_2)H_6$, **hydroferricyanic acid,** hexabasic (see potassium and iron salts).

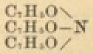
HYDROXYLAMIN DERIVATIVES.

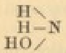
Hydroxylamin, itself an amin (see p. 105), still contains three atoms of hydrogen which may be replaced by radicals to form primary, secondary, and tertiary derivatives (see p. 274) whose relations to the corresponding ammonia derivatives are indicated by the following formulæ:

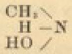

Ammonia.

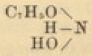

Methylamin.

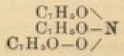

Benzamid.


Tribenzamid.


Hydroxylamin.


Methyl-hydroxylamin.


Benzhydroxamic acid.


Tribenzhydroxylamin.

Hydroxylamin also enters into reaction directly with aldehydes, acetones and nitrils to form compounds called **oxims**.

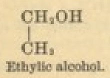
The derivatives of the aldehydes are called **aldoxims,** whose general formula is $R—C\Big\langle{H \atop NOH}$, and those of the acetones are known as **acetoxims,** whose general formula is $R—C\Big\langle{R \atop NOH}$, in which R is a hydrocarbon radical. They are both formed by the action of the hydroxylamin chlorid upon the corresponding aldehyde or acetone.

The **amidoxims** are formed by direct union of the nitrils with hydroxylamin, and have the general formula $R—C\Big\langle{NH_2 \atop N,OH}$. The first of the series, **Isuretin,** or **Carbamidoxim,** $H—C\Big\langle{NH_2 \atop N,OH}$, is isomeric with urea, and is produced by direct union of hydroxylamin and hydrocyanic acid.

SULFUR DERIVATIVES OF THE PARAFFINS.

Sulfur and oxygen, being equal in valence, may replace each other in organic compounds as, for instance, in sulfocyanic acid **CNSH,** corresponding to cyanic **CNOH.**

There exist many derivatives of the paraffins in which S thus takes the place of O. Thus:



$$\begin{array}{c} CH_2OH \\ | \\ CH_3 \end{array}$$

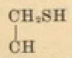
Ethylic alcohol.

$$\begin{array}{l} C_2H_5 \\ C_2H_5 \end{array}\Big\rangle O$$

Ethylic ether, or ethyl oxid.

$$CH_3—CH\Big\langle\begin{array}{l} OC_2H_5 \\ OC_2H_5 \end{array}$$

Acetal.



$$\begin{array}{c} CH_2SH \\ | \\ CH \end{array}$$

Thioalcohol or mercaptan.

$$\begin{array}{l} C_2H_5 \\ C_2H_5 \end{array}\Big\rangle S$$

Ethyl sulfid.

$$CH_3—CH\Big\langle\begin{array}{l} SC_2H_5 \\ SC_2H_5 \end{array}$$

Mercaptal.

Methyl Sulfids.—Three are known. The **monosulfid,** **$(CH_3)_2S$,** is a colorless liquid, boils at 41° (105°.8 F.), has a very disagreeable odor, as have all the alcoholic sulfids and sulfhydrates. It is formed by the action of gaseous methyl chlorid on potassium monosulfid. The **bisulfid,** **$(CH_3)_2S_2$,** is similarly formed from potassium bisulfid, and is a colorless liquid, boiling at 116°–118° (240°.8–244°.4 F.). The **trisulfid,** **$(CH_3)_2S_3$,** is formed in the same way from potassium pentasulfid, and boils at 200° (392° F.).

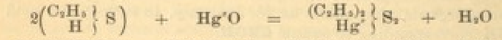
Ethyl sulfids are formed in the same manner as the methyl compounds, and have the same constitution.

Methyl hydrosulfid—Methyl mercaptan—H,CH_2SH—is a very offensive liquid formed by distilling together calcium methylsulfate and potassium hydrosulfid.

Ethyl sulfhydrate—Thioalcohol—Mercaptan—CH_3,CH_2SH—is best prepared by treating alcohol with H_2SO_4, as in the preparation of sulfovinic acid (q.v.); mixing the crude product with excess of potash; separating from the crystals of potassium sulfate; saturating with H_2S; and distilling.

It is a mobile, colorless liquid; sp. gr. 0.8325; has an intensely disagreeable odor, combined of those of garlic and H_2S; boils at 36°.2 (97°.2 F.); ignites readily and burns with a blue flame; may be readily frozen by the cold produced by its own evaporation; neutral in reaction; sparingly soluble in H_2O, soluble in all proportions in alcohol and ether; dissolves I, S and P.

Potassium and sodium act with mercaptan as with alcohol, replacing the extra-radical hydrogen. In its behavior toward the oxids it more closely resembles the acids than the alcohols, being capable even of entering into double decomposition to form salts, called **sulfethylates** or **mercaptids**. Its action with mercuric oxid is characteristic, forming a white, crystalline sulfid of ethyl and mercury:



$$2\left(\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S\right) + Hg''O = \left.\begin{matrix}(C_2H_5)_2\\Hg''\end{matrix}\right\}S_2 + H_2O$$

Ethyl sulfhydrate. Mercuric oxid. Ethyl-mercuric sulfid. Water.

When a mixture of one molecule of a mercaptan with two molecules of an aldehyde is treated with dry HCl, a stable compound is produced which is called a **mercaptal**, being an acetal whose O is replaced by S.

If the reaction take place with an acetone, in place of with an aldehyde, a **mercaptol** is produced, which differs from the mercaptal in that an alcoholic radical is substituted for the remaining H atom of the methane:

$$\begin{matrix}H\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$$

Acetal.

$$\begin{matrix}H\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}$$

Mercaptal.

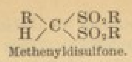
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}$$

Mercaptol.

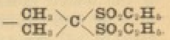
Ethyl mercaptol—$(CH_3)_2 = C = (SC_2H_5)_2$—is formed as one of the steps in the manufacture of sulfonal. It is produced by the action of dry HCl upon a mixture of acetone and ethylmercaptan, or upon a mixture of sodium ethylthiosulfate, C_2H_5,SO_2ONa, and acetone. It is a mobile liquid, whose odor is not disagreeable. When heated it begins to boil at about 80° (176° F.) and the temperature rises rather regularly to 192° (377°.6 F.).

Oxidizing agents act readily upon the mercaptals and mercaptols to produce compounds called **sulfones**, whose constitution is represented by one of the three following formulæ, in which **R** is a univalent alcoholic radical:


$$\begin{matrix}H \\ H\end{matrix}\!>\!C\!<\!\begin{matrix}SO_2R \\ SO_2R\end{matrix}$$
Methylendisulfone.


$$\begin{matrix}R \\ H\end{matrix}\!>\!C\!<\!\begin{matrix}SO_2R \\ SO_2R\end{matrix}$$
Methenyldisulfone.


$$\begin{matrix}R \\ R\end{matrix}\!>\!C\!<\!\begin{matrix}SO_2R \\ SO_2R\end{matrix}$$
Ketondisulfone.

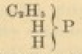

Sulfonal — Diethylsulfondimethylmethane — $\begin{matrix}CH_3 \\ CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}SO_2C_2H_5 \\ SO_2C_2H_5\end{matrix}$ --is obtained by the oxidation of ethyl-mercaptol, prepared as above described, by potassium permanganate. It crystallizes in thick, colorless prisms, difficultly soluble in cold water or alcohol, readily soluble in hot water or alcohol, and in ether, benzene and chloroform. It fuses at 130°–131° (266°–267°.8 F.), and boils at 300° (572° F.), suffering partial decomposition. It dissolves in concentrated H_2SO_4, and is decomposed by the acid when heated, but may be precipitated from the cold solution unchanged by dilution with H_2O. Nitric acid does not affect it, even when heated. It is not attacked by Br, by caustic alkalies or by nascent H.

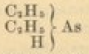
Ichthyol—is the Na salt of a complex sulfonic acid, having the empirical formula $C_{28}H_{36}S_3Na_2O_6$, obtained by the distillation and purification of an ozocerite-like mineral deposit. It is a dark brown, pitch-like mass having a disagreeable odor.

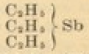
COMPOUNDS OF THE ALCOHOLIC RADICALS WITH OTHER ELEMENTS.

Phosphins, arsins, and **stibins,** are compounds resembling the amins in constitution, in which the N is replaced by P, As, or Sb. Like the amins, they may be primary, secondary, or tertiary :


$$\left.\begin{matrix}C_2H_5 \\ H \\ H\end{matrix}\right\}N$$
Ethylamin (primary).


$$\left.\begin{matrix}C_2H_5 \\ H \\ H\end{matrix}\right\}P$$
Ethylphospin (primary).

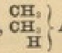

$$\left.\begin{matrix}C_2H_5 \\ C_2H_5 \\ H\end{matrix}\right\}As$$
Diethyl-arsin (secondary).


$$\left.\begin{matrix}C_2H_5 \\ C_2H_5 \\ C_2H_5\end{matrix}\right\}Sb$$
Triethyl-stibin (tertiary).

There also exist compounds containing P, As, or Sb, which are similar in constitution to the hydroxids and salts of ammonium, and of the compound ammoniums :

NH_4I	$N(CH_3)_4I$	$As(CH_3)_4I$
Ammonium iodid.	Tetramethyl ammonium iodid.	Tetramethyl arsenium iodid.

Most of these compounds, which are very numerous, are as yet only of theoretic interest. One of them, however, is deserving of notice here :


Dimethyl Arsin, $\left.\begin{matrix}\mathbf{CH_3} \\ \mathbf{CH_3} \\ \mathbf{H}\end{matrix}\right\}$ **As**—106—which may be considered as being the hydrid of the radical $[As(CH_3)_2]$, does not exist as such. There is, however, a liquid known as the **fuming liquor of Cadet,**

or **alkarsin**, which is obtained by distilling a mixture of potassium acetate and arsenic trioxid. This liquid contains the oxid of the above radical, and a substance which ignites on contact with air, and which consists of the same radical united to itself, $2[As(CH_3)_2]$. This radical, called **cacodyle** (κακός = evil), is capable of entering into a great number of other combinations. Cacodyle and its compounds are all exceedingly poisonous, especially the cyanid, an ethereal liquid, very volatile, the presence of whose vapor in inspired air, even in minute traces, produces symptoms referable both to arsenic and to hydrocyanic acid.

It is probable that during the putrefaction of cadavers injected with arsenical embalming liquids one or more arsins may be formed.

Organo-metallic substances are compounds of the alcoholic radicals with metals. They are very numerous, usually obtained by the action of the iodid of the alcoholic radical upon the metallic element, in an atmosphere of H. They are substances which, although they have been put to no uses in the arts or in medicine, have been of great service in chemical research. As typical of this class of substances we may mention :

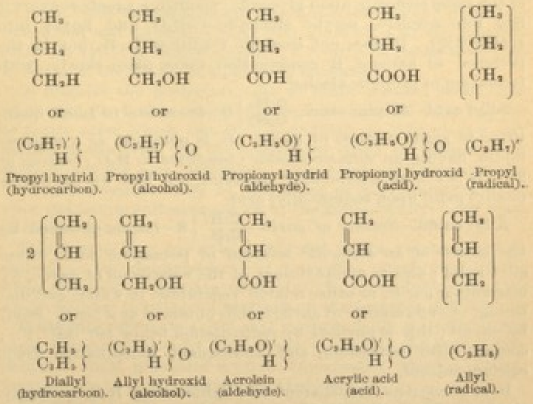
Zinc-ethyl — $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\} Zn$—123—obtained by heating at 130° (266° F.) in a sealed tube a mixture of perfectly dry zinc amalgam with ethyl iodid : the contents of the tube are then distilled in an atmosphere of coal-gas, or H, and the distillate collected in a receiver, in which it can be sealed by fusion of the glass without contact with air.

It is a colorless, transparent, highly refracting liquid ; sp. gr. 1.182 ; boils at 118° (244°.4 F.). On contact with air it ignites and burns with a luminous flame, bordered with green, and gives off dense clouds of zinc oxid, a property which renders it very dangerous to handle. On contact with H_2O it is immediately decomposed into zinc hydrate and ethyl hydrid. It is chiefly useful as an agent by which the radical ethyl can be introduced into organic molecules.

ALLYLIC SERIES.

The compounds heretofore considered may be derived more or less directly from the saturated hydrocarbons; in the derivatives, as in the hydrocarbons, the valences of the C atoms are all satisfied, and that in the simplest and most complete manner, two neighboring C atoms always exchanging a *single* valence. There exist, however, other compounds containing less H in proportion to C than those already considered, and yet resembling them in being monoatomic. These compounds have usually been considered as *non-saturated*, because all the *possible* valences are not satisfied, and the substances are therefore capable of forming products of *addition*, while the *saturated* compounds can only form products of *substitution*.

In this sense the substances composing this series are non-saturated, but they are not so in the sense that they contain C or other atoms whose valences are not satisfied. The following formulæ indicate the constitution of the substances of this series, and their relation to those of the previous one. It will be observed that in the allyl compounds, two neighboring C atoms exchange *two* valences:



$$\begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CH_2H \end{matrix} \qquad \begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CH_2OH \end{matrix} \qquad \begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ COH \end{matrix} \qquad \begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ COOH \end{matrix} \qquad \left(\begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \end{matrix}\right)$$

or — or — or — or

$$\left.\begin{matrix} (C_3H_7)' \\ H \end{matrix}\right\} \qquad \left.\begin{matrix} (C_3H_7)' \\ H \end{matrix}\right\} O \qquad \left.\begin{matrix} (C_3H_5O)' \\ H \end{matrix}\right\} \qquad \left.\begin{matrix} (C_3H_5O)' \\ H \end{matrix}\right\} O \qquad (C_3H_7)'$$

Propyl hydrid (hydrocarbon). Propyl hydroxid (alcohol). Propionyl hydrid (aldehyde). Propionyl hydroxid (acid). Propyl (radical).

$$2\left[\begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CH_2 \end{matrix}\right] \qquad \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{matrix} \qquad \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ COH \end{matrix} \qquad \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ COOH \end{matrix} \qquad \left(\begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CH_2 \\ | \end{matrix}\right)$$

or — or — or — or

$$\left.\begin{matrix} C_3H_5 \\ C_3H_5 \end{matrix}\right\} \qquad \left.\begin{matrix} (C_3H_5)' \\ H \end{matrix}\right\} O \qquad \left.\begin{matrix} (C_3H_3O)' \\ H \end{matrix}\right\} \qquad \left.\begin{matrix} (C_3H_3O)' \\ H \end{matrix}\right\} O \qquad (C_3H_5)$$

Diallyl (hydrocarbon). Allyl hydroxid (alcohol). Acrolein (aldehyde). Acrylic acid (acid). Allyl (radical).

Diallyl—$\left.\begin{matrix} C_3H_5 \\ C_3H_5 \end{matrix}\right\}$—82—formerly known as *allyl*, is obtained by the action of sodium upon allyl iodid, and is not, as its empirical formula would seem to indicate, a superior homologue of acetylene and allylene (*q.v.*).

It is a colorless liquid, having a peculiar odor, somewhat resembling that of horseradish; boils at 59° (138°.2 F.); sp. gr. 0.684 at 14° (57°.2 F.).

Vinyl hydrate—Vinyl alcohol—$\left.\begin{matrix}C_2H_3\\ H\end{matrix}\right\}O$—is produced by distilling vinyl sulfuric acid, $(C_2H_3)H.SO_4$, formed by the action of H_2SO_4 on acetylene, with H_2O. It is an unstable liquid, having a very pungent odor.

Allyl hydrate—Allylic alcohol—$\left.\begin{matrix}C_3H_5\\ H\end{matrix}\right\}O$—58—may be obtained by the action of sodium upon dichlorhydrin in ethereal solution; or by heating four parts of glycerol with one part of crystallized oxalic acid.

Allylic alcohol is a colorless, mobile liquid; solidifies at −54° (−65°.2 F.); boils at 97° (206°.6 F.); sp. gr. 0.8507 at 25° (77° F.); soluble in H_2O; has an odor resembling the combined odors of alcohol and essence of mustard; burns with a luminous flame.

Allyl alcohol is isomeric with propylic aldehyde and with acetone. Being an unsaturated compound, it is capable of forming products of addition with Cl, Br and I, etc., which are isomeric or identical with products of substitution obtained by the action of the same elements upon glycerol. Oxidizing agents convert it first into acrolein, acrylic aldehyde, C_3H_4O, and finally into acrylic acid. It does not combine readily with H, but in the presence of nascent H combination takes place slowly, with formation of propylic alcohol.

Allyl oxid—Allylic ether—$\left.\begin{matrix}C_3H_5\\ C_3H_5\end{matrix}\right\}O$—98—exists in small quantities in crude essence of garlic. It is obtained as a colorless liquid, having an alliaceous odor; insoluble in H_2O; boiling at 82° (179°.6 F.), by a number of reactions, but best by the action of allyl iodid upon sodium-allyl oxid.

Allyl sulfid—*Essence of garlic*—$\left.\begin{matrix}C_3H_5\\ C_3H_5\end{matrix}\right\}S$—114—is obtained by the action of an alcoholic solution of potassium sulfid upon allyl iodid; also as a constituent of the volatile oil of garlic, by macerating garlic, or other related vegetables, in water, and distilling. Crude essence of garlic is thus obtained as a heavy, fetid, brown oil; this is purified by redistillation below 140° (284° F.); contact with potassium, and subsequent redistillation from calcium chlorid.

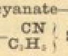
It is a colorless, transparent oil; lighter than H_2O, sparingly soluble in H_2O, very soluble in alcohol and ether; boils at 140° (280° F.); has an intense odor of garlic. It does not exist naturally in the plant, but is formed during the process of extraction by the action of H_2O, probably in a manner similar to that in which essence of mustard is formed under similar circumstances. It is to the formation of allyl sulfid, which is highly volatile, that garlic owes the odor which it emits.

Allyl chlorid—C_3H_5Cl—a colorless liquid, boils at 46° (114°.8 F.), has an irritating odor; formed by slowly adding PCl_3 to allyl alcohol.

Allyl bromid—C_3H_5Br—a liquid boiling at 71° (159°.8 F.), obtained in the same manner as the chlorid, using PBr_3.

Allyl iodid—C_3H_5I—a colorless liquid having a peculiar odor; boils at 101°.5 (214°.7 F.); insoluble in H_2O; obtained by carefully mixing allyl alcohol, red P, and I, and distilling after 24 hours.

Allyl tribromid—$(C_3H_5Br)_3$—a colorless liquid, very soluble in ether, boiling at 217° (422° F.), solidifying at −10° (14° F.); obtained by acting upon allyl iodid with 2½ times its weight of Br. Has been recommended as a nervous sedative.

Allyl sulfocyanate—*Essential oil of mustard*—**Oleum sinapis volatile (U. S.)**— $\left.\begin{matrix}CN\\C_3H_5\end{matrix}\right\}S$—99.—If the seeds of white or black mustard be strongly expressed, a bland, neutral oil is obtained, which resembles rape-seed and colza oils in its physical properties, and in being composed of the glycerids of stearic, oleic, and erucic acids. The cake remaining after the expression of this oil from *black mustard*, or the black-mustard seeds themselves, pulverized and moistened with H_2O, gives off a strong, pungent odor. If the H_2O be now distilled, a volatile oil passes over with it, which is the crude essential oil of mustard.

In practice the powdered cake of black-mustard seeds, from which the fixed oil has been expressed, is digested with H_2O for 24 hours, after which the H_2O is distilled as long as any oily matter passes over; the oil is collected, dried by contact with calcium chlorid, and redistilled. Essence of mustard may also be obtained synthetically by the action of allyl bromid or iodid upon potassium sulfocyanate, or by the action of allyl iodid upon silver sulfocyanate.

This essence does not exist preformed in the mustard, but results from the decomposition of a peculiar constituent of the seeds, **potassium myronate**, determined by cryptolytic action set up by another constituent, **myrosin**, in the presence of H_2O.

Potassium myronate exists only in appreciable quantity in the black variety of mustard, from which it may be obtained in the shape of short prismatic crystals, transparent, odorless, bitter; very soluble in H_2O, sparingly so in alcohol.

Myrosin is a nitrogenized cryptolite, existing in the white as well as in the black mustard, and in other seeds. It may be obtained from white mustard seeds, in an impure form, by extraction with cold H_2O, filtering and evaporating the solution at a temperature below 40° (104° F.); the syrupy fluid so obtained is precipitated with alcohol, the precipitate washed with alcohol, redissolved in H_2O, and the solution evaporated below 40° (104° F.) to dryness.

At temperatures above 40° (104° F.) myrosin becomes coagulated and incapable of decomposing potassium myronate, a change which is also produced by contact with acetic acid. As the rubefacient and vesicant actions of mustard when moistened with H_2O, are due to the production of allyl sulfocyanate, neither vinegar, acetic acid, nor heat greater than 40° (104° F.) should be used in the preparation of mustard cataplasms.

Pure allyl sulfocyanate is a transparent, colorless oil; sp. gr. 1.015 at 20° (68° F.); boils at 143° (289°.4 F.); has a penetrating, pungent odor, sparingly soluble in H_2O, very soluble in alcohol and ether. When exposed to the light it gradually turns brownish-yellow and deposits a resinoid material. When applied to the skin it produces rubefaction, quickly followed by vesication.

ACIDS AND ALDEHYDES OF THE ACRYLIC SERIES.

These substances bear the same relation to the alcohols of the allyl series that the volatile fatty acids and the corresponding aldehydes bear to the ethylic series of alcohols.

The acids of this series differ from those containing the same number of C atoms in the formic series, by containing two atoms of H less; they are readily converted into acids of the formic series by the action of potassium hydroxid in fusion.

Acrylic acid—$\left.\begin{matrix} C_3H_3O \\ H \end{matrix}\right\} O$—72—is obtained by oxidation of acrolein by silver oxid, and is formed in a number of other reactions. It is a colorless, highly acid liquid; has a penetrating odor; solidifies at 7° (44°.6 F.); boils at 140° (284° F.). Nascent H unites with it to form propionic acid. It forms crystalline salts and ethers.

Acrylic aldehyde—Allylic aldehyde—Acrolein—$\left.\begin{matrix} C_3H_3O \\ H \end{matrix}\right\}$—56.—When the fats and fixed oils are decomposed by heat, a disagreeable, irritating odor is produced, which is due to the formation of acrolein by the dehydration of the glycerol contained in the fatty material. Acrolein may be obtained by heating glycerol with strong H_2SO_4, or with hydropotassic sulfate. Glycerol is the alcohol (hydroxid) of a radical having the same composition as allyl, but so differing from it in constitution as to be trivalent in place of univalent.

$$\underset{\text{Glycerol.}}{(C_3H_5)'''(OH)_3} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Acrolein.}}{(C_3H_3O)'H}$$

Acrolein is a colorless, limpid liquid; lighter than H_2O; boils at 52°.4 (126°.3 F.); sparingly soluble in H_2O, more soluble in alcohol; very volatile; its vapor is very pungent and irritating. When freshly prepared it is neutral in reaction, but on contact with air it rapidly becomes acid by oxidation. For the same reason it does not keep well, even in closed vessels; on standing it deposits a flocculent material, which has been called **disocryl,** while at the same time formic, acetic, and acrylic acids are formed. Oxidizing agents convert it into acrylic acid, or, if they be energetic, into a mixture of formic and acetic acids. The caustic alkalies produce from it resinoid substances similar to those formed from acetic aldehyde. With NH_3 it forms a crystalline, odorless compound, which behaves as a base.

Acrolein is formed whenever glycerin, or any substance containing it or its compounds with the fatty acids, is heated to a temperature sufficient to effect its decomposition; for this reason and because of the irritating action of the acrolein, the heavy petroleum-oils are preferable to those of vegetable or animal origin for the lubricating of machinery operated in enclosed places.

Crotonic acid—$\left.\begin{matrix}C_4H_5O\\H\end{matrix}\right\}O$—86—was first obtained from croton-oil, *oleum tiglii* (*U. S.*), *oleum crotonis* (*Br.*), in which it exists in combination with glycerin, and accompanied by the glycerin ethers of several other fatty acids; it is, however, neither the vesicant nor the purgative principle of the oil. It may be obtained by saponification of croton-oil, or, better, by the action of potassium hydroxid upon allyl cyanid.

It is an oily liquid; solidifies at −5° (23° F.); acrid in taste; gives off highly irritating vapors at temperatures slightly above 0° (32° F.). When taken internally it acts as an irritant poison.

An acid obtained by oxidation of crotonic aldehyde is probably an isomere, as it is in the form of crystals at ordinary temperatures, and only fuses at 73° (163°.4 F.).

Crotonic aldehyde—$\left.\begin{matrix}C_4H_5O\\H\end{matrix}\right\}$—70.—If aldehyde, H_2O, and HCl be mixed together at a low temperature, and the mixture exposed to diffused daylight for some days, an oily liquid is formed, which, after purification, has the composition $C_4H_8O_2$. This substance, known as **aldol**, when exposed to heat, is decomposed into water and crotonic aldehyde: $C_4H_8O_2 = H_2O + C_4H_6O$.

Crotonic aldehyde is a colorless liquid; boils at 105° (221° F.); gives off highly irritating vapors. It bears the same relation to croton chloral that aldehyde does to chloral.

Angelic acid—$\left.\begin{matrix}C_5H_7O\\H\end{matrix}\right\}O$—100—exists in angelica root, in the flowers of chamomile, *Anthemis* (U. S.), and in croton-oil.

It crystallizes in colorless prisms, which fuse at 45°.5 (113°.9 F.); boils at 185° (365° F.); has an aromatic odor and an acid, pungent taste; sparingly soluble in cold H_2O; readily soluble in hot H_2O, alcohol, and ether. By the action of heat it is converted into its isomere, **methylcrotonic acid**, $\left.\begin{matrix}C_4H_4(CH_3)O\\H\end{matrix}\right\}O$.

Oleic acid—Acidum oleicum (U. S.)—$\left.\begin{matrix}C_{18}H_{33}O\\H\end{matrix}\right\}O$—246—exists as its glyceric ether, **olein**, in most, if not in all the fats and in all fixed oils. It is obtained in an impure form on a large scale as a by-product in the manufacture of candles. This product is, however, very impure. To purify it, it is first cooled to 0° (32° F.), the liquid portion collected; cooled to −10° (14° F.), expressed, and the solid portion collected; this is melted and treated with half its weight of massicot; the lead oleate so obtained is dissolved out by ether; the decanted ethereal solution is shaken with HCl, the ethereal layer decanted and evaporated, when it leaves oleic acid, contaminated with a small quantity of oxyoleic acid, from which it can be purified only by a tedious process.

Pure oleic acid is a white, pearly, crystalline solid, which fuses to a colorless liquid at 14° (57°.2 F.); it is odorless and tasteless; soluble in alcohol, ether, and cold H_2SO_4; insoluble in H_2O; sp. gr. 0.808 at 19° (66°.2 F.). Neutral in reaction. It can be distilled in vacuo without decomposition, but when heated in contact with air, it is decomposed with formation of hydrocarbons, volatile fatty acids, and sebacic acid. It dissolves the fatty acids readily, forming mixtures whose consistency varies with the proportions of liquid and solid acid which they contain. The solid acid is but little altered by exposure to air, but when liquid it absorbs O rapidly, becomes yellow, rancid, acid in reaction, and incapable of solidifying when cooled; these changes take place the more rapidly the higher the temperature.

When heated with a small amount of chlorin, bromin or iodin under pressure to 270°–280° (518°–536° F.) for several hours, oleic acid is converted into a mixture of solid fatty acids containing 70 per cent. of stearic acid.

Cl and Br under ordinary pressure attack oleic acid with formation of products of substitution. If oleic acid be heated with an excess of caustic potassa to 200° (392° F.), it is decomposed into palmitic and acetic acids: $C_{18}H_{34}O_2 + 2KHO = C_{16}H_{31}O_2K + C_2H_3O_2K + H_2$; a reaction which is utilized industrially to obtain hard soaps, palmitates, from olein, which itself only forms soft soaps. Cold H_2SO_4 dissolves oleic acid, and deposits it unaltered on the addition of H_2O, but if the acid solution be heated it turns brown and gives off SO_2. Nitric acid oxidizes it energetically, with formation of a number of volatile fatty acids and acids of another series—suberic, adipic, etc. The oleates of the alkali metals are soft, soluble soaps; those of the earthy metals are insoluble in H_2O, but soluble in alcohol and in ether.

Elaidic acid is an isomere of oleic acid, produced by the action upon it of nitrous acid in the preparation of *Unguentum hydrargyri nitratis* (*U. S.; Br.*). The nitrous fumes formed convert the oleic acid, contained in the oil and lard used, into elaidic acid, which exists in the ointment in combination with mercury.

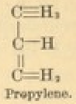
SECOND SERIES OF HYDROCARBONS—OLEFINS.

SERIES C_nH_{2n}.

The terms of this series contain two H atoms less than the corresponding terms of the first series. They differ in constitution in this, that, while in the first series a single valence is exchanged between each two neighboring C atoms, in the second series two valences are exchanged between two of the C atoms:

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

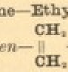
Propane.



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

Propylene.

They are designated as **olefins**; or, to distinguish them from the terms of the first series, by the terminations **ylene** or **ene**, thus the second is called **ethylene** or **ethene**. They behave as bivalent radicals.

Ethene—Ethylene—Olefiant gas—*Elayl*—*Heavy carburetted hydrogen*—  $\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array}$ —28—is formed by the dry distillation of fats, resins, wood, and coal, and is one of the most important constituents of illuminating gas. It is also obtained by the dehydration of alcohol or ether.

It has been obtained synthetically: (1) by passing a mixture of H_2S and carbon monoxid over iron or copper heated to redness; (2) by heating acetylene in the presence of H, or by the action of nascent H upon copper acetylid; (3) by the action of H upon the chlorid C_2Cl_4, obtained by the action of Cl upon carbon disulfid. It is prepared in the laboratory by the dehydration of alcohol: a mixture of 4 pts. H_2SO_4 and 1 pt. alcohol is placed in a flask containing enough sand to form a thin paste, and gradually heated to about 170° (338° F.); the gas, which is given off in abundance, is purified by causing it to pass through wash-bottles containing H_2O, an alkaline solution, and concentrated H_2SO_4.

Pure ethylene is a colorless gas; tasteless; has a faint odor resembling that of salt water, or an ethereal odor when impure; irrespirable; sparingly soluble in H_2O, more soluble in alcohol. It burns with a luminous, white flame, and forms explosive mixtures with air and oxygen.

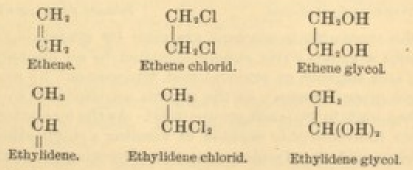
When heated for some time at a dull red heat it is converted into acetylene, ethyl and methyl hydrids, a tarry product, and carbon.

Ethylene readily enters into combination. It unites with H to form ethyl hydrid, C_2H_6. With O it unites explosively on the approach of a flame, with formation of carbon dioxid and H_2O.

Oxidizing agents, such as potassium permanganate in alkaline solution, convert it into oxalic acid and H_2O. A mixture of Cl and ethene, in the proportion of two volumes of the former to one of the latter, unite with an explosion on contact with flame, the union being attended with a copious deposition of C and the formation of HCl. Chlorin and ethene, mixed in equal volumes and exposed to diffused daylight, unite slowly, with formation of an oily liquid; **ethene chlorid, $C_2H_4Cl_2$=Dutch liquid,** to whose formation ethene owes the name **olefiant gas**. By suitable means ethene may also be made to yield chlorinated products of substitution, the highest of which is **carbon dichlorid, C_2Cl_4**. Br and I also form products of addition and of substitution with ethene. By union with $(OH)_2$ it forms glycol (*q.v.*). It slowly dissolves in ordinary H_2SO_4, with formation of sulfovinic acid. With fuming H_2SO_4 it combines with elevation of temperature and formation of ethionic anhydrid.

When inhaled, diluted with air, ethene produces effects somewhat similar to those of nitrous oxid.

The name **ethylidene** is given to a grouping of C_2H_4 which would be isomeric with ethene were it capable of free existence. It has not been isolated, but exists in a series of compounds whose relations to the ethene derivatives is shown in the following formulæ:



$$\begin{array}{ccc} CH_2 & CH_2Cl & CH_2OH \\ \| & | & | \\ CH_2 & CH_2Cl & CH_2OH \\ \text{Ethene.} & \text{Ethene chlorid.} & \text{Ethene glycol.} \\ CH_3 & CH_3 & CH_3 \\ | & | & | \\ CH & CHCl_2 & CH(OH)_2 \\ \| & & \\ \text{Ethylidene.} & \text{Ethylidene chlorid.} & \text{Ethylidene glycol.} \end{array}$$

Two of the isomeric lactic acids (see p. 314) are derived from ethene and ethylidene by addition of CO_2H_2.

Ethene chlorid—Bichlorid of ethylene—Dutch liquid—$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}$—99—is obtained by passing a current of ethene through a retort in which Cl is being generated, and connected with a cooled receiver. The distillate is washed with a solution of caustic potassa, afterward with H_2O, and is finally rectified.

It is a colorless, oily liquid, which boils at 82°.5 (180°.5 F.); has a sweetish taste and an ethereal odor. It is isomeric with the chlorid of monochlorinated ethyl, $\begin{array}{l} C_2H_4Cl \\ | \\ Cl \end{array}$, which boils at 64°(147°.2 F.). It is capable of fixing other atoms of Cl by substitution for H, and thus forming a series of chlorinated derivatives, the highest of which is C_2Cl_6.

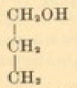
Pentene—*Amylene* or *valerene*—$\mathbf{C_5H_{10}}$—70—a colorless, mobile liquid, boiling at 39° (102°.2 F.); obtained by heating alcohol with a concentrated solution of zinc chlorid.

Its use as an anæsthetic has been suggested.

DIATOMIC ALCOHOLS.

SERIES $C_nH_{2n+2}O_2$.

These substances are designated as **glycols.** They are the hydroxids of the hydrocarbons of the series C_nH_{2n}, and consist of those hydrocarbons, playing the part of bivalent radicals, united with two groups OH; their general typical formula is then $\left.\begin{array}{r}(C_nH_{2n})''\\ H_2\end{array}\right\}O_2$. We have seen (p. 238) that the primary monoatomic alcohols contain the group of atoms (CH_2OH), united with $n(C_nH_{2n+1})$; the **primary glycols** are similarly constructed, and consist of twice the group (CH_2OH), united in the higher terms to $n(CH_2)$. The constitution of the glycols and their relations to the monoatomic alcohols are indicated by the following formulæ:



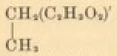
$$\begin{array}{l}CH_2OH\\ |\\ CH_2\\ |\\ CH_3\end{array}$$

Primary propyl alcohol.

$$\begin{array}{l}CH_2OH\\ |\\ CH_2\\ |\\ CH_2OH\end{array}$$

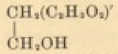
Primary propyl glycol.

As the monoatomic alcohols are such by containing in their molecules a group (OH), closely attached to an electro-positive group, and capable of removal and replacement by an electro-negative group or atom, so the glycols are *diatomic* by the fact that they contain two such groups (OH). As the monoatomic alcohols are therefore only capable of forming a single ether with a monobasic acid, the glycols are capable of forming two such ethers:



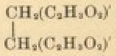
$$\begin{array}{l}CH_2(C_2H_3O_2)'\\ |\\ CH_3\end{array}$$

Ethyl acetate.



$$\begin{array}{l}CH_2(C_2H_3O_2)'\\ |\\ CH_2OH\end{array}$$

Monoacetic glycol.

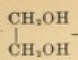


$$\begin{array}{l}CH_2(C_2H_3O_2)'\\ |\\ CH_2(C_2H_3O_2)'\end{array}$$

Diacetic glycol.

Methene glycol, which would have the composition $H_2C{<}\begin{array}{l}OH\\ OH\end{array}$, is not known. Its haloid ethers are, however, known. A condensation product corresponding to it exists as **methene dimethylate,** $\mathbf{H_2C{<}\begin{array}{l}OCH_3\\ OCH_3\end{array}}$, also called **methylal** and **formal**, as a thin liquid, boiling at 42° (107°.6 F.), soluble in alcohol, ether, and water, sp. gr. 0.855; formed by oxidizing methyl alcohol with H_2SO_4 and MnO_2. It has been used as a medicine.

Ethene glycol—**Ethylene glycol** or **Alcohol** or **Hydroxid**—

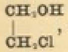


$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$$

—62.—This, the best known of the glycols, is prepared by the action of dry silver acetate upon ethylene bromid. The ether so obtained is purified by redistillation, and decomposed by heating for some time with barium hydroxid.

It is a colorless, slightly viscous liquid; odorless; faintly sweet; sp. gr. 1.125 at 0° (32° F.); boils at 197° (386°.6 F.); sparingly soluble in ether; very soluble in water and in alcohol.

It is not oxidized by simple exposure to air, but on contact with platinum-black it is oxidized to glycolic acid; more energetic oxidants transform it into oxalic acid. Chlorin acts slowly upon glycol in the cold; more rapidly under the influence of heat, producing chlorinated and other derivatives. By the action of dry HCl upon cooled glycol, a product is formed, intermediate between it and ethylene chlorid, a neutral compound—**ethene chlorhydrin,**



$$\begin{array}{l}\mathbf{CH_2OH}\\ |\\ \mathbf{CH_2Cl}\end{array}$$

, which boils at 130° (266° F.).

Ethene oxid—Ethylene oxid—$(C_2H_4)''O$—44.—This substance, isomeric with aldehyde, is obtained by the action of potassium hydroxid upon ethene chlorhydrate.

It is a transparent, volatile liquid; boils at 13°.5 (54°.3 F.); gives off inflammable vapors; mixes with H_2O in all proportions. It is capable of uniting directly with H_2O to form glycol; and with HCl gas to regenerate ethene chlorhydrin.

Taurin—$SO_3C_2H_7N$—125—is isomeric with a derivative of glycol, **isethionamid.** It is obtained from ox-bile by boiling with dilute HCl; decanting and concentrating the liquid; separating from the sodium chlorid which crystallizes; evaporating further, and precipitating with alcohol. The deposit is purified by recrystallization from alcohol.

It crystallizes in large, transparent, oblique, rhombic prisms, permanent in air, soluble in H_2O, almost insoluble in absolute alcohol and ether.

Taurin has acid properties and forms salts; it is not attacked by H_2SO_4, HNO_3, or nitromuriatic acid, but is oxidized by nitrous acid, with formation of H_2O, N, and isethionic acid.

It exists in the animal economy, in the bile in taurocholic acid (*q.v.*); and has also been detected in the intestine and fæces, muscle, blood, liver, kidneys, and lungs. The **pneumic acid,** described as existing in the lung, is taurin. When taken internally, it is eliminated by the urine, not in its own form, but as **taurocarbamic or isethionuric acid, $C_3H_8N_2SO_4$.**

ACIDS DERIVED FROM THE GLYCOLS.

As the acids of the acetic series are obtained from the primary monoatomic alcohols by the substitution of O for H_2 in the characterizing group CH_2OH:

$$\begin{array}{ccc} CH_3 & \qquad & CH_3 \\ | & & | \\ CH_2,OH & & CO,OH \end{array}$$

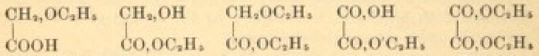
Ethyl alcohol. Acetic acid.

so the diatomic alcohols may, by oxidation, be made to yield acids, formed by the same substitution of O for H_2. But the glycols differ from the monoatomic alcohols in containing two groups CH_2OH, and they consequently yield two acids, as the substitution occurs in one or both of the alcoholic groups:

$$\begin{array}{ccc} CH_2,OH & CH_2,OH & CO,OH \\ | & | & | \\ CH_2,OH & CO,OH & CO,OH \end{array}$$

Ethene glycol. Glycolic acid. Oxalic acid.

A study of these two acids shows them to be possessed of peculiar differences of function. Each of them contains two groups (OH), whose hydrogen is capable of replacement by an acid or alcoholic radical:



$$\begin{array}{ccccc} CH_2,OC_2H_5 & CH_2,OH & CH_2OC_2H_5 & CO,OH & CO,OC_2H_5 \\ | & | & | & | & | \\ COOH & CO,OC_2H_5 & CO,OC_2H_5 & CO,O'C_2H_5 & CO,OC_2H_4 \end{array}$$

Ethylglycolic acid. Ethyl glycolate. Ethyl ethylglycolate. Ethyloxalic acid. Ethyl oxalate.

They are, therefore, both said to be **diatomic.** The ability, however, of the two acids to form salts is not the same, for while oxalic acid is capable of forming two salts of univalent metals, and a salt of a bivalent metal with a single molecule of the acid; glycolic acid only forms a single salt of an univalent metal, and two of its molecules are required to form a salt of a bivalent metal; in other words, glycolic acid is **monobasic,** while oxalic acid is **dibasic.** It is only that H atom which is contained in the electro-negative group COOH which is replaceable as acid hydrogen, while that of the electro-positive group CH_2OH is only replaceable, as is the corresponding hydrogen of an alcohol.

In general terms, therefore, the **atomicity** of an organic acid may be greater than its **basicity,** the former representing the number of H atoms contained in its molecule which are capable of being displaced by alcoholic radicals, while the latter represents the number of H atoms replaceable by electro-positive elements or radicals, with formation of salts or of ethers.

There may, therefore, be obtained from the glycols, by more or less complete oxidation, two series of acids; those of the first are diatomic and monobasic; those of the second diatomic and dibasic.

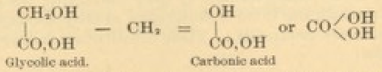
DIATOMIC AND MONOBASIC ACIDS.

SERIES $C_nH_{2n}O_3$.

The acids of this series at present known are:

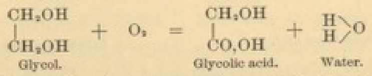
(Carbonic acid).........	CO_3H_2	Oxyvaleric acid........	$C_5O_3H_{10}$
Glycolic acid............	$C_2O_3H_4$	Leucic acid..............	$C_6O_3H_{12}$
Ethyleno-lactic acid....	$C_3O_3H_6$	(?) Œnanthic acid.....	$C_{14}O_3H_{28}$
Butylactic acid.......	$C_4O_3H_8$		

The first-named of these acids, although not capable, so far as yet known, of existing in the free state, is widely represented in nature in the shape of its salts, the carbonates. Its position in this series is an anomaly, and at first sight a contradiction, as it is certainly not a monobasic, but a distinctly dibasic acid, or, more properly speaking, would be such were it obtained in a state of purity. It is, however, in this position, as the inferior homologue of glycolic acid, that carbonic acid is most naturally placed, and the dibasic nature of the latter acid does not present any valid objection to such a position, for, if we consider one term of a series as derivable from its superior homologue by the subtraction of CH_2, and if we bear in mind that the basic nature of the hydrogen atom in a group OH depends upon its close union with the group CO (or with some other electro-negative group), it will become evident that the inferior homologue of glycolic acid must contain two groups OH united to one CO, and must, therefore, be dibasic:



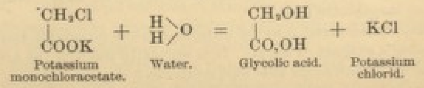
$$\underset{\text{Glycolic acid.}}{\begin{array}{c}CH_2OH\\ |\\ CO,OH\end{array}} - CH_2 = \underset{\text{Carbonic acid}}{\begin{array}{c}OH\\ |\\ CO,OH\end{array}} \text{ or } CO\begin{array}{l}\diagup OH\\ \diagdown OH\end{array}$$

The other acids of the series are formed: (1.) By the partial oxidation of the corresponding glycol:



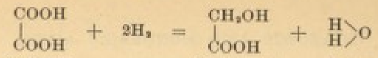
$$\underset{\text{Glycol.}}{\begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}} + O_2 = \underset{\text{Glycolic acid.}}{\begin{array}{c}CH_2OH\\ |\\ CO,OH\end{array}} + \underset{\text{Water.}}{\begin{array}{c}H\\ H\end{array}\!\!>\!O}$$

(2.) By the combined action of water and silver oxid upon the monochloracid of the acetic series, or by heating the alkaline salt of such an acid with water or potassium hydroxid:



$$\underset{\text{Potassium monochloracetate.}}{\begin{array}{c}CH_2Cl\\ |\\ COOK\end{array}} + \underset{\text{Water.}}{\begin{array}{c}H\\ H\end{array}\!\!>\!O} = \underset{\text{Glycolic acid.}}{\begin{array}{c}CH_2OH\\ |\\ CO,OH\end{array}} + \underset{\text{Potassium chlorid.}}{KCl}$$

(3.) By reducing the corresponding acid of the oxalic series by nascent hydrogen:



$$\begin{array}{l}\text{COOH}\\ |\\ \text{COOH}\end{array} + 2H_2 = \begin{array}{l}\text{CH}_2\text{OH}\\ |\\ \text{COOH}\end{array} + \begin{array}{l}H\\ H\end{array}\!\!>O$$

Oxalic acid. Glycolic acid. Water.

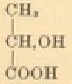
Carbonic acid—$\mathbf{CO}\!<\!\begin{array}{l}\mathbf{OH}\\ \mathbf{OH}\end{array}$—62.—Although this acid has not been isolated, it probably exists in aqueous solutions of CO_2, which have an acid reaction, while dry CO_2 is neutral. Its salts, the carbonates, are well characterized.

Ethers are also known corresponding to **orthocarbonic acid, $\mathbf{C(OH)_4}$**, although the acid itself is unknown.

Glycollic acid—$\begin{array}{l}\mathbf{CH_2OH}\\ |\\ \mathbf{COOH}\end{array}$—76—is formed by the oxidation of glycol, by the action of nitrous acid on glycocol, and by the action of potash on monochloracetic acid.

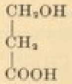
It forms deliquescent, acicular crystals; very soluble in water; soluble in alcohol and ether; has a strongly acid taste and reaction; fuses at 78° (172°.4 F.); is decomposed at 150° (302° F.); at an intermediate temperature it loses H_2O, forming **glycollid, or glycollic anhydrid, $\mathbf{C_2H_2O_2}$.**

Lactic acids—$\mathbf{C_3H_6O_3}$—90.—There are probably three, certainly two, acids having this composition. Two of these would seem, from their products of decomposition, to be of similar constitution, while the molecular composition of the third is distinct. The two of similar constitution are sometimes designated as **ethylidene lactic acids,** because of their containing the group of atoms CH_3, while the third is designated as **ethyleno-lactic acid,** as it contains the group CH_2. Their constitution is expressed by the formulæ:



$$\begin{array}{l}\text{CH}_3\\ |\\ \text{CH,OH}\\ |\\ \text{COOH}\end{array}$$

Ethylidene lactic acid.



$$\begin{array}{l}\text{CH}_2\text{OH}\\ |\\ \text{CH}_2\\ |\\ \text{COOH}\end{array}$$

Ethyleno-lactic acid.

Obviously it is the ethylene acid which is the superior homologue of glycollic acid.

Ethyleno-lactic Acid.—Muscular tissue contains a mixture of this and optically active ethylidene lactic acid, which has been known as **sarcolactic acid.**

Ethyleno-lactic acid may be obtained from muscular tissue or from Liebig's extract of meat. It is optically inactive, as are also solutions of its salts; its zinc salt contains 2 Aq, and is very soluble in water and quite soluble in alcohol. When oxidized by chromic acid it yields malonic acid.

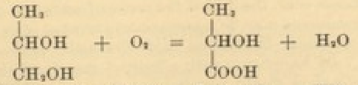
Of the two **ethylidene lactic acids,** that which is *optically active* is the one accompanying ethylene lactic acid, and predominating over it in amount, in dead muscle. It is to this acid that the name **paralactic acid** is most properly applied. It may be obtained from Liebig's meat extract.

Paralactic acid differs from its two isomeres in that its solutions are dextrogyrous, and the solutions of its salts are lævogyrous. The specific rotary power of the acid is $[\alpha]_D = +3^\circ.5$; that of the zinc salt $[\alpha]_D = -7^\circ.6$; and of the calcium salt $[\alpha]_D = -3^\circ.8$. Its products of decomposition are the same as those of ordinary lactic acid.

Ordinary Lactic Acid—*Lactic acid of fermentation—Optically inactive ethylidene lactic acid*—**Acidum lacticum** (**U. S.**)—exists in nature, widely distributed in the vegetable kingdom, and as the product of a fermentation which is designated as the lactic, in milk, sour-krout, fermented beet-juice, and rice, and in the liquid refuse of starch factories and tanneries.

Lactic acid is obtained as a product of the fermentation of certain sugars, milk-sugar and grape-sugar; as a result of the processes of nutrition of a minute vegetable, the lactic ferment, in which the sugar is converted into its inferior polymere: $C_6H_{12}O_6 = 2C_3H_6O_3$. It is usually produced by allowing a mixture of cane-sugar, tartaric acid, water, rotten cheese, skim milk and chalk to ferment for 10 days at 35° (95° F.). The calcium lactate produced is separated, purified and decomposed with an equivalent quantity of H_2SO_4.

It has also been obtained synthetically by oxidation of the propylglycol of Wurtz, which is a secondary glycol, a synthesis which indicates its constitution:



$$\begin{matrix} CH_3 & & & & CH_3 & & \\ | & & & & | & & \\ CHOH & + & O_2 & = & CHOH & + & H_2O \\ | & & & & | & & \\ CH_2OH & & & & COOH & & \end{matrix}$$

Propylglycol. Oxygen. Lactic acid. Water.

It is a colorless, syrupy liquid; sp. gr. 1.215 at 20° (68° F.); does not solidify at −24° (−11°.2 F.); soluble in water, alcohol, and ether; is not capable of distillation without decomposition; when heated to 130° (266° F.) it loses water and is converted into **dilactic acid,** $\mathbf{C_6H_{10}O_5}$, and, when heated to 250° (482° F.), into **lactid,** $\mathbf{C_3H_4O_2}$. It is a good solvent of tricalcic phosphate.

Oxidizing agents convert this acid into formic and acetic acids, without the formation of any malonic acid.

The three lactic acids occur in animal nature, either free or in combination. Free lactic acid of fermentation occurs in the contents of the small intestine, and, when vegetable food has been taken, in the stomach. It is not, however, the acid to which the *normal, unmixed* gastric juice owes its acidity. Its salts have been found to exist in the contents of the stomach and those of the intestines, chyle, bile, parenchymatous fluid of spleen, liver, thymus, thyroid, pancreas, lungs, and brain; urine. Pathologically in the blood in leucocythæmia, pyæmia, puerperal fever, and after excessive muscular effort; in the fluids of ovarian cysts and transudations. In the urine it is abundant in phosphorus-poisoning, in acute atrophy of the liver, and in rachitis and osteomalachia.

Muscular tissue, after death or continued contractions, contains the mixture of acids known as sarcolactic acid. Normal, quiescent muscle is neutral in reaction; but, when rigor mortis appears, or if the muscle be tetanized, its reaction becomes acid from the liberation of sarcolactic acid. Whether these acids are formed *de novo* during the contraction of the muscle, or whether they are produced by the decomposition of lactates existing in the quiescent muscle, is still undetermined; certain it is, however, that a given quantity of muscle has when separated from the circulation, a fixed maximum of acid-producing capacity, which is greater in a muscle that has been tetanized during the interval between its removal and the establishment of rigor, than in one which has been at rest.

There exist no grounds upon which to base the supposition that, in rheumatic fever, lactic acid is present in the blood.

OXIDS AND SULFIDS OF CARBON.

As the saturated compound of carbon and oxygen is the anhydrid of carbonic acid, the first of the series of acids just considered, it and its congeners may be appropriately treated of in this place.

Carbon monoxid—Carbonous oxid—Carbonic oxid—CO—28—is formed: (1.) By burning C with a limited supply of air. (2.) By passing dry carbon dioxid over red-hot charcoal. (3.) By heating oxalic acid with H_2SO_4: $C_2O_4H_2=H_2O+CO+CO_2$; and passing the gas through sodium hydroxid to separate CO_2. (4.) By heating potassium ferrocyanid with H_2SO_4.

It is a colorless, tasteless gas; sp. gr. 0.9678A; very sparingly soluble in H_2O and in alcohol.

It burns in air with a blue flame and formation of carbon dioxid; it forms explosive mixtures with air and oxygen; it is oxidized to carbon dioxid by cold chromic acid. It is a valuable reducing agent, and is used for the reduction of metallic oxids at a red heat. Ammoniacal solutions of the cuprous salts absorb it readily. Being non-saturated, it unites readily with O to form CO_2, and with Cl to form **$COCl_2$**, the latter a colorless, suffocating gas, known as **phosgene**, or **carbonyl chlorid**.

Toxicology.—Carbon monoxid is an exceedingly poisonous gas, and is the chief toxic constituent of the gases given off from blast-furnaces, from defective flues, and open coal or charcoal fires, and of illuminating gas. An atmosphere containing but a small proportion of this gas produces asphyxia and death, even if the quantity of oxygen present be equal to or even greater than that normally existing in the atmosphere; 0.5 per cent. of CO in air is sufficient to kill a small bird in a few moments, and one per cent. proves fatal to small mammals.

Poisoning by CO may occur in several ways. By inhalation of the gases discharged from blast-furnaces and from copper-furnaces, the former containing 25 to 32 per cent., and the latter 13 to 19 per cent. of CO. By the fumes given off from charcoal burned in a confined space, which consist of a mixture of the two oxids of carbon, the dioxid predominating largely, especially when the combustion is most active. The following is the composition of an atmosphere produced by burning charcoal in a confined space, and which proved rapidly fatal to a dog: oxygen, 19.19; nitrogen, 76.62; carbon dioxid, 4.61; carbon monoxid, 0.54; marsh-gas, 0.04. Obviously the deleterious effects of charcoal-fumes are more rapidly fatal in proportion as the combustion is imperfect and the room small and ill-ventilated.

A fruitful source of CO poisoning, sometimes fatal, but more frequently producing languor, headache, and debility, is to be found in the stoves, furnaces, etc., used in heating our dwellings and other buildings, especially when the fuel is anthracite coal. This fuel produces in its combustion, when the air-supply is not abundant, considerable quantities of CO, to which a further addition may be made by a reduction of the dioxid, also formed, in passing over red-hot iron.

Of late years cases of fatal poisoning by illuminating gas are of very frequent occurrence, caused either by accidental inhalation, by inexperienced persons blowing out the gas, or by suicides. The most actively poisonous ingredient of illuminating gas is CO, which exists in the ordinary coal-gas in the proportion of 4 to 7.5 per cent., and in water-gas, made by decomposing superheated steam by passage over red-hot coke, and subsequent charging with vapor of hydrocarbons, in the large proportion of 30-35 per cent.

The method in which CO produces its fatal effects is by forming with the blood-coloring matter a compound which is more stable than oxyhæmoglobin, and thus causing asphyxia by destroying the power of the blood-corpuscles of carrying O from the air to the tissues. This compound of CO and hæmoglobin is quite stable, and hence the symptoms of this form of poisoning are very persistent, lasting until the place of the coloring-matter thus rendered useless is supplied by new formation. The prognosis is very unfavorable when the amount of the gas inhaled has been at all considerable. The treatment usually followed, *i.e.*, artificial respiration, and inhalation of O, failing to restore the altered coloring-matter. There would seem to be no form of poisoning in which transfusion of blood is more directly indicated than in that by CO.

Detection after death.—The blood of those asphyxiated by CO is persistently bright red in color. When suitably diluted and examined with the spectroscope, it presents an absorption spectrum (Fig. 36) of two bands similar to that of oxyhæmoglobin (Fig. 16, No. 11), but in which the two bands are more equal and somewhat nearer the violet end of the spectrum. Owing to the greater stability of the CO compound, its spectrum may be readily distinguished from that of the O compound by the addition of a reducing agent (an ammoniacal solution of ferrous tartrate), which changes the spectrum of oxyhæmoglobin to the single-band spectrum of hæmoglobin (Fig. 16, No. 12), while that of the CO compound remains unaltered, or only fades partially.

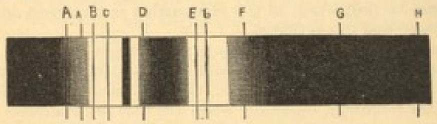


FIG. 36.

If a solution of caustic soda of sp. gr. 1.3 be added to normal blood a black, slimy mass is formed, which, when spread upon a white plate, has a greenish-brown color. The same reagent added to blood altered by CO forms a firmly clotted mass, which in thin layers upon a white surface is bright red in color.

A piece of gun-cotton upon which platinum-black has been dusted fires in air containing 2.5 in 1,000 of CO.

For the method of determining CO in gaseous mixtures, see p. 325.

Carbon dioxid—Carbonic anhydrid—Carbonic acid gas—CO_2—44 —is obtained: (1.) By burning C in air or O. (2.) By decomposing a carbonate (marble=$CaCO_3$) by a mineral acid (HCl diluted with an equal volume of H_2O).

At ordinary temperatures and pressures it is a colorless, suffocating gas; has an acidulous taste; sp. gr. 1.529A; soluble in an equal volume of H_2O at the ordinary pressure; much more soluble as the pressure increases. **Soda water** is a solution of carbonic acid in H_2O under increased pressure. When compressed to the extent of 38 atmospheres at 0° (32° F.); 50 atm. at 15° (59° F.); or 73 atm. at 30° (86° F.) it forms a transparent, mobile liquid, by whose evaporation, when the pressure is relieved, sufficient cold is produced to solidify a portion into a snow-like mass, which, by spontaneous evaporation in air, produces a temperature of −90° (−130° F.).

Carbon dioxid neither burns nor does it support combustion. When heated to 1,300° (2,370° F.), it is decomposed into CO and O. A similar decomposition is brought about by the passage through it of electric sparks. When heated with H it yields CO and H_2O. When K, Na or Mg is heated in an atmosphere of CO_2, the gas is decomposed with formation of a carbonate and separation of carbon. When caused to pass through solutions of the hydroxids of Na, K, Ca, or Ba, it is absorbed, with formation of the carbonates of those elements, which, in the case of the last two, are deposited as white precipitates. Solution of potash is frequently used in analysis to absorb CO_2, and lime and baryta water as tests for its presence. The hydroxids mentioned also absorb CO_2 from moist air.

Atmospheric Carbon Dioxid.—Carbon dioxid is a constant constituent of atmospheric air in small and varying quantities; the mean amount in free country air being about 4 in 10,000. The variation in amount under different conditions is shown in the following table:

AMOUNT OF CARBON DIOXID IN AIR.

Collected at	Parts in 10,000.	Determined by
Paris	3.190	Boussingault and Lewy.
Andilly—twenty miles from Paris	2.989	Boussingault and Lewy.
Paris—Day	3.9	Boussingault.
Night	4.2	Boussingault.
Ocean—Day	5.42	Lewy.
Night	3.346	Lewy.
Geneva	4.68	Saussure.
Meadow—three-fourths mile from Geneva		
Dry months	4.79 to 5.18	Saussure.
After long rains	3.57 to 4.56	Saussure.
December, damp and cloudy	3.85 to 4.25	Saussure.
January, frost	4.57	Saussure.
January, thaw	4.27	Saussure.
Lake Geneva	4.39	Saussure.
Arctic regions	4.83 to 6.41	Moss.
Gosport Barracks	6.45	Chaumont.
Anglesey Barracks	14.04	Chaumont.
Hilsey Hospital	4.72	Chaumont.
Portsmouth Hospital	9.76	Chaumont.
Cell in Pentonville Prison	9.89	Chaumont.
Cell in Chatham Prison	16.91	Chaumont.
Boys' school—69 cubic feet per head	31.0	Roscoe.
Room—51 cubic feet per head	52.8	Weaver.
Girls' school—150 cubic feet per head	72.3	Pettenkofer.
Greenhouse—Jardin des Plantes	1.0	
Theatre—Parquet	23.0	
Near ceiling	43.0	
Lead mine—Lamps burn	80.0	F. Leblanc.
Lamps extinguished	390.0	F. Leblanc.
Grotto del Cane	7,360.0	F. Leblanc.

It will be observed that on land the amount is greater by night than by day, while the reverse is the case at sea; on land the green parts of plants absorb CO_2 during the hours of sunlight, but not during those of darkness. The increase in the amount in air over large bodies of water during the daytime is due to the less solubility of CO_2 in the surface-water when heated by the sun's rays. The absence of vegetation accounts for the large quantity of CO_2 in the air of the polar regions, and the same cause, aided by an increased production, for its excess in the air of cities over that of the country.

The sources of atmospheric CO_2 are:

(1.) *The respiration of animals.*—The air expired from the lungs of animals contains a quantity of CO_2, varying with the age, sex, food, and muscular development and activity, while, at the same time, a much smaller quantity is discharged by the skin and in solution in the urine.

The expired air under ordinary conditions contains about 4.5 per cent. by volume of CO_2, the proportion being greater the slower the respiration.

(2.) *Combustion.*—The greater part of the atmospheric CO_2 is a product of the oxidation of C in some form as a source of light and heat. In the table on p. 321 are given the amounts of CO_2 produced, and of air consumed, by different kinds of fuel and illuminating materials. In equal times, an ordinary gas-burner produces nearly six times as much CO_2, and consumes nearly ten times as much air as a man. The amount of air consumed by fuel is, for practical purposes, greater than that given in the table, as the oxidation is never complete, the air in the chimney frequently containing ten per cent. of oxygen by volume.

(3.) *Fermentation.*—Most fermentations, including putrefactive changes, are attended by the liberation of CO_2. Thus, alcoholic fermentation takes place according to the equation:

$$\underset{180}{C_6H_{12}O_6} = \underset{92}{2C_2H_6O} + \underset{88}{2CO_2}$$

and consequently discharges into the air 88 parts by weight of CO_2 for every 92 parts of alcohol formed, or 384 litres of gas for every litre of absolute alcohol obtained.

(4.) *Tellural sources.*—Volcanoes in activity discharge enormous quantities of CO_2, and, in volcanic countries, the same gas is thrown out abundantly through fissures in the earth. All waters, sweet and mineral, hold this gas in solution, and those which have become charged with it under pressure in the earth's crust, upon being relieved of the pressure when they reach the surface, discharge the excess into the air.

(5.) *Manufacturing processes.*—Large quantities of CO_2 are added to the air in the vicinity of lime- and brick-kilns, cement-works, etc.

(6.) *In mines*, after explosions of "fire-damp." These explosions are caused by the sudden union of the C and H of CH_4, with the O of the air, and are consequently attended by the formation of large volumes of CO_2, known to miners as *after-damp*.

COMBUSTION OF FUEL.

Fuel.	Average amount burned in one hour.	Average percentage of		Carbon dioxid produced by				Air deoxidized by				Heat units.	Light in standard candles, 100.
		Carbon.	Hydrogen.	One volume in volumes.	One part by wt. in parts by weight.	In one hour.		One volume in volumes.	One kilo in cubic metres.	In one hour.			
						In kilos.	In litres.			In kilos.	In litres.		
Hydrogen	...	...	100.00	...	...	...	...	2.39	26.89	...	...	34462	...
Carbon to CO_2	...	100.0	...	...	3.65	...	...	...	9.83	...	...	8080	...
Carbon to CO	...	100.0	...	...	...	...	...	...	4.93	...	...	2474	...
Carbon monoxid	...	42.86	...	1.0	1.57	...	...	2.39	0.44	...	...	2403	...
Marsh-gas	...	75.0	25.09	1.0	2.75	...	...	9.55	13.45	...	...	13063	...
Ethene	...	85.72	14.28	2.0	3.14	...	...	14.33	12.67	...	...	11857	...
Coal-gas	140 litres	40.0	55.0	0.80	1.67	0.221	112	7.14	11.04	1.293	1000	11000	...
Crude petroleum	...	84.0	13.0	...	3.08	...	...	...	12.07	...	...	11775	...
Kerosene	15 gr.	87.0	13.0	...	3.17	0.048	25	...	12.12	0.235	182	11055	180
Wax	10 gr.	79.2	13.2	...	2.89	0.029	15	...	11.24	0.146	113	10496	100
Stearic acid	10 gr.	76.05	12.68	...	2.9	0.029	15	...	8 69	0.112	86.9	9716	84
Colza-oil	42 gr.	70.43	10.5	...	2.81	0.118	60	...	8.28	0.450	348	...	159
Wood (dry pine)	...	39.10	4.90	...	1.43	...	...	...	5.16	...	...	3600	...
Wood charcoal	...	85.0	...	...	3.10	...	...	...	8.36	...	...	7540	...
Peat	...	45.0	1.5	...	1.64	...	...	...	4.82	...	...	3000	...
Coke	...	87.0	...	...	3.17	...	...	...	8.55	...	...	...	...
Anthracite	...	90.0	2.5	...	3.29	...	...	...	9.22	...	...	6000	...
Alcohol	...	52.17	13.04	...	1.90	...	...	...	8.64	...	...	7183	...
Adult man	10 gr. C.	...	...	...	...	0.037	19	...	...	0.134	104	...	...

Constancy of the amount of atmospheric carbon dioxid.—It has been roughly estimated by Poggendorff that 2,500,000,000,000 cubic metres of CO_2 are annually discharged into our atmosphere, and that this quantity represents one-eighty-sixth of the total amount at present existing therein. This being the case, with the present production, the percentage of atmospheric CO_2 would be doubled in eighty-six years. No such increase has, however, been observed, and the average percentage found by Angus Smith, in 1872, is about the same as that observed by Boussingault in 1840, *i.e.*, four parts in ten thousand. The CO_2 discharged into the air is, therefore, removed from it about as fast as it is produced. This removal is effected in two ways: (1) by the formation of deposits of earthy carbonates by animal organisms, corals, mollusks, etc.; (2) principally by the process of nutrition of vegetables, which absorb CO_2 both by their roots and leaves, and in the latter, under the influence of the sun's rays, decompose it, retaining the C, which passes into more complex molecules; and discharging a volume of O about equal to that of the CO_2 absorbed.

Air contaminated with excess of carbon dioxid, and its effects upon the organism.—When, from any of the above sources, the air of a given locality has received sufficient CO_2 to raise the proportion above 7 in 10,000 by volume, it is to be considered as contaminated; the seriousness of the contamination depending not only upon the amount of the increase, but also upon the source of the CO_2. If the gas be derived from fermentation, or from tellural or manufacturing sources, it is simply added to the otherwise unaltered air, and the absolute amount of oxygen present remains the same. When, however, it is produced in a confined space by the processes of combustion and respiration, the composition of the air is much more seriously modified, as not only is there addition of a deleterious gas, but a simultaneous removal of an equal volume of O; hence the importance of providing, by suitable ventilation, for the supply of new air from without to habitations and other places where human beings are collected within doors, especially where the illumination is artificial.

Although an adult man deoxidizes a little over 100 litres of air in an hour, a calculation of the quantity which he would require in a given time cannot be based exclusively upon that quantity, as the deoxidation cannot be carried to completeness; indeed, when the proportion of CO_2 in air exceeds five per cent., it becomes incapable of supporting life, while a much smaller quantity, one per cent., is provocative of severe discomfort, to say the least.

In calculating the quantity of air which should be supplied to a given enclosed space, most authors have agreed to adopt as a basis that the percentage of CO_2 should not be allowed to exceed 0.6 volume per 1,000; of which 0.4 is normally present in air, and 0.2 the product of respiration or combustion. Taking the amount of CO_2 eliminated by an adult at 19 litres (=0.7 cubic foot) per hour, a man will have brought the air of an air-tight space of 100 cubic metres (=3,500 cubic feet) up to the permissible maximum of impurity in an hour.

Practically, owing to the imperfect closing of doors and windows, and to ventilation by chimneys, inhabited spaces are never hermetically closed, and a less quantity of air-supply than would be required in an air-tight space will suffice.

A sleeping-room occupied by a single person should have a cubic space of 30 to 50 cubic metres (=1,050 to 1,800 cubic feet), conditions which are fulfilled in rooms measuring 10×13×8 feet, and 13×15.6×9 feet.

In calculating the space of dormitories to be occupied by several healthy people, the smallest air-space that should, under any circumstances, be allowed, is 12 cubic metres (=420 cubic feet) for each person. To determine the number of individuals that may sleep in a room, multiply its length, width, and height together, and divide the product by 420 if the measurement be in feet, or by 12 if it be in metres. Thus, a dormitory 40 feet long, 20 feet wide, and 10 feet high, is fitted for the accommodation of 19 persons at most; for 40×20×10=8,000 and $\frac{8000}{420}$=19.05.

As a rule, in places where many persons are congregated, it is necessary to resort to some scheme of ventilation by which a sufficient supply of fresh air shall be introduced and the vitiated air removed, the quantity to be supplied varying according to circumstances. Experiment has shown that, in order to keep the air pure to the senses, the quantity of air which must be supplied per head and per hour in temperate climates is as shown in the table:

Situation.	Cubic metres.	Cubic feet.	Situation.	Cubic metres.	Cubic feet.
Barracks (day-time)	35	1,236	Hospital wards (surgical).	170	6,004
Barracks (night-time)	70	2,472	Contagious and lying-in	170	6,004
Workshops (mechanical)	70	2,472	Mines, metaliferous	150	5,297
School-rooms	35	1,236	Mines, coal	170	6,004
Hospital wards	85	3,002			

The amounts given are the smallest permissible, and should be exceeded wherever practicable.

Lights.—Each cubic foot of illuminating-gas consumes in its combustion a quantity of O equal to that contained in 7.14 cubic feet of air, and produces 0.8 cubic feet of CO_2, besides a large quantity of watery vapor, and less amounts of H_2SO_4, SO_2, and sometimes CO; and an ordinary gas-burner consumes about three feet per hour. It is obvious, therefore, that a much larger quantity of pure air must be furnished to maintain the atmosphere of an apartment at the standard of 0.6 per 1,000 of CO_2, when the vitiation is produced by the combustion of gas, than when it is the result of the respiration of a human being, and that to such an extent that a single three-foot burner requires a supply of air which would be sufficient for six human beings.

In theatres the contamination of the air by the burning of gas should be entirely eliminated by placing the burners either under the dome ventilator, or in boxes which open to the air of the house only below the level of the burner, and which are in communication with a ventilating-shaft.

When artificial illumination is obtained from lamps or candles, or from gas in small quantity and for a short time, the contamination of the air is sufficiently compensated by the ventilation through imperfect closing of the windows. A room without a window should never be used for human habitation.

One important advantage of the electric light is that it consumes no O and produces no CO_2.

Although, by the combustion of fuel, O is consumed and CO_2 produced, heating arrangements only become a source of vitiation of air when they are improperly constucted. Indeed, in the majority of cases, if properly arranged, they are the means of ventilation, either by aspirating the vitiated air of the apartment, or by the introduction of air from without.

Action on the economy.—An animal introduced into an atmosphere of pure CO_2 dies almost instantly, and without entrance of the gas into the lungs, death resulting from spasm of the glottis, and consequent apnœa.

When diluted with air, the action of CO_2 varies according to its proportion, and according to the proportion of O present.

When the proportion of O is not diminished, the poisonous action of CO_2 is not as manifest, in equal quantities, as when the air is poorer in oxygen. An animal will die rapidly in an atmosphere composed of 21 per cent. O, 59 per cent. N, and 20 per cent. CO_2 by volume; but will live for several hours in an atmosphere whose composition is 40 per cent. O, 37 per cent. N, 23 per cent. CO_2. If CO_2 be added to normal air, of course the relative quantity of O is slightly diminished, while its absolute quantity remains the same. This is the condition of affairs existing in nature when the gas is discharged into the air; under these circumstances an addition of 10–15 per cent. of CO_2 renders an air rapidly poisonous, and one of 5–8 per cent. will cause the death of small animals more slowly. Even a less proportion than this may become fatal to an individual not habituated.

In the higher states of dilution, CO_2 produces immediate loss of muscular power, and death without a struggle; when more dilute, a sense of irritation of the larynx, drowsiness, pain in the head, giddiness, gradual loss of muscular power, and death in coma.

If the CO_2 present in air be produced by respiration, or combustion, the proportion of O is at the same time diminished, and much smaller absolute and relative amounts of the poisonous gas will produce the effects mentioned above. Thus, an atmosphere containing in volumes 19.75 per cent. O, 74.25 per cent. N, 6 per cent. CO_2, is much more rapidly fatal than one composed of 21 per cent. O, 59 per cent. N, 20 per cent. CO_2. With a corresponding reduction of O, 5 per cent. of CO_2 renders an air sufficiently poisonous to destroy life; 2 per cent. produces severe suffering; 1 per cent. causes great discomfort, while 0.1 per cent., or even less, is recognized by a sense of closeness.

The **treatment** in all cases of poisoning by CO_2 consists in the inhalation of pure air (to which an excess of O may be added), aided, if necessary, by artificial respiration, the cold douche, galvanism, and friction.

Detection of carbon dioxid and analysis of confined air.—Carbon dioxid, or air containing it, causes a white precipitate when caused to bubble through lime or baryta water. Normal air contains enough of the gas to form a scum upon the surface of these solutions when exposed to it.

It was at one time supposed that air in which a candle continued to burn was also capable of maintaining respiration. This is, however, by no means necessarily true. A candle introduced into an atmosphere in which the normal proportion of O is contained, burns readily in the presence of 8 per cent. of CO_2; is perceptibly dulled by 10 per cent.; is usually extinguished with 13 per cent.; always extinguished with 16 per cent. Its extinction is caused by a less proportion of CO_2, 4 per cent., if the quantity of O be at the same time diminished. Moreover, a contaminated atmosphere may not contain enough CO_2 to extinguish, or perceptibly dim the flame of a candle, and at the same time contain enough of the monoxid to render it fatally poisonous if inhaled.

The presence of CO_2 in a gaseous mixture is determined by its absorption by a solution of potash; its quantity either by measuring the diminution in bulk of the gas, or by noting the increase in weight of an alkaline solution.

To determine the proportions of the various gases present in air the apparatus shown in Fig. 37 is used. A is an aspirator of known capacity, filled with water at the beginning of the operation. It connects by a flexible tube from its upper part with an absorbing apparatus consisting of *a*, a U-shaped tube containing fragments of pumice-stone, moistened with H_2SO_4; by the increase in weight of this tube the weight of watery vapor in the volume of air drawn through by the aspirator is determined; *b*, a Liebig's bulb filled with a solution of potash; *c*, a U-tube filled with fragments of pumice moistened with H_2SO_4; *b* and *c* are weighed together and their increase in weight is the weight of

CO_2 in the volume of air operated on. Every gram of increase in weight represents 0.50607 litre, or 31.60356 cubic inches; *d* is a tube of difficultly fusible glass, filled with black oxid of copper and heated to redness; *e* is a U-tube filled with pumice moistened with H_2SO_4; its increase in weight represents H_2O obtained from decomposition of CH_4. Every gram of increase in weight of *e* represents 0.444 gram, or 0.621 litre, or 38.781 cubic inches of marsh-gas; *f* and *g* are similar to *b* and *c*, and their increase in weight represents CO_2 formed by oxidation of CO and CH_4 in *d*. From this the amount of CO is thus calculated: First, 2.75 grams are deducted from the increase of weight of *f* and *g* for each gram of CH_4 formed by *e*; of the remainder, every gram represents 0.6364 gram, or 0.5085 litre, or 31.755 cubic inches of CO. The air is drawn through the apparatus by opening the stopcock of A to such an extent that about 30 bubbles a minute pass through *b*.

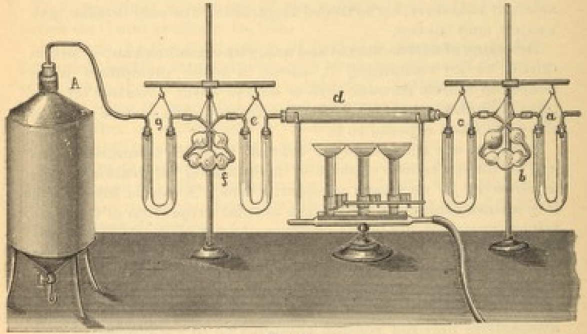


FIG. 37.

Carbon disulfid — Bisulfid of carbon — Carbonei bisulfidum (U. S.)—CS_2—76—is formed by passing vapor of S over C heated to redness, and is partly purified by rectification.

It is a colorless liquid; when pure it has a peculiar, but not disagreeable odor, the nauseating odor of the commercial product being due to the presence of another sulfurated body; boils at 47° (116°.6 F.); sp. gr. 1.293; very volatile; its rapid evaporation in vacuo produces a cold of −60° (−76° F.); it does not mix with H_2O; it refracts light strongly.

It is highly inflammable, and burns with a bluish flame, giving off CO_2 and SO_2; its vapor forms highly explosive mixtures with air, which detonate on contact with a glass rod heated to 250° (482° F.). Its vapor forms a mixture with nitrogen dioxid, which, when ignited, burns with a brilliant flame, rich in actinic rays.

There also exists a substance intermediate in composition between CO_2 and CS_2, known as **carbon oxysulfid, CSO,** which is an inflammable, colorless gas, obtained by decomposing potassium sulfocyanate with dilute H_2SO_4.

Toxicology.—Cases of acute poisoning by CS_2 have hitherto only been observed in animals; its action is very similar to that of chloroform.

Workmen engaged in the manufacture of CS_2 and in the vulcanization of rubber, as well as others exposed to the vapor of the disulfid, are subject to a form of chronic poisoning which may be divided into two stages. The first, or stage of excitation, is marked by headache, vertigo, a disagreeable taste, cramps in the legs; the patient talks, laughs, sings, and weeps immoderately, and sometimes becomes violently delirious. In the second stage the patient becomes sad and sleepy, sensibility diminishes, sometimes to the extent of complete anæsthesia, especially of the lower extremities, the headache becomes more intense, the appetite is greatly impaired, and there is general weakness of the limbs, which terminates in paralysis.

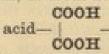
The only remedy which has been suggested is thorough ventilation of the workshops, and abandonment of the trade at the first appearance of the symptoms.

DIATOMIC AND DIBASIC ACIDS.

SERIES $CH_{2n-2}O_4$.

Oxalic acid	$C_2O_4H_2$	Pimelic acid	$C_7O_4H_{12}$
Malonic acid	$C_3O_4H_4$	Suberic acid	$C_8O_4H_{14}$
Succinic acid	$C_4O_4H_6$	Azelaic acid	$C_9O_4H_{16}$
Deoxyglutanic acid	$C_5O_4H_8$	Sebacic acid	$C_{10}O_4H_{18}$
Adipic acid	$C_6O_4H_{10}$	Roccellic acid	$C_{17}O_4H_{32}$

They are derived from the primary glycols by complete oxidation; they are diatomic and dibasic, and contain two groups, CO, OH. They form two series of salts with the univalent metals, and two series of ethers, one of which contains neutral, and the other acid ethers. They may be obtained from the corresponding glycols, or from acids of the preceding series, by oxidation.

Oxalic acid—
$\begin{matrix}\mathbf{COOH}\\|\\\mathbf{COOH}\end{matrix}$—90—$\mathbf{C_2O_4H_2,2Aq}$—126—does not occur free in nature, but in the oxalates of K, Na, Ca, Mg, and Fe in the juices of many plants: sorrel, rhubarb, cinchona, oak, etc.; as a native ferrous oxalate; and in small quantity in human urine. It is prepared artificially by oxidizing sugar or starch by HNO_3, or by the action of an alkaline hydroxid in fusion upon sawdust. The soluble alkaline oxalate obtained by the latter method is con-

verted into the insoluble Ca or Pb salt, which is washed and decomposed by an equivalent quantity of H_2SO_4 or H_2S; and the liberated acid purified by recrystallization.

Oxalic acid is also formed by the oxidation of many organic substances—alcohol, glycol, sugar, etc.; by the action of potassa in fusion upon the alkaline formates; and by the action of K or Na upon CO_2.

It crystallizes in transparent prisms, containing 2Aq, which effloresce on exposure to air, and lose their Aq slowly but completely at 100° (212° F.), or in a dry vacuum. It fuses at 98° (208°.4 F.) in its Aq; at 110°–132° (230°–269°.6 F.) it sublimes in the anhydrous form, while a portion is decomposed; above 160° (320° F.) the decomposition is more extensive; H_2O, CO_2, CO, and formic acid are produced, while a portion of the acid is sublimed unchanged. It dissolves in 15.5 parts of water at 10° (50° F.); the presence of HNO_3 increases its solubility. It is quite soluble in alcohol. It has a sharp taste and an acid reaction in solution.

Oxalic acid is readily oxidized; in watery solution it is converted into CO_2 and H_2O, slowly by simple exposure to air, more rapidly in the presence of platinum-black or of the salts of platinum and gold; under the influence of sunlight; or when heated with HNO_3, manganese dioxid, chromic acid, Br, Cl, or hypochlorous acid. Its oxidation, when it is triturated dry with lead dioxid, is sufficiently active to heat the mass to redness. H_2SO_4, H_3PO_4, and other dehydrating agents decompose it into H_2O, CO, and CO_2.

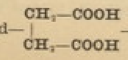
Analytical Characters.—(1.) In neutral or alkaline solution a white ppt. with a solution of a Ca salt. (2.) Silver nitrate, a white ppt., soluble in HNO_3 and in NH_4HO. The ppt. does not darken when the fluid is boiled, but, when dried and heated on platinum foil, it explodes. (3.) Lead acetate, in solutions not too dilute, a white ppt., soluble in HNO_3, insoluble in acetic acid.

Toxicology.—Although certain oxalates are constant constituents of vegetable food and of the human body, the acid itself, as well as hydropotassic oxalate, is a violent poison when taken internally, acting both locally as a corrosive upon the tissues with which it comes in contact, and as a true poison, the predominance of either action depending upon the concentration of the solution. Dilute solutions may produce death without pain or vomiting, and after symptoms resembling those of narcotic poisoning. Death has followed a dose of ʒ i. of the solid acid, and recovery a dose of ℥ i. in solution. When death occurs, it may be almost instantaneously, usually within half an hour; sometimes after weeks or months, from secondary causes.

The treatment, which must be as expeditious as possible, consists in the administration, *first*, of lime or magnesia, or a soluble salt of Ca or Mg suspended or dissolved in a *small* quantity of H_2O or mucilaginous fluid; afterward, if vomiting have not occurred spontaneously, and if the symptoms of corrosion have not been severe, an emetic may be given. In the treatment of this form of poisoning several points of negative caution are to be observed. As in all cases in which a corrosive has been taken internally, the use of the stomach-pump is to be avoided. The alkaline carbonates are of no value in cases of oxalic-acid poisoning, as the oxalates which they form are soluble, and almost as poisonous as the acid itself. The ingestion of water, or the administration of warm water as an emetic, is contraindicated when the poison has been taken in the solid form (or where doubt exists as to what form it was taken in), as they dissolve, and thus favor the absorption of the poison.

Analysis.—In fatal cases of poisoning by oxalic acid the contents of the stomach are sometimes strongly acid in reaction; more usually, owing to the administration of antidotes, neutral, or even alkaline. In a systematic analysis the poison is to be sought for in the residue of the portion examined for prussic acid and phosphorus; or, if the examination for those substances be omitted, in the residue or final alkaline fluid of the process for alkaloids. If oxalic acid alone is to be sought for, the contents of the stomach, or other substances *if acid*, are extracted with water, the liquid filtered, the filtrate evaporated, the residue extracted with alcohol, the alcoholic fluid evaporated, the residue redissolved in water (solution No. 1). The portion undissolved by alcohol is extracted with alcohol acidulated with hydrochloric acid, the solution evaporated after filtration, the residue dissolved in water (solution No. 2). Solution No. 1 contains any oxalic acid which may have existed free in the substances examined; No. 2 that which existed in the form of soluble oxalates. If lime or magnesia have been administered as an antidote, the substances must be boiled for an hour or two with potassium carbonate (not the hydroxid), filtered, and the filtrate treated as above. In the solutions so obtained, oxalic acid is characterized by the tests given above. The urine is also to be examined microscopically for crystals of calicum oxalate. The stomach may contain small quantities of oxalates as normal constituents of certain foods.

Malonic acid—$CH_2\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right.$—is a product of the oxidation of malic acid, or of normal propyl glycol. It forms large prismatic crystals, soluble in water, alcohol and ether; fusible at 132° (269°.6 F.), and decomposed at about 150° (302° F.) into acetic acid and carbon dioxid.



Succinic acid—$\begin{matrix}CH_2\text{—}COOH\\|\\CH_2\text{—}COOH\end{matrix}$—118—exists in amber, coal, fossil wood, and in small quantity in animal and vegetable tissues. Its presence has been detected in the normal urine after the use of fruits and of asparagus, in the parenchymatous fluids of the spleen, thyroid, and thymus, and in the fluids of hydrocele and of hydatid cysts. It is also formed in small quantity during alcoholic fermentation; as a product of oxidation of many fats and fatty acids; and by synthesis from ethylene cyanid.

It may be obtained by dry distillation of amber, or, preferably, by the fermentation of malic acid.

It crystallizes in large prisms or hexagonal plates, which are colorless, odorless, permanent in air, acid in taste, soluble in water, sparingly so in ether and in cold alcohol. It fuses at 180° (356° F.), and distils with partial decomposition at 235° (455° F.). It withstands the action of oxidizing agents; reducing agents convert it into the corresponding acid of the fatty series, butyric acid; with Br it forms products of substitution; H_2SO_4 is without action upon it; phosphoric anhydrid removes H_2O and converts it into **succinic anhydrid, $C_4H_4O_3$.**

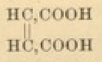
Isosuccinic acid—$CH_3-CH\left\langle\begin{array}{l}COOH\\COOH\end{array}\right.$—is formed by the action of hydrating agents upon cyanopropionic acid. It forms prismatic crystals, fusible at 130° (266° F.), and is decomposed at higher temperatures into propionic acid and carbon dioxid.

UNSATURATED ACIDS $C_nH_{2n-4}O_4$.

These acids contain two atoms of H less than the corresponding acids of the oxalic series, like which, they are dibasic. In the higher terms there are many instances of isomerism, as shown in the formulæ of the derivatives of aconitic acid given below.

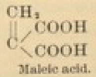
They are obtainable by the action of KI upon the dibrominated derivatives of the acids of the oxalic series.

Fumaric and **Maleic Acids—$C_4H_4O_4$**—are produced together by the dry distillation of malic acid, by loss of the elements of a molecule of water. The difference in their molecular structure is shown by the formulæ:



$$\begin{array}{l}HC,COOH\\ \|\\ HC,COOH\end{array}$$

Fumaric acid.

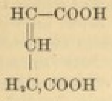


$$\begin{array}{l}CH_2\\ \|\\ C\left\langle\begin{array}{l}COOH\\COOH\end{array}\right.\end{array}$$

Maleic acid.

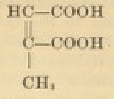
Fumaric acid exists in many plants, is a solid, crystalline body, sparingly soluble in cold, readily soluble in hot water. Nascent H converts it into succinic acid.

Mesaconic, Citraconic, Itaconic and Paraconic Acids—$C_5H_6O_4$— may be considered as being the homologues, the first two of fumaric acid, the last two of maleic acid :



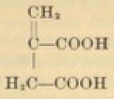
$$\begin{array}{l} \mathrm{HC{-}COOH} \\ \| \\ \mathrm{CH} \\ | \\ \mathrm{H_2C,COOH} \end{array}$$

Mesaconic acid.



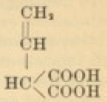
$$\begin{array}{l} \mathrm{HC{-}COOH} \\ \| \\ \mathrm{C{-}COOH} \\ | \\ \mathrm{CH_3} \end{array}$$

Citraconic acid.



$$\begin{array}{l} \mathrm{CH_2} \\ \| \\ \mathrm{C{-}COOH} \\ | \\ \mathrm{H_2C{-}COOH} \end{array}$$

Itaconic acid.



$$\begin{array}{l} \mathrm{CH_2} \\ \| \\ \mathrm{CH} \\ | \\ \mathrm{HC}\begin{array}{l}\diagup \mathrm{COOH} \\ \diagdown \mathrm{COOH}\end{array} \end{array}$$

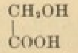
Paraconic acid.

Citraconic and itaconic acids are produced by the action of heat upon citric acid. Mesaconic and paraconic by the action of heat upon citrachloropyrotartaric and itachloropyrotartaric acids respectively.

COMPOUND ETHERS OF THE ACIDS OF THE SERIES

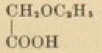
$C_nH_{2n}O_3$ AND $C_nH_{2n-2}O_4$.

The members of both of these series contain two atoms of H replaceable by alcoholic radicals. In those of the series $C_nH_{2n}O_3$ (with the exception of carbonic acid), being monobasic, although diatomatic, it is not immaterial which H is so replaced. If it be that of the group CH_2OH, the resulting compound is a monobasic acid, in which the H of the group COOH may be replaced by another alcoholic radical to form a neutral ether of the new acid. If, on the other hand, the H of the group COOH be first replaced, a neutral compound ether is formed. In the members of the series $C_nH_{2n-2}O_4$, which are dibasic, the substitution of an alcoholic radical for the H of either group COOH produces a monobasic acid, in which the H of the other COOH may be replaced by another radical to form a neutral ether. The following formulæ indicate the differences in the nature of these compounds :



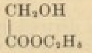
$$\begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{COOH} \end{array}$$

Glycolic acid.



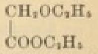
$$\begin{array}{l} \mathrm{CH_2OC_2H_5} \\ | \\ \mathrm{COOH} \end{array}$$

Ethylglycolic acid.



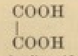
$$\begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{COOC_2H_5} \end{array}$$

Ethyl glycolate.



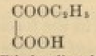
$$\begin{array}{l} \mathrm{CH_2OC_2H_5} \\ | \\ \mathrm{COOC_2H_5} \end{array}$$

Ethyl ethylglycolate.



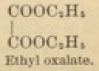
$$\begin{array}{l} \mathrm{COOH} \\ | \\ \mathrm{COOH} \end{array}$$

Oxalic acid.



$$\begin{array}{l} \mathrm{COOC_2H_5} \\ | \\ \mathrm{COOH} \end{array}$$

Ethyloxalic acid.



$$\begin{array}{l} \mathrm{COOC_2H_5} \\ | \\ \mathrm{COOC_2H_5} \end{array}$$

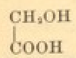
Ethyl oxalate.

ALDEHYDES AND ANHYDRIDS OF THE SERIES

$C_nH_{2n}O_3$ AND $C_nH_{2n-2}O_4$.

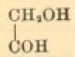
In treating of the monoatomic compounds, it was stated that substances existed corresponding to the fatty acids, known as aldehydes and anhydrids, the former differing from the acids in that they contained the group COH instead of COOH ; the latter being the oxids of the acid radicals. Similar compounds exist corresponding to the acids of these two series.

The aldehydes corresponding to the series $C_nH_{2n}O_3$ contain the group COH in place of the group COOH, and as they also contain the group CH_2OH, they are possessed of the double function of primary alcohol and aldehyde. Those of the series $C_nH_{2n-2}O_4$ form two series ; in one of which only one of the groups COOH is deoxidized to COH ; in the other, both. Those of the first series, still containing a group COOH, are monobasic acids as well as aldehydes :



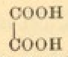
$\begin{array}{c} CH_2OH \\ | \\ COOH \end{array}$

Glycolic acid.



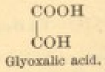
$\begin{array}{c} CH_2OH \\ | \\ COH \end{array}$

Glycolic aldehyde.



$\begin{array}{c} COOH \\ | \\ COOH \end{array}$

Oxalic acid.



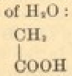
$\begin{array}{c} COOH \\ | \\ COH \end{array}$

Glyoxalic acid.

$\begin{array}{c} COH \\ | \\ COH \end{array}$

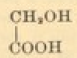
Glyoxol.

While the anhydrids of the fatty series may be considered as derived from the acids by the subtraction of H_2O from two molecules of the acid ; those of both the series of acids under consideration are derived from a single molecule of the acid by the subtraction of H_2O :



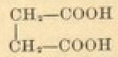
$\begin{array}{c} CH_3 \\ | \\ COOH \end{array}$

Acetic acid.



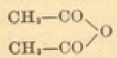
$\begin{array}{c} CH_2OH \\ | \\ COOH \end{array}$

Glycolic acid.



$\begin{array}{l} CH_2{-}COOH \\ | \\ CH_2{-}COOH \end{array}$

Succinic acid.

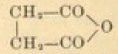


$\begin{array}{l} CH_3{-}CO \\ CH_3{-}CO \end{array}\!\!>O$

Acetic anhydrid.

$\begin{array}{l} CH_2 \\ | \\ CO \end{array}\!\!>O$

Glycolic anhydrid.



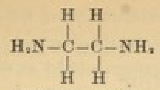
$\begin{array}{l} CH_2{-}CO \\ | \\ CH_2{-}CO \end{array}\!\!>O$

Succinic anhydrid.

DIAMINS AND TRIAMINS.

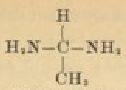
The **diamins** are derived from a double molecule of NH_3, or of ammonium hydroxid, by the substitution of the diatomic radicals of the glycols (hydrocarbons of the series C_nH_{2n}) for an equivalent number of H atoms.

When it is considered that in the formation of these substances any number of groups C_nH_{2n} of different constitution may be introduced between two NH_2 groups, thus:



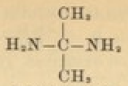
$H_2N-CH_2-CH_2-NH_2$

Dimethylendiamin.



$H_2N-CH(CH_3)-NH_2$

Ethylendiamin.



$H_2N-C(CH_3)_2-NH_2$

Propylendiamin.

that the remaining hydrogen atoms may be replaced by univalent or bivalent radicals; that the H atoms may be replaced by OH, etc.; and finally that similar compounds of P, As and Sb exist, it is not astonishing that the study of the great number of substances, the possibility of whose existence is thus indicated, is still in its infancy.

Among the diamins are included several of the alkaloidal products of putrefaction known as **ptomains** (see pp. 276; 334).

Trimethylendiamin—$H_2N-(CH_2)_3-NH_2$—is said to have been obtained from the cultures of the comma bacillus.

Putrescin — Tetramethylendiamin? — $H_2N-(CH_2)_4-NH_2$ — is produced along with cadaverin during the putrefaction of muscular tissue, internal organs of man and animals, and of fish, and in the culture media of the comma bacillus from three days to four months. The free base is a colorless liquid, having a seminal odor, which absorbs CO_2 from the air and unites with acids to form crystalline salts. It is not actively poisonous.

Cadaverin—Pentamethylendiamin—$H_2N-(CH_2)_5-NH_2$—is isomeric with neuridin and is produced during the later stages of putrefaction of many animal tissues, the cholin disappearing as this and the other diamins are formed. The free base is a clear syrupy liquid, having a strong, disagreeable odor, resembling that of coniin, boils at 175°, and fumes in air. It absorbs CO_2 rapidly with formation of a crystalline carbonate. Its salts are crystalline. The chlorid on dry distillation is decomposed into ammonium chlorid and piperidin (*q. v.*).

Neuridin—$C_5H_{14}N_2$—a diamin of undetermined constitution, is produced, along with cholin (*q. v.*), during the earlier stages of putrefaction, particularly of gelatinoid substances, and increases in quantity as putrefaction advances, while the quantity of cholin diminishes. The free base is a gelatinous substance, having a very marked seminal odor, readily soluble in water, insoluble in alcohol and in ether. Its chlorid is crystalline and very soluble in water. It seems to be non-poisonous when pure.

Saprin—$C_5H_{14}N_2$—another diamin of undetermined constitution, has been obtained from putrid spleens and livers after three weeks' putrefaction.

(See Ptomains, pp. 276, 334, 424, 470.)

Among the diamins are included the **amidins**, having the constitution $R—C\begin{cases}NH\\NH_2\end{cases}$, in which R is a hydrocarbon radical; and these, on oxidation, yield a class of substances known as **amidoxims**, having the constitution $R—C\begin{cases}NOH\\NH_2\end{cases}$.

The **guanidins** are triamins, more or less modified by substitution. The type of the group is

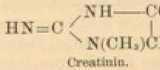
Guanidin—Carbotriamin—CH_5N_3—first obtained by oxidation of guanin (see p. 352). Its synthesis has been accomplished by heating together ethyl orthocarbonate, $C(OC_2H_5)_4$, and NH_3. It is a crystalline substance, which absorbs CO_2 and H_2O from the air and forms crystalline salts. Some of its derivatives are important physiologically.

Methyl-guanidin — Methyluramin — $HN - C(NH_2)NH(CH_3)$ — was first obtained by the oxidation of creatin and of creatinin (see below). It has also been obtained as a product of putrefaction of muscular tissue at a low temperature in closed vessels, when it probably results from the decomposition of creatin. It is a colorless, crystalline, deliquescent, strongly alkaline substance, and is highly poisonous.

The relations of guanidin and methyl-guanidin to each other and to creatin and creatinin is shown by the following formulæ:

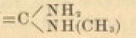
$$HN=C\begin{cases}NH_2\\NH_2\end{cases}$$

Guanidin.



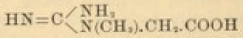
$$HN=C\begin{cases}NH—CO\\N(CH_3)CH_2\end{cases}$$

Creatinin.



$$HN=C\begin{cases}NH_2\\NH(CH_3)\end{cases}$$

Methyl-guanidin.



$$HN=C\begin{cases}NH_2\\N(CH_3).CH_2.COOH\end{cases}$$

Creatin.

Creatin—$C_4H_9N_3O_2$ + Aq—is, as is shown by the above graphic formula, a complex amido-acid. It is a normal constituent of the juices of muscular tissue, brain, blood, and amniotic fluid.

It is best obtained from the flesh of the fowl, which contains 0.32 per cent., or from beef-heart, which contains 0.14 per cent. It is soluble in boiling H_2O and in alcohol, insoluble in ether; crystallizes in brilliant, oblique, rhombic prisms; neutral, tasteless, loses aq at 100° (212° F.); fuses and decomposes at higher temperatures. When long heated with H_2O or treated with concentrated acids, it loses H_2O, and is converted into creatinin. Baryta water decomposes it into sarcosin and urea. It is not precipitated by silver nitrate, except when it is in excess and in presence of a small quantity of potassium hydroxid. The white precipitate so obtained is soluble in excess of potash, from which a jelly separates, which turns black, slowly at ordinary temperatures, rapidly at 100° (212° F.). A white precipitate, which turns black when heated, is also formed when a solution of creatin is similarly treated with mercuric chlorid and potash.

Creatinin—$C_4H_7N_3O$—113—a product of the dehydration of creatin, is a normal and constant constituent of the urine and amniotic fluid, and also exists in the blood and muscular tissue.

It crystallizes in oblique, rhombic prisms, soluble in H_2O and in hot alcohol, insoluble in ether. It is a strong base, has an alkaline taste and reaction; expels NH_3 from the ammoniacal salts, and forms well-defined salts, among which is the double chlorid of zinc and creatinin, $(C_4H_7N_3O)_2ZnCl_2$, obtained in very sparingly soluble, oblique prismatic crystals, when alcoholic solutions of creatinin and zinc chlorid are mixed.

The quantity of creatinin eliminated is slightly greater than that of uric acid, 0.6–1.3 gram (9.25–20 grains) in 24 hours. It is not increased by muscular exercise, but is diminished in progressive muscular atrophy. It is obtained from the urine by precipitation with zinc chlorid.

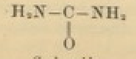
Cruso-creatinin — $C_5H_8N_4O$ — is an orange-yellow, crystalline solid, alkaline in reaction; **Xantho-creatinin—$C_5H_{10}N_4O$—**is in yellow crystalline plates; **Amphi-creatinin—$C_9H_{19}N_7O_4$—**forms yellowish-white prismatic crystals. These are basic substances, forming crystalline chlorids and belonging to the class of **leucomains,** which include alkaloidal substances produced by physiological processes. (See p. 470.) They are obtained from the juices of muscular tissue, and from Liebig's meat extract, in which they accompany creatin and creatinin.

DIAMIDS—IMIDS—AND CARBAMIC ACIDS.

Among these substances, derivable from the acids of the series $C_nH_{2n}O_2$ and $C_nH_{2n-2}O_4$, are several of great medical interest.

The **diamids** correspond to the diamins (see p. 332), from which they differ in that the substituted groups are oxidized in place of hydrocarbon. The **imids** differ from the secondary monamids (see p. 278) in that the group NH is attached to a bivalent group in place of to two univalent groups. The **-amic acids** are dibasic acids of the series mentioned above in which an OH is replaced by NH_2.

The constitution and relations of these bodies are shown by the following graphic formulæ of those derived from carbonic acid:

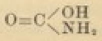


$$H_2N-\underset{\underset{O}{\|}}{C}-NH_2$$

Carbamid.
Primary diamid.

$O=C=NH$

Carbimid.
Imid—Secondary monamid.



$$O=C\begin{matrix}\diagup OH\\ \diagdown NH_2\end{matrix}$$

Carbamic acid.

Carbimid—CONH—is identical with cyanic acid (p. 295).

Carbamid—Urea—$H_2N-CO-NH_2$—60—does not occur in the vegetable world. It exists principally in the urine of the mammalia; also in smaller quantity in the excrements of birds, fishes, and some reptiles; in the mammalian blood, chyle, lymph, liver, spleen, lungs, brain, vitreous and aqueous humors, saliva, perspiration, bile, milk, amniotic and allantoic fluids, muscular tissue, and in serous fluids (see below).

It is formed—(1.) As a product of the decomposition of uric acid, usually by oxidation:

$$\underset{\text{Uric acid.}}{C_5H_4N_4O_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Oxygen.}}{O} = \underset{\text{Urea.}}{CON_2H_4} + \underset{\text{Alloxan.}}{C_4H_2N_2O_4}$$

(2.) By the oxidation of oxamid.

(3.) By the action of caustic potassa upon creatin:

$$\underset{\text{Creatin.}}{C_4H_9N_3O_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Urea.}}{CON_2H_4} + \underset{\text{Sarcosin.}}{C_3H_7NO_2}$$

4.) By the limited oxidation of albuminoid substances, by potassium permanganate, and during the processes of nutrition.

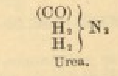
(5.) By the action of carbon oxychlorid on dry ammonia.

(6.) By the action of ammonium hydroxid on ethyl carbonate at 180° (356° F.).

(7.) By heating ammonium carbonate in sealed tubes to 130° (266° F.).

(8.) By the slow evaporation of an aqueous solution of hydrocyanic acid.

(9.) By the molecular transformation of its isomerid, ammonium isocyanate:



$$\underset{\text{Ammonium cyanate.}}{\begin{matrix} CN \\ | \\ O\,(NH_4) \end{matrix}} = \underset{\text{Urea.}}{\left.\begin{matrix} (CO) \\ H_2 \\ H_2 \end{matrix}\right\} N_2}$$

It is obtained:

(1.) *From the urine.*—Fresh urine is evaporated to the consistency of a syrup over the water-bath; the residue is cooled and mixed with an equal volume of colorless HNO_3 of sp. gr. 1.42; the crystals are washed with a small quantity of cold H_2O, and dissolved in hot H_2O; the solution is decolorized, so far as possible, without boiling, with animal charcoal, filtered, and neutralized with potassium carbonate; the liquid is then concentrated over the water-bath, and decanted from the crystals of potassium nitrate which separate; then evaporated to dryness over the water-bath, and the residue extracted with strong, hot alcohol; the alcoholic solution, on evaporation, leaves the urea more or less colored by urinary pigment.

(2.) *By synthesis.*—Urea is more readily obtained in a state of purity from potassium isocyanate. This is dissolved in cold H_2O, and dry ammonium sulfate is added to the solution. Potassium sulfate crystallizes out, and is separated by decanting the liquid, which is then evaporated over the water-bath, fresh quantities of potassium sulfate crystallizing and being separated during the first part of the evaporation; the dry residue is extracted with strong, hot alcohol; this, on evaporation, leaves the urea, which, by a second crystallization from alcohol, is obtained pure.

Urea crystallizes from its aqueous solution in long, flattened prisms, and by spontaneous evaporation of its alcoholic solution in quadratic prisms with octahedral ends. It is colorless and odorless; has a cooling, bitterish taste, resembling that of saltpetre; is neutral in reaction; soluble in one part of H_2O at 15° (59° F.), the solution being attended with diminution of temperature; soluble in five parts of cold alcohol (sp. gr. 0.816) and in one part of boiling alcohol; very sparingly soluble in ether. When its powder is mixed with that of certain salts, such as sodium sulfate, the Aq of the salt separates, and the mass becomes soft or even liquid. When pure it is not deliquescent, but is slightly hygrometric. Fuses at 130° (266° F.).

Heated a few degrees above 130° (266° F.) urea boils, giving off ammonia and ammonium carbonate, and leaves a residue of **ammelid**, $\mathbf{C_6H_9N_9O_3}$. When heated to 150°–170° (302°–338° F.), it is decomposed, leaving a mixture of ammelid, cyanuric acid, and biuret:

$$\underset{\text{Urea.}}{8CON_2H_4} = \underset{\text{Carbon dioxid.}}{2CO_2} + \underset{\text{Ammelid.}}{C_6H_9N_9O_3} + \underset{\text{Ammonia.}}{7NH_3} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\text{Urea.}}{3CON_2H_4} = \underset{\text{Cyanuric acid.}}{C_3O_3N_3H_3} + \underset{\text{Ammonia.}}{3NH_3}$$

$$\underset{\text{Urea.}}{2CON_2H_4} = \underset{\text{Biuret.}}{C_2H_5N_3O_2} + \underset{\text{Ammonia.}}{NH_3}$$

If urea is maintained at 150°–170° (302°–338° F.) for some time, a dry, grayish mass remains, which consists principally of cyanuric acid. In this reaction, the volatile products contain urea, not that that substance is volatile, but because a portion of the cyanuric acid and ammonia unite to regenerate urea by the reverse action to that given above.

Dilute aqueous solutions of urea are not decomposed by boiling; but if the solution be concentrated, or the boiling prolonged for a long time, the urea is partially decomposed into CO_2 and NH_3. The same decomposition takes place more rapidly and completely when a solution of urea is heated under pressure to 140° (284° F.). A pure aqueous solution of urea is not altered by exposure to filtered air. If urine be allowed to stand, putrefactive changes take place under the influence of a peculiar, organized ferment, or of a diastase-like body which is a constituent of normal urine.

Chlorin decomposes urea with production of CO_2, N, and HCl. Solutions of the alkaline hypochlorites and hypobromites effect a similar decomposition in the presence of an excess of alkali, according to the equation :

$$\underset{\text{Urea.}}{CON_2H_4} + \underset{\text{Sodium hypochlorite.}}{3NaClO} = \underset{\text{Carbon dioxid.}}{CO_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Nitrogen.}}{N_2} + \underset{\text{Sodium chlorid.}}{3NaCl}$$

Upon this decomposition are based the quantitative processes of Knop, Hüfner, Yvon, Davy, Leconte, etc.

Nitrous acid, or HNO_3 charged with nitrous vapors, decomposes urea according to the equation :

$$\underset{\text{Urea.}}{CON_2H_4} + \underset{\text{Nitrogen trioxid.}}{N_2O_3} = \underset{\text{Carbon dioxid.}}{CO_2} + \underset{\text{Nitrogen.}}{N_4} + \underset{\text{Water.}}{2H_2O} \quad (1)$$

or the equation :

$$\underset{\text{Urea.}}{2CON_2H_4} + \underset{\text{Nitrogen trioxid.}}{N_2O_3} = \underset{\text{Ammonium carbonate.}}{CO_3(NH_4)_2} + \underset{\text{Nitrogen.}}{N_4} + \underset{\text{Carbon dioxid.}}{CO_2} \quad (2)$$

If the mixture be made in the cold, of one molecule of nitrogen trioxid to two molecules of urea, the decomposition is that indicated by Equation 2. If, on the other hand, the trioxid be gradually added to the previously warmed urea solution in the same proportion, half the urea is decomposed while the remainder is left unaltered, and, upon the addition of a further and sufficient quantity of the trioxid, all the urea is decomposed according to Equation 1. Upon this reaction are based the processes of Gréhant, Boymond, Draper, etc.

When heated with mineral acids or alkalies, urea is decomposed with formation of CO_2 and NH_3; if the decomposing agent be an acid, CO_2 is given off, and an ammoniacal salt remains; if an alkali, a carbonate of the alkaline metal remains, and NH_3 is given off. Upon this decomposition are based the processes of Heintz and Ragsky, Bunsen, etc.

Urea forms definite compounds, not only with acids, but also with certain oxids and salts. Of the compounds which it forms with acids, the most important are those with nitric and oxalic acids.

Urea nitrate—CON_2H_4,HNO_3—is formed as a white, crystalline mass when a concentrated solution of urea is treated, in the cold, with HNO_3. It is much less soluble in H_2O than is urea, especially in the presence of an excess of HNO_3. It decomposes the carbonates with liberation of urea. If a solution of urea nitrate be evaporated over the water-bath, it is decomposed, bubbles of gas being given off beyond a certain degree of concentration, and large crystals of urea, covered with smaller ones of urea nitrate, separate.

Urea oxalate—$2CON_2H_4,H_2C_2O_4$—separates as a fine, crystalline powder from mixed aqueous solutions of urea and oxalic acid of sufficient concentration. It is acid in taste and reaction, less soluble in cold H_2O than the nitrate, and less soluble in the presence of an excess of oxalic acid than in pure H_2O. Its solution may be evaporated at the temperature of the water-bath without suffering decomposition.

Of the compounds of urea with oxids, the most interesting are those with mercuric oxid, three in number:

α. $CON_2H_4,2HgO$ is formed by gradually adding mercuric oxid to a solution of urea, heated to near its boiling-point; the filtered liquid, on standing twenty-four hours, deposits crystalline crusts of the above composition.

β. $CON_2H_4,3HgO$ is formed as a gelatinous precipitate when mercuric chlorid solution is added to a solution of urea containing potassium hydroxid.

γ. $CON_2H_4,4HgO$ is formed as a white, amorphous precipitate when a dilute solution of mercuric nitrate is gradually added to a dilute alkaline solution of urea, and the excess of acid neutralized from time to time. A yellow tinge in the precipitate indicates the formation of mercuric subnitrate after the urea has been all precipitated (Liebig's process).

Of the compounds of urea with salts, that with sodium chlorid is the only one of importance:

$CON_2H_4,NaCl,H_2O$.—It is obtained in prismatic crystals when solutions of equal molecules of urea and sodium chlorid are evaporated together. It is deliquescent and very soluble in water. Its solution, when mixed with solution of oxalic acid, only forms urea oxalate after long standing, or on evaporation.

Urea is a constant constituent of normal mammalian blood and urine, and is the chief product of the oxidation of albuminoid substances which occur in the body; the bulk of the N assimilated from the food ultimately making its exit from the body in the form of urea in the urine.

The determinations of the amount of urea in the blood and fluids other than the urine are, owing to imperfections in the processes of analysis, not as accurate as could be desired, the error being generally a minus one.

The average proportion of urea in parts per 1000 in animal fluids other than urine is: In blood of dog, normal, 0.24–0.53; same three hours after nephrectomy, 0.45–0.93; same twenty-seven hours later, 2.06–2.76; human blood, normal, 0.14–0.4; human placental blood, 0.28–0.62; human fœtal blood, 0.27; human blood in cholera, 2.4–3.6; human blood in Bright's, 15.0; lymph and chyle (cow), 0.19; milk, 0.13; saliva, 0.35; bile, 0.3; fluid of ascites, 0.15; perspiration, 0.38–0.88.

Under normal conditions, the quantity of urea voided in twenty-four hours is subject to considerable variations, as is shown in the subjoined table:

AMOUNT OF UREA IN HUMAN URINE—NORMAL.

	Parts per 1,000.	Grams in total urine of 24 hours.	
Urine of sp. gr. 1009.2	9.88	......	Millon.
Urine of sp. gr. 1011.6	11.39	......	Millon.
Urine of sp. gr. 1019.0	18.58	......	Boymond.
Urine of sp. gr. 1026.0	25.80	......	Millon.
Urine of sp. gr. 1027.7	29.70	......	Millon.
Urine of sp. gr. 1028.0	27.08	......	Boymond.
Urine of sp. gr. 1029.0	31.77	......	Millon.
Urine of adult male (average)	30.0	......	Berzelius.
Urine of adult male (average)	....	28.052	Lecanu.
Urine of adult male (average)	25–32	22–35	Neubauer.
Urine of adult male (average)	....	32–43	Kerner.
Urine of adult male (average)	23.3	35	Vogel.
Urine of adult male, animal food	....	51–92	Franque.
Urine of adult male, mixed food	....	36–38	Franque.
Urineof adult male, vegetable food	....	24–28	Franque.
Urine of adult male, non-nitrogenized food	....	16	Franque.
Urine of old men, 84–86 years	....	8.11	Lecanu.
Urine of adult female (average)	....	19.116	Lecanu.
Urine of pregnant female	....	30–38	Quinquand.
Urine of female 24 hours after delivery	....	20–22	Quinquand.
Urine of infant, first day	....	0.03–0.04	Quinquand.
Urine of infant, fifth day	....	0.12–0.15	Quinquand.
Urine of infant, eighth day	....	0.2 –0.28	Quinquand.
Urine of infant, fifteenth day	....	0.3 –0.04	Quinquand.
Urine of child four years old	....	4.505	Lecanu.
Urine of child eight years old	....	13.471	Lecanu.
Urine of boy eighteen months old	....	8–12	Harley.
Urine of girl eighteen months old	....	6–9	Harley.

The variations are produced by:

(1.) *Age.*—In new-born children the elimination of urea is insignificant. By growing children the amount voided is absolutely less than that discharged by adults, but, relatively to their weight, considerably greater; thus, Harley gives the following amounts of urea in grams for each pound of body-weight in twenty-four hours: Boy, eighteen months, 0.4; girl, eighteen months, 0.35; man, twenty-seven years, 0.25; woman, twenty-seven years, 0.20. During adult life the mean elimination of urea remains stationary, unless modified by other causes than age.

In old age the amount sinks to below the absolute quantity discharged by growing children.

(2.) *Sex.*—At all periods of life females eliminate less urea than males. The proportion given by Beigel differs slightly from that of Harley, viz.: one kilo of male, 0.35 gram urea in twenty-four hours; one kilo of female, 0.25 gram. During pregnancy females discharge more urea than males; very shortly after delivery the amount sinks to the normal, below which it passes during lactation.

(3.) *Food.*—The quantity of urea eliminated is in direct proportion to the amount of N contained in the food. The ingestion of large quantities of watery drinks increases the amount, and a contrary effect is produced by tea, coffee, and alcohol. With insufficient food the excretion of urea is diminished, although not arrested, even in extreme starvation.

(4.) *Exercise.*—The question whether the elimination of urea is increased during violent muscular exercise is one which has been the subject of many observations and of much discussion. An examination of the various results shows that, while the excretion of urea is slightly greater during violent exercise than during periods of rest, the increase is so insignificant in comparison to the work done, and, in some instances, to the loss of body-weight, as to render the assumption that muscular force is the result of the oxidation of the nitrogenized constituents of muscle improbable. (See Gamgee, "Physiological Chemistry," I., pp. 385–401, for a full review of the subject.)

The percentage of urea in the urine of the same individual is not the same at different times of the day. The minimum hourly elimination is in the morning hours; an increase begins immediately after the principal meal, and reaches its height in about six hours, when a diminution sets in and progresses to the time of the next meal. Gorup-Besanez gives a curve representing the hourly variations in the elimination of urea, which, reduced to figures, gives the following:

Hour.	Urea in Grams.	Hour.	Urea in Grams.	Hour.	Urea in Grams.
8–9 A.M.	1.5	4–5 P.M.	2.6	12–1 A.M	1.9
9–10 A.M.	1.5	5–6 P.M.	3.1	1–2 A.M	1.9
10–11 A.M.	1.4	6–7 P.M.	2.8	2–3 A.M	1.9
11 A.M.–12 M.	1.3	7–8 P.M.	2.5	3–4 A.M	1.8
12 M.–1 P.M.	1.8	8–9 P.M.	2.3	4–5 A.M	1.6
1–2 P.M.	1.9	9–10 P.M.	2.0	5–6 A.M	1.6
2–3 P.M.	2.1	10–11 P.M.	2.0	6–7 A.M	1.6
3–4 P.M.	2.3	11–12 P.M.	2.3	7–8 A.M	1.5

The total of which, however, represents a quantity above the normal.

The absolute amount of urea eliminated in twenty-four hours is increased by the exhibition of diuretics, alkalies, colchicum, turpentine, rhubarb, alkaline silicates, and compounds of antimony, arsenic, and phosphorus. It is diminished by digitalis, caffein, potassium iodid, and lead acetate; not sensibly affected by quinin.

In acute febrile diseases both the relative and absolute amounts of urea eliminated augment, with some oscillations, until the fever is at its height. There is, however, no constant relation between the amount of urea eliminated and the body temperature. During the period of defervescence, the amount of urea eliminated in twenty-four hours is diminished below the normal; during convalescence it again sowly increases. If the malady terminate in death the diminution of urea is continuous to the end. In intermittent fever the amount of urea discharged is increased on the day of the fever and diminished during the interval. In cholera, during the algid stage, the elimination of urea by the kidneys is almost completely arrested, while the quantity in the blood is greatly increased. When the secretion of urine is again established, the excretion of urea is greatly increased (60–80 grams = 926–1235 grains a day), and the abundant perspiration is also rich in urea. In cardiac diseases, attended with respiratory difficulty, but without albuminuria, the elimination of urea is diminished and that of uric acid increased. In nephritis, attended with albuminuria, the elimination of urea at first remains normal; later it diminishes, and the urea, accumulating in the blood, has been considered by many as the cause of uræmic poisoning. It appears more probable, however, that the symptoms of uræmia are due to the retention in the blood of alkaloidal poisons normally excreted in small amount. The quantity of urea in the urine is also diminished in all diseases attended with dropsical effusions; but is increased when the dropsical fluid is reabsorbed. In true diabetes the amount of urea in the urine of twenty-four hours is greater than normal. In chronic diseases the elimination of urea is below the normal, owing to imperfect oxidation.

To detect the presence of urea in a fluid, it is mixed with three to four volumes of alcohol, and filtered, after having stood several hours in the cold; the filtrate is evaporated on the water-bath, and the residue extracted with strong alcohol; the filtered alcoholic fluid is evaporated, and the residue tested as follows:

(1.) A small portion is heated in a dry test-tube to about 160° (320° F.), until the odor of ammonia is no longer observed; the residue is treated with a few drops of caustic potassa solution and one drop of cupric sulfate solution. If urea be present, the biuret resulting from its decomposition by heat causes the solution of the cupric oxid with a reddish-violet color. The same appearance is produced in solutions containing peptone.

(2.) A portion of the residue is dissolved in a drop or two of H_2O, and an equal quantity of *colorless* concentrated HNO_3 added; if urea be present in sufficient quantity there appear white, shining, hexagonal or rhombic, crystalline plates or six-sided prisms of urea nitrate.

(3.) A portion dissolved in water, as in (2), is treated with a solution of oxalic acid; rhombic plates of urea oxalate crystallize.

Determination of Quantity of Urea in Urine.—It must not be forgotten that, in all quantitative determinations of constituents of the urine, the question to be solved is not how much of that constituent is contained in a given quantity of urine, but how much of that substance the patient is discharging in a given time, usually twenty-four hours. Quantitative determinations are, therefore, in most cases, barren of useful results, unless the quantity of urine passed by the patient in twenty-four hours is known; and, in view of diurnal variations in elimination, unless the urine examined be a sample taken from the *mixed urine of twenty-four hours.*

The process giving the most accurate results is that of Bunsen, in which the urea is decomposed into CO_2 and NH_3, the former of which is weighed as barium carbonate. Unfortunately, this process requires an expenditure of time and a degree of skill in manipulation which render its application possible only in a well-appointed laboratory.

A process which is described in most text-books upon urinary analysis, and which is much used by physicians, is that of Liebig. As this method is one, however, which contains more sources of error than any other, and as it can only be made to yield approximately correct results by a very careful elimination, as far as possible, of those defects, it is not one which is adapted to the use of the physician.

Probably the most satisfactory process in the hands of the practitioner is that of Hüfner, based upon the reaction, to which attention was first called by Knop, of the alkaline hypobromites upon urea (p. 338); using, however, Dietrich's apparatus, or the more simple modification suggested by Rumpf, in place of that of Hüfner. The apparatus (Fig. 38) consists of a burette of 30–50 c.c. capacity, immersed in a tall glass cylinder filled with water, and supported in such a way as to admit of being raised or lowered at pleasure. The upper end of the burette communicates with the evolution bottle *a*, which has a capacity of 75 c.c., by means of a rubber tube.

The reagent required is made as follows: 27 c.c. of a solution of caustic soda, made by dissolving 100 grams NaHO in 250 c.c. H_2O, are brought into a glass-stoppered bottle, 2.5 c.c. bromin are added, the mixture shaken, and diluted with water to 150 c.c. The caustic soda solution may be kept in a glass-stoppered bottle whose stopper is well paraffined, but the mixture must be made up as required, a fact which, owing to the irritating character of the Br vapor, renders the use of this reagent in a physician's office somewhat troublesome. The Br is best measured by a pipette of suitable size, having a compressible rubber ball at the upper end.

To conduct a determination, about 20 c.c. of the hypobromite solution are placed in the bottle *a*; 5 c.c. of the urine to be examined are placed in the short test-tube, which is then introduced into the position shown in the figure, care being had that no urine escapes. The cork with its fittings is then introduced, the pinch-cock *b* opened, and closed again when the level of liquid in the burette is the same as that in the cylinder. The decomposing vessel *q* is then inclined so that the urine and hypobromite solution mix; the decomposition begins at once, and the evolved N passes into the burette, which is raised from time to time so as to keep the external and internal levels of water about equal; the CO_2 formed is retained by the soda solution. In about an hour (the decomposition is usually complete in fifteen minutes, but it is well to wait an hour) the height is so adjusted that the inner and outer levels of water are exactly even, and the graduation is read, while the standing of the barometer and thermometer are noted at the same time.

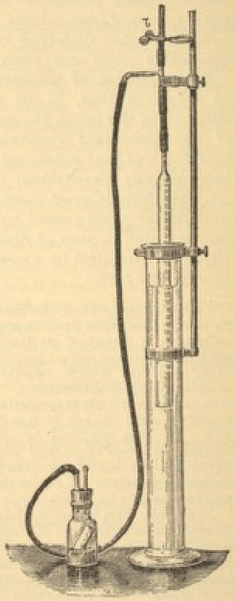


FIG 38.

In calculating the percentage of urea from the volume of N obtained, it is essential that a correction should be made for differences of temperature and pressure, without which the result from an ordinary sample of urine may be vitiated by an error of ten per cent. If, however, the temperature and barometric pressure have been noted, the correction is readily made by the use of the table (see Appendix B, III.), computed by Dietrich, giving the weight of 1 c.c. N at different temperatures and pressures.

In the square of the table in which the horizontal line of the observed temperature crosses the vertical line of the observed barometric pressure will be found the weight, in milligrams, of a c.c. of N; this, multiplied by the observed volume of N, gives the weight of N produced by the decomposition of the urea contained in 5 c.c. urine. But as 60 parts urea yield 28 parts N, the weight of N, multiplied by 2.14, gives the weight of urea in milligrams in

5 c.c. urine. This quantity, multiplied by twice the amount of urine in 24 hours, and divided by 10,000, gives the amount of urea eliminated in 24 hours in grams. If the result be desired in grains the amount in grams is multiplied by 15.434.

Example.—5 c.c. urine decomposed; barometer = 736 mm.; thermometer = 10°; burette reading before decomposition = 64.2; same after decomposition = 32.6: c.c. N collected = 31.6. From the table 1 c.c. N at 10° and 736 mm BP weighs 1.1593. The patient passes 1500 c.c. urine in 24 hours:

$$31.6 \times 1.1593 = 36.6339 = \text{milligr. N in 5 c.c. urine.}$$

$$36.6339 \times 2.14 = 78.3965 = \text{milligr. urea in 5 c.c. urine.}$$

$$\frac{78.3965 \times 3000}{10.000} = 23.519 = \text{grams urea in 24 hours.}$$

$$23.519 \times 15.434 = 362.99 = \text{grains urea in 24 hours.}$$

In using this process it is well to have the urea solution as near the strength of one per cent. as possible; therefore if the urine be concentrated, it should be diluted. Even when carefully conducted, the process is not strictly accurate; creatinin and uric acid are also decomposed with liberation of N, thus causing a slight plus error: on the other hand, a minus error is caused by the fact that in the decomposition of urea by the hypobromite, the theoretical result is never obtained within about eight per cent. in urine. These errors may be rectified to a great extent by multiplying the result by 1.044.

A process which does not yield as accurate results as the preceding, but which is more easy of application, is that of Fowler, based upon the loss of sp. gr. of the urine after the decomposition of its urea by hypochlorite. To apply this method the sp. gr. of the urine is carefully determined, as well as that of the liq. sodæ chlorinatæ (Squibb's). One volume of the urine is then mixed with exactly seven volumes of the liq. sod. chlor., and, after the first violence of the reaction has subsided, the mixture is shaken from time to time during an hour, when the decomposition is complete; the sp. gr. of the mixture is then determined. As the reaction begins instantaneously when the urine and reagent are mixed, the sp. gr. of the mixture must be calculated by adding together once the sp. gr. of the urine and seven times the sp. gr. of the liq. sod. chlor., and dividing the sum by 8. From the quotient so obtained the sp. gr. of the mixture after decomposition is subtracted; every degree of loss in sp. gr. indicates 0.7791 gram of urea in 100 c.c. of urine. The sp. gr. determinations must all be made at the same temperature; and that of the mixture only when the evolution of gas has ceased entirely.

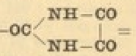
Finally, when it is only desired to determine whether the urea is greatly in excess or much below the normal, advantage may be taken of the formation of crystals of urea nitrate. Two samples of the urine are taken, one of 5 drops and one of 10 drops; the latter is evaporated, at a low temperature, to the bulk of the former, and cooled; to each, three drops of colorless HNO_3 are added. If crystals do not form within a few moments in the concentrated sample, the quantity of urea is below the normal; if they do in the unconcentrated sample, it is in excess. In using this very rough method, regard must be had to the quantity of urine passed in 24 hours; the above applies to the normal amount of 1200 c.c.; if the quantity be greater or less, the urine must be concentrated or diluted in proportion. The *amorphous* white ppt. caused by HNO_3 in albuminous urine must not be mistaken for the *crystalline* deposit of urea nitrate.

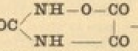
COMPOUND UREAS.

These compounds, which are exceedingly numerous, may be considered as formed by the substitution of one or more alcoholic or acid radicals for one or more of the remaining H atoms of urea.

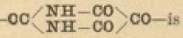
Those containing alcoholic radicals may be obtained, as urea is obtained from ammonium isocyanate, from the cyanate of the corresponding compound ammonium; or by the action of NH_3, or of the compound ammonias, upon the cyanic ethers.

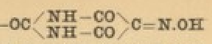
Those containing acid radicals have received the distinctive name of ureids. Of these some are **monureids,** derived from a single molecule of urea, others **diureids,** derived from two molecules of urea. Among the monureids are the following:

Oxalylurea = Parabanic acid— $\mathrm{OC}\left\langle\begin{array}{l}\mathrm{NH-CO}\\ \qquad\quad|\\ \mathrm{NH-CO}\end{array}\right.$ $= C_3H_2N_2O_3$—which is urea in which H_2 has been replaced by the bivalent radical of oxalic acid (C_2O_2)=*oxalyl.* It is produced by oxidizing uric acid or alloxan with hot HNO_3, or may be formed synthetically from pyruvic diureid.

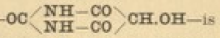
Oxaluric acid— $\mathrm{OC}\left\langle\begin{array}{l}\mathrm{NH-O-CO}\\ \qquad\qquad\;|\\ \mathrm{NH \;—\; CO}\end{array}\right.$ —occurs in its ammonium salt, as a normal constituent, in small quantity, in human urine. It may be obtained by heating oxalylurea with calcium carbonate.

It is a white, sparingly soluble powder, which is converted into urea and oxalic acid when boiled with water or alkalies. Its ammonium salt crystallizes in white, glistening, sparingly soluble needles. Its ready conversion into urea and oxalic acid and its formation from oxalylurea, itself a product of oxidation of uric acid, render it probable that oxaluric acid is one of the many intermediate products of the oxidation of the nitrogenous constituents of the body.

Alloxan = Oxymalonylurea— $\mathrm{OC}\left\langle\begin{array}{l}\mathrm{NH-CO}\\ \mathrm{NH-CO}\end{array}\right\rangle\mathrm{CO}$—is a product of the limited oxidation of uric acid. It has been found in the intestinal mucus in diarrhœa. It forms colorless crystals, readily soluble in H_2O. It turns red in air, and stains the skin red.



Violuric acid = Nitroso-malonylurea—$OC\langle\begin{matrix}NH-CO\\NH-CO\end{matrix}\rangle C=N.OH$—is produced, along with alloxan, by the action of nitric acid upon hydurilic acid. It forms small, readily soluble, octahedral crystals. It is a strong monobasic acid, whose salts are brilliantly colored.



Dialuric acid = Tartronylurea—$OC\langle\begin{matrix}NH-CO\\NH-CO\end{matrix}\rangle CH.OH$—is a dibasic acid produced by the reduction of alloxan. Nitrous acid converts it into allantoïn. By boiling with H_2O it is converted into *tartronamic acid.*

The **diureids** may be considered as consisting of two molecules of urea united together by loss of hydrogen and interposition of a group of proper valence (see formulæ of uric acid, etc., below). The best known of the group is:

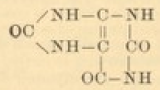
Uric acid—Lithic acid—$C_5H_4N_4O_3H_2$—168.—It exists in the urine of man and of the carnivora, and in that of the herbivora when, during early life or starvation, they are for the time being carnivora; as a constituent of urinary calculi; and, very abundantly, in the excrement of serpents, tortoises, birds, mollusks, and insects, also in guano. It is present in very small quantity in the blood of man, more abundantly in that of gouty patients and in that of birds. The so-called "chalk-stones" deposited in the joints of gouty patients are composed of sodium urate. It also occurs in the spleen, lungs, liver, pancreas, brain, and muscular fluid.

Although uric acid may be obtained from calculi, urine, and guano, the source from which it is most readily obtained is the solid urine of large serpents, which is composed almost entirely of uric acid and the acid urates of sodium, potassium, and ammonium. This is dried, powdered, and dissolved in a solution of potassium hydroxid; the solution is boiled until all odor of NH_3 has disappeared. Through the filtered solution CO_2 is passed, through a wide tube, until the precipitate, which was at first gelatinous, has become granular and sinks to the bottom; the acid potassium urate so formed is collected on a filter, and washed with cold H_2O until the wash-water becomes turbid when added to the first filtrate; the deposit is now dissolved in hot dilute caustic potassa solution, and the solution filtered hot into HCl, diluted with an equal volume of H_2O. The precipitated uric acid is washed and dried.

Uric acid, when pure, crystallizes in small, white, rhombic, rectangular or hexagonal plates, or in rectangular prisms, or in dendritic crystals of a hydrate, $C_5H_4N_4O_3,2H_2O$. As crystallized from urine it is more or less colored with urinary pigments, and forms rectangular or rhombic plates, usually with the angles rounded so as to form lozenges, which are arranged in bundles, daggers, crosses, or dendritic groups, sometimes of considerable size. It is almost insoluble in H_2O, requiring for its solution 1900 parts of boiling H_2O and 15,000 parts of cold H_2O; insoluble in alcohol and ether; its aqueous solution is acid to test-paper; cold HCl dissolves it more readily than H_2O, and on evaporation deposits it in rectangular plates. It is tasteless and odorless.

When heated, it is decomposed without fusion or sublimation. Its constitution has been recently established (see below), and shows it to be the diureid of tartronic acid. Heated in Cl it yields cyanuric acid and HCl. When Cl is passed for some time through H_2O holding uric acid in suspension, alloxan, parabanic and oxalic acids, and ammonium cyanate are formed. Similar decomposition is produced by Br and I. It is simply dissolved by HCl. It is dissolved by H_2SO_4; from a hot solution in which a deliquescent, crystalline compound, $C_5H_4N_4O_3$, $4H_2SO_4$ is deposited; it is partly decomposed by H_2SO_4 at 140° (284° F.). It dissolves in cold HNO_3 with effervescence and formation of alloxan, alloxantin, and urea; with hot HNO_3 parabanic acid is produced. Solutions of the alkalies dissolve uric acid with formation of neutral urates. It is decomposed by sodium hypobromite, giving up half of its N in the cold and the whole if heated. It reduces solutions of $CuSO_4$.

The synthesis of uric acid has been accomplished by heating together a mixture of glycocol and urea at 230° (446° F)., and purifying the product. From this synthesis and from the products of decomposition of uric acid its constitution has been established. Its molecule consists of two urea remainders, $CO(NH)_2$, united unsymmetrically by a group of three carbon and one oxygen atoms, in the manner represented by the formula:



Uric acid is dibasic, forming two series of salts.

Ammonium urates.—The neutral salt, $C_5H_2N_4O_3(NH_4)_2$, is unknown. The acid salt, $C_5H_3N_4O_3(NH_4)$, exists as a constituent of the urine of the lower animals, and occurs, accompanying other urates and free uric acid, in urinary sediments and calculi. Sediments of this salt are rust-yellow or pink in color, amorphous, or composed of globular masses, set with projecting points, or elongated dumb-bells, and are formed in alkaline urine. It is very sparingly soluble in H_2O; soluble in warm HCl, from which solution crystalline plates of uric acid are deposited.

Potassium urates.—The neutral salt, $C_5H_2N_4O_3K_2$, is obtained when a solution of potassium hydroxid, free from carbonate, is saturated with uric acid; the solution on concentration deposits the salt in fine needles. It is soluble in 44 parts of cold H_2O and in 35 parts of boiling H_2O. It is alkaline in taste, and absorbs CO_2 from the air.

The acid salt, $C_5H_3N_4O_3K$, is formed as a granular (at first gelatinous) precipitate when a solution of the neutral salt is treated with CO_2. It dissolves in 800 parts of cold H_2O and in 80 parts of boiling H_2O. The occurrence of potassium urates in urinary sediments and calculi is very exceptional.

Sodium urates.—The neutral salt, $C_5H_2N_4O_3Na_2$, is formed under similar conditions as the corresponding potassium salt. It forms nodular masses, soluble in 77 parts of cold H_2O and in 75 of boiling H_2O; it absorbs CO_2 from the air.

The acid salt, $C_5H_3N_4O_3Na$, is formed when the neutral salt is treated with CO_2. It is soluble in 1200 parts of cold H_2O and in 125 parts of boiling H_2O. It occurs in urinary sediments and calculi, very rarely crystallized. The arthritic calculi of gouty patients are almost exclusively composed of this salt, frequently beautifully crystallized.

Calcium urates.—The neutral salt, $C_5H_2N_4O_3Ca$, is obtained by dropping a solution of neutral potassium urate into a boiling solution of calcium chlorid until the precipitate is no longer redissolved, and then boiling for an hour. A granular powder, soluble in 1500 parts of cold H_2O and in 1440 parts of boiling H_2O.

The acid salt, $(C_5H_3N_4O_3)_2Ca$, is obtained by decomposing a boiling solution of acid potassium urate with calcium chlorid solution. It crystallizes in needles, soluble in 603 parts of cold H_2O and in 276 parts of boiling H_2O. It occurs occasionally in urinary sediments and calculi, and in "chalk-stones."

Lithium urates.—The acid salt, $C_5H_3N_4O_3Li$, is formed by dissolving uric acid in a warm solution of lithium carbonate. It crystallizes in needles, which dissolve in 60 parts of H_2O at 50° (122° F.) and do not separate when the solution is cooled. It is partly with a view to the formation of this, the most soluble of the acid urates, that the compounds of lithium are given to patients suffering with the uric acid diathesis.

Uric acid exists in the economy chiefly in combination as its sodium salts; it is occasionally found free, and from the probable method of its formation it is difficult to understand how all the uric acid in the economy should not have existed there free, at least at the instant of its formation. It can scarcely be doubted that uric acid is one of the products of the oxidation of the albuminoid substances—an oxidation intermediate in the production of urea; and that consequently diseases in which there is an excessive formation of uric acid, such as gout, have their origin in defective oxidation.

In human urine the quantity of uric acid varies with the nature of the food in the same manner as does urea, and in about the same proportion :

	Urea.	Uric Acid.	Proportion of Uric Acid to Urea.
Animal food...............	71.5	1.25	57.2
Mixed food................	37.0	0.76	48.7
Vegetable food............	26.0	0.50	52.0
Non-nitrogenized food	16.0	0.34	47.0

The mean elimination of uric acid in the urine is from one-thirty-fifth to one-sixtieth of that of urea, or about 0.5 to 1.0 gram (7.7–15.4 grains) in twenty-four hours. With a strictly vegetable diet the elimination of twenty-four hours may fall to 0.3 gram (4.6 grains), and with a surfeit of animal food it may rise to 1.5 gram (23 grains). The hourly elimination is increased after meals, and diminished by fasting and by muscular and mental activity.

Deposits of free uric acid occur in acid, concentrated urines. In gout the proportion of uric acid in the urine is diminished, although, owing to the small quantity of urine passed, it may be relatively great ; during the paroxysms the quantity of uric acid is increased, both relatively and absolutely. The proportion of uric acid in the blood is invariably increased in gout.

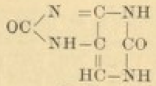
Uric acid may be recognized by its crystalline form and by the **murexid test.** The substance is moistened with HNO_3, which is evaporated nearly to dryness at a low temperature ; the cooled residue is then moistened with ammonium hydroxid solution. If uric acid be present, a yellow residue—sometimes pink or red when the uric acid was abundant—remains after the evaporation of the HNO_3, and this, on the addition of the alkali, assumes a rich purplish-red color.

To detect uric acid in the blood, about two drachms of the serum are placed in a flat glass dish and faintly acidulated with acetic acid ; a very fine fibril of linen thread is placed in the liquid, which is set aside and allowed to evaporate to the consistency of a jelly ; the fibril is then examined microscopically. If the blood contain uric acid in abnormal proportion, the thread will have attached to it crystals of uric acid.

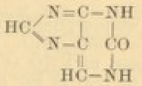
The best method for the determination of the quantity of uric acid in urine is the following : 250 c.c. of the filtered urine are acidulated with 10 c.c. of HCl, and the mixture set aside for twenty-four hours in a cool place. A small filter is washed, first with dilute HCl and then with H_2O, dried at 100° (212° F.), and weighed. At the end of twenty-four hours this filter is moistened in a funnel, and the crystals of uric acid collected upon it (those which adhere to the walls of the precipitating vessel are best separated by a small section of rubber tubing passed over the end of a glass rod, and used as a brush). No H_2O is to be used in this part of the process, the filtered urine being made use of to bring all the crystals upon the filter. The deposit on the filter is now washed with 35 c.c. of pure H_2O, added in small portions at a time; the filter and its contents are then dried and weighed. The difference between this weight and that of the dry filter alone is the weight of uric acid in 250 c.c. of urine. If from any cause more than 35 c.c. of wash-water have been used, $0^{mgr.}.043$ must be added to this weight for every c.c. of extra wash-water.

If the urine contain albumen, this must first be separated by adding two or three drops of acetic acid, heating to near 100° (212° F.), until the coagulum becomes flocculent, and filtering.

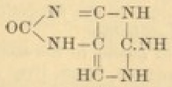
Reducing agents convert uric acid into **xanthin** and then into **hypoxanthin**, which with **guanin** and **adenin** constitute a series of leucomains, of great physiological interest. Their relations to each other and to uric acid, of which they may all be considered as products of reduction, will be understood by a comparison of the formula of uric acid (p. 348) with the following:



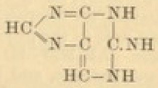
Xanthin.



Hypoxanthin.



Guanin.



Adenin.

Xanthin—*Xanthic acid*—*Urous acid*—$\mathbf{C_5H_4N_4O_2}$—152—occurs in a rare form of urinary calculus; in the pancreas, spleen, liver, thymus, and brain of mammals and fishes; and in human urine after the use of sulfur baths or inunctions.

It is formed synthetically, either by the reduction of uric acid by sodium amalgam, or by oxidation of guanin.

It is an amorphous, yellowish-white powder; very slightly soluble in cold H_2O. If dissolved in HNO_3 and the solution evaporated, xanthin leaves a yellowish residue, which turns reddish-yellow on the addition of potash solution, and violet-red when heated.

By the action of methyl iodid upon its lead compound xanthin is converted into *theobromin*, the natural alkaloid of cocoa, by introduction of two methyl groups; and by the introduction of a third methyl group into caffein, the alkaloid of coffee.

Xanthin calculi vary in size from that of a pea to that of a pigeon's egg. They are rather hard, brownish-yellow, smooth, shining, and made up of well-defined, concentric layers. Their broken surfaces assume a waxy polish when rubbed.

Hypoxanthin—Sarcin—$C_5H_4N_4O$ — 136 — occurs in the spleen, muscular tissue, thymus, suprarenal capsules, brain, and other animal tissues. In the urine it is present in very small quantity in health, but in leucocythæmia it is increased in the urine and has been found in the blood. It also occurs in numerous seeds and pollen of plants, and is also produced during putrefaction of albumen. It appears to be a product of decomposition of nuclein (see p. 369). It may be obtained from the mother liquor of the preparation of creatin (see p. 334). It is also found as a product of the action of gastric juice, of pancreatic juice, or of dilute acids upon fibrin. It is produced by the action of nitrous acid upon adenin; by the acton of sodium amalgam upon uric acid or upon xanthin; and, in small quantity, by the action of acids upon nuclein.

It is a white crystalline powder; soluble in 300 parts of cold and 78 parts of boiling H_2O. It dissolves in acids and alkalies. It is decomposed by KHO at 200° (392° F.) into NH_3 and potassium cyanid; by H_2O at 200° (392° F.) into CO_2, formic acid and NH_3; and is oxidized to xanthin by HNO_3.

It is probably, along with creatin, xanthin, guanin, and other leucomaines, an intermediate product in the formation of uric acid and urea in the processes of metabolism.

Guanin—$C_5H_5N_5O$—151—occurs in guano, in the excrements of the lower animals, and in the pancreas, lungs, liver and other organs of animals as well as in the young leaves and pollen of certain plants. It has not been found in the urine. Like hypoxanthin and xanthin it is a product of decomposition of nuclein. It is a white or yellowish, amorphous, odorless and tasteless solid; almost insoluble in H_2O, alcohol and ether; readily soluble in acids and alkalies, with which it forms compounds. It gives the xanthin reaction with HNO_3 and KHO. Nitrous acid oxidizes it to xanthin. Potassium permanganate oxidizes it to urea, oxalic acid and *oxyguanin*. Hydrochloric acid and potassium chlorate oxidize it to CO_2, guanidin (p. 334), and oxalylurea (p. 346).

Adenin—$C_5H_5N_5$—is a leucomain of great physiological interest recently separated from extract of pancreas, in which it is found along with the bases described above by decomposition of nuclein. It is widely distributed in both animal and vegetable kingdoms, and has been found in tissues abounding in nucleated cells, in the spleen, kidneys, lymphatic glands, and in the blood and urine in leucocythæmia, as well as in yeast and in tea leaves.

Adenin crystallizes in nacreous plates or in long needles, containing 3 Aq., which they lose only at 110° (230° F.) although they become opaque at 53° (127°. 4 F.). Very soluble in hot H_2O, it requires 1086 parts of cold H_2O for solution. The aqueous solution is neutral. It is insoluble in alcohol, ether and chloroform; readily soluble in acids and alkalies, with which it forms compounds.

It resists oxidizing and hydrating actions obstinately. Nitrous acid, however, converts it into hypoxanthin. Adenin is a polymere of hydrocyanic acid, and when heated to 200° (392° F.) it produces potassium cyanid. It has not been obtained synthetically from hydrocyanic acid, although the closely related xanthin and methylxanthin have been formed by heating hydrocyanic acid, water and acetic acid together under pressure.

Carnin—$C_7H_8N_4O_3+H_2O$—196 + 18—is obtained from Liebig's meat extract in chalky, microscopic crystals, readily soluble in warm H_2O. It forms compounds with acids and alkalies, similar to those of hypoxanthin.

Heteroxanthin or **Methylxanthin**—$C_6H_6N_4O_2$—and **Paraxanthin=Dimethylxanthin**—$C_7H_8N_4O_2$—the homologues of xanthin, are leucomains existing in small quantity in urine.

Allantoin—$C_4H_6N_4O_3$—is a diureid which occurs in the allantoic fluid of the cow; in the urine of sucking calves, in that of dogs and cats when fed on meat, in that of children during the first eight days of life, in that of adults after the ingestion of tannin, and in that of pregnant women. It is produced artificially by oxidizing uric acid, suspended in boiling H_2O, with lead dioxid.

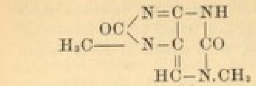
It crystallizes in small, tasteless, neutral, colorless prisms; sparingly soluble in cold H_2O, readily soluble in warm H_2O. Heated with alkalies it yields oxalic acid and NH_3; and with dilute acids, allanturic acid, $C_3H_4N_2O_3$.

Allantoin has been obtained synthetically by heating together mesoxalic acid, $C_3H_4O_6$, and urea.

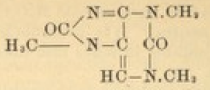
Alloxantin—$C_8H_4N_4O_7$—is a diureid crystallizing in small, brilliant, very sparingly soluble prisms, produced by the action of reducing agents upon alloxan, whose action is less powerful than that required to convert alloxan into dialuric acid.

Murexid—*Ammonium purpurate*—$C_8H_4(NH_4)N_5O_6$—is produced by oxidation of uric acid, of alloxan, and of a number of other derivatives of uric acid with subsequent contact of ammonium hydroxid. It is supposed to be the ammonium salt of a hypothetical and non-isolated acid. The ammonium salt is of a brilliant, but evanescent purple color. (See p. 350.)

Two vegetable alkaloids, theobromin and caffein, are diureids whose relations to each other and to the uric acid series will be seen by comparison of their formulæ with those on pp. 348, 351:



Theobromin.



Caffein.

Theobromin—$C_7H_8N_4O_2$—occurs in the seeds of *theobroma cacao* in the proportion of about two per cent. It is a colorless crystalline powder, bitter in taste; difficultly soluble in water, alcohol, ether, and chloroform; soluble in acids, with which it forms salts. When heated with chlorin water so that the fluid gradually evaporates it leaves a red-brown residue, which turns to a fine purple-violet with ammonium hydroxid.

Caffein—Thein—Guaranin—Caffeina (**U. S.**)—$C_8H_{10}N_4O_2+Aq$—194+18—exists in coffee, tea, Paraguay tea, and other plants. It crystallizes in long, silky needles; faintly bitter; soluble in 75 pts. H_2O at 15° (59° F.): less soluble in alcohol and ether. Hot fuming HNO_3 converts it into a yellow liquid, which after evaporation turns purple with NH_4HO. It gives the same reaction with chlorin water and ammonium hydroxid as theobromin.

CARBAMIC ACIDS.

Carbamic acid— $OC\left\langle\begin{matrix}OH\\NH_2\end{matrix}\right.$—is produced whenever NH_3 and CO_2 come in contact. It is formed during the combustion of organic nitrogenized substances, and appears to exist in animal fluids, particularly in blood serum. Its salts are much less stable than its ethers. The latter are known as *urethans.*

Ethyl carbamate—Urethan— $OC\left\langle\begin{matrix}O.C_2H_5\\NH_2\end{matrix}\right.$—is formed (1) by the action of cyanogen chlorid on alcohol; (2) by the action of alcohol upon urea nitrate under pressure at 120°–130° (248°–266° F.); (3) by the action of ethylcarbonic ether, $CO_3(C_2H_5)_2$, on alcohol. It forms thin, large, transparent, crystalline plates, fusible at about 50° (122° F.); boils at 180° (356° F.), very soluble in alcohol and in water.

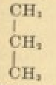
Chloral-urethan—Uralium—Somnal—$C_7H_{12}Cl_3O_3N$ (?)—is a product obtained by the action of chloral upon urethan in the presence of ethylic alcohol. It is a very deliquescent, crystallizable solid, readily soluble in alcohol; decomposed by hot H_2O into chloral and urethan. It is questionable whether this is a definite compound or a mere mixture.

Phenyl-urethan—$OC\left\langle\begin{matrix}O.C_6H_5\\NH_2\end{matrix}\right.$—used as an antipyretic under the name "*euphorine*," is a light white powder, having faintly aromatic odor and taste, almost insoluble in water, very soluble in alcohol.

TRIATOMIC ALCOHOLS.

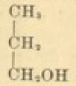
SERIES $C_nH_{2n+2}O_3$.

These substances are known as **glycerins** or more properly **glycerols**. Their relation to the monoatomic and diatomic alcohols is shown by the following formulæ:



$$\begin{array}{c}CH_3\\|\\CH_2\\|\\CH_3\end{array}$$

Propane.



$$\begin{array}{c}CH_3\\|\\CH_2\\|\\CH_2OH\end{array}$$

Propyl alcohol.

$$\begin{array}{c}CH_2OH\\|\\CH_2\\|\\CH_2OH\end{array}$$

Propyl glycol.

$$\begin{array}{c}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}$$

Glycerin.

They are obtained by the saponification of their ethers, either those existing in nature or those produced artificially.

They combine with acids to form three series of ethers, known as **monoglycerids, diglycerids,** and **triglycerids,** formed by the combination of one molecule of the alcohol with one, two, or three molecules of a monobasic acid.

Glycerol—Glycerin—Propenyl Alcohol—Glycerinum (U. S.)—$\mathbf{C_3H_5(OH)_3}$—92—was first obtained as a secondary product in the manufacture of lead plaster; it is now produced as a by-product in the manufacture of soaps and of stearin candles. It exists free in palm-oil and in other vegetable oils. It is produced in small quantity during alcoholic fermentation, and is consequently present in wine and beer. It is much more widely disseminated in its ethers, the neutral fats, in the animal and vegetable kingdoms.

It has been obtained by partial synthesis, by heating for some time a mixture of allyl tribromid, silver acetate and acetic acid, and saponifying the triacetin so obtained.

The glycerol obtained by the process now generally followed—the decomposition of the neutral fats and the distillation of the product in a current of superheated steam—is free from the impurities which contaminated the product of the older processes. The only impurity likely to be present is water, which may be recognized by the low sp. gr.

Glycerol is a colorless, odorless, syrupy liquid, has a sweetish taste; sp. gr. 1.26 at 15° (59° F.). Although it cannot usually be caused to crystallize by the application of the most intense cold, it does so sometimes under imperfectly understood conditions, forming small, white needles of sp. gr. 1.268, and fusible between 17° and 18° (62°.6 and 64°.6 F.). It is soluble in all proportions in water and alcohol, insoluble in ether and in chloroform. The sp. gr. of mixtures of glycerol and water increase with the proportion of glycerol. It is a good solvent for a number of mineral and organic substances (*glycerites* and *glyceroles*). It is not volatile at ordinary temperatures. When heated, a portion distils unaltered at 275°–280° (527°–536° F.), but the greater part is decomposed into acrolein, acetic acid, carbon dioxid, and combustible gases. It may be distilled unchanged in a current of superheated steam between 285° and 315° (545°–599° F.), and distils under ordinary conditions when perfectly pure.

Concentrated glycerol, when heated to 150° (302° F.) ignites and burns without odor and without leaving a residue, and with a pale blue flame. It may also be burnt from a short wick.

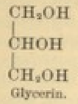
Glycerol is readily oxidized, yielding different products with different degrees of oxidation. Platinum-black oxidizes it, with formation, finally, of H_2O and CO_2. Oxidized by manganese dioxid and H_2SO_4, it yields CO_2 and formic acid. If a layer of glycerol diluted with an equal volume of H_2O be floated on the surface of HNO_3 of sp. gr. 1.5, a mixture of several acids is formed: oxalic, $C_2O_4H_2$; glyceric, $C_3H_6O_4$; formic, CH_2O_2; glycollic, $C_2H_4O_3$; glyoxylic, $C_2H_4O_4$; and tartaric, $C_4H_6O_6$. When glycerol is heated with potassium hydroxid, a mixture of potassium acetate and formiate is produced. When glycerol, diluted with 20 volumes of H_2O, is heated with Br; CO_2, bromoform, glyceric acid, and HBr are produced. Phosphoric anhydrid removes the elements of H_2O from glycerol, with formation of acrolein (see p. 304). A similar action is effected by heating with H_2SO_4, or with potassium hydrosulfate. Heated with oxalic acid, glycerol yields CO_2 and formic acid.

The presence of glycerol in a liquid may be detected as follows: Add NaHO to feebly alkaline reaction, and dip into it a loop of Pt wire holding a borax bead; then heat the bead in the blowpipe flame, which is colored green if the liquid contain $\frac{1}{100}$ of glycerol.

The glycerol used for medicinal purposes should respond to the following tests: (1) its sp. gr. should not vary much from that given above; (2) it should not rotate polarized light; (3) it should not turn brown when heated with sodium nitrate; (4) it should not be colored by H_2S; (5) when dissolved in its own weight of alcohol, containing one per cent. of H_2SO_4, the solution should be clear; (6) when mixed with an equal volume H_2SO_4, of sp. gr. 1.83, it should form a limpid, brownish mixture, but should not give off gas.

ACIDS DERIVABLE FROM THE GLYCEROLS.

Three series of acids are derivable from the glycerols by substitution of O for H_2 in the group CH_2OH :

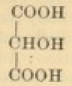


$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Glycerin.

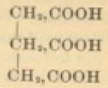
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ COOH \end{array}$$

Glyceric acid.



$$\begin{array}{l} COOH \\ | \\ CHOH \\ | \\ COOH \end{array}$$

Tartronic acid.



$$\begin{array}{l} CH_2,COOH \\ | \\ CH_2,COOH \\ | \\ CH_2,COOH \end{array}$$

Tricarballylic acid.,

The terms of each series are triatomic ; those of the glyceric series are monobasic, those of the tartronic series are dibasic, and those of the tricarballylic series are tribasic.

Malic acid—$C_4H_6O_5$—134—is the second term of the tartronic series, and is therefore dibasic. It exists in the vegetable kingdom ; either free or combined with K, Na, Ca, Mg, or organic bases ; principally in fruits, such as apples, cherries, etc. ; accompanied by citrates and tartrates.

It crystallizes in brilliant, prismatic needles ; odorless ; acid in taste ; fusible at 100° (212° F.) ; loses H_2O at 140° (284° F.) ; deliquescent ; very soluble in H_2O and in alcohol. Heated to 175°–180° (347°–356° F.), it is decomposed into H_2O and **maleic acid, $C_4H_4O_4$.** The malates are oxidized to carbonates in the body.

TRIBASIC UNSATURATED ACIDS.

Aconitic Acid—$C_3H_3(COOH)_3$—exists in its Ca salt in the different species of *aconitum* and of *equisetum*. It forms white, crystalline crusts, or by slow crystallization white plates or prisms ; odorless ; sour ; soluble in water, alcohol and ether ; fuses at 186° (366°.8 F.). Its salts are soluble and crystalline. It is decomposed by heat into itaconic acid and CO_2.

Citric acid—Acidum citricum (U. S., Br.)—$C_6H_8O_7+Aq$—192+18—is best considered in this place, although it is tetratomic, while the other acids of the series are triatomic. It exists in the juices of many fruits—lemon, strawberry, etc., and in cow's milk in the proportion of about 0.1%, as calcium citrate.

It is obtained from lemon-juice, which is filtered, boiled, and saturated with chalk. The insoluble calcium citrate is separated and decomposed with H_2SO_4, the solution filtered, and evaporated to crystallization.

It crystallizes in large, right rhombic prisms, which lose their aq at 100° (212° F.); very soluble in water, less soluble in alcohol, sparingly soluble in ether; heated to 100° (212° F.) it fuses; at 175° (347° F.) it is decomposed, with loss of H_2O and formation of *aco-*

nitic acid, $C_6H_6O_6$; at a higher temperature CO_2 is given off, and *itaconic acid*, $C_5H_6O_4$, and *citraconic acid*, $C_5H_6O_4$, are formed.

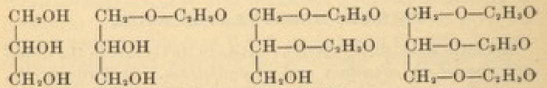
Concentrated H_2SO_4 decomposes it with evolution of CO; oxidizing agents convert it into formic acid and CO_2, or into acetone and CO_2, or into oxalic and acetic acids and CO_2. It is tetratomic and tribasic. In the body its salts are oxidized to carbonates.

Citric acid may be distinguished from tartaric and malic acids by the following reaction: Add glycerol, fuse in a porcelain capsule, heat until acrolein is given off, dissolve in NH_4HO. Expel NH_4HO by heat, add two drops HNO_3—a green color, changing to blue when heated.

ETHERS OF GLYCEROL.

GLYCERIDS.

As glycerol is a triatomic alcohol, it contains three oxhydryl groups which may be removed, combining with H from an acid to form H_2O, and leaving a univalent, bivalent, or trivalent remainder, which may replace the H of monobasic acids to form three series of ethers. As, further, the OH groups differ from each other in that two of them are contained in the primary group CH_2OH, the other in the secondary group CHOH, there exist two isomeres of each mono- and di-glycerid:



$$\begin{array}{llll} CH_2OH & CH_2{-}O{-}C_2H_3O & CH_2{-}O{-}C_2H_3O & CH_2{-}O{-}C_2H_3O \\ | & | & | & | \\ CHOH & CHOH & CH{-}O{-}C_2H_3O & CH{-}O{-}C_2H_3O \\ | & | & | & | \\ CH_2OH & CH_2OH & CH_2OH & CH_2{-}O{-}C_2H_3O \end{array}$$

Glycerin. Manoacetin. Diacetin. Triacetin.

Of the many substances of this class, only a few, principally those entering into the composition of the neutral fats, require consideration here.

Tributyrin—$C_3H_5(O,C_4H_7O)_3$—302—exists in butter. It may also be obtained by heating glycerol with butyric acid and H_2SO_4. It is a pungent liquid, very prone to decomposition, with liberation of butyric acid.

Trivalerin—$C_3H_5(O,C_5H_9O)_3$—344—exists in the oil of some maritime mammalia, and is identical with the *phocenin* of Chevreul.

Tricaproin—$C_3H_5(O,C_6H_{11}O)_3$—386—**Tricaprylin**—$C_3H_5(O,C_8H_{15}O)_3$—470—and **Tricaprin**—$C_3H_5(O,C_{10}H_{19}O)_3$—554—exist in small quantities in milk, butter, and cocoa-butter.

Tripalmitin—$C_3H_5(O,C_{16}H_{31}O)_3$—806—exists in most animal and vegetable fats, notably in palm-oil; it may also be obtained by heating glycerol with 8 to 10 times its weight of palmitic acid for

8 hours at 250° (482° F.). It forms crystalline plates, very sparingly soluble in alcohol, even when boiling; very soluble in ether. It fuses at 50° (122° F.) and solidifies again at 46° (114°.8 F.).

Trimargarin—$C_3H_5(O,C_{17}H_{33}O)_3$—848—has probably been obtained artificially as a crystalline solid, fusible at 60° (140° F.), solidifiable at 52° (125°.6 F.). The substance formerly described under this name as a constituent of animal fats is a mixture of tripalmitin and tristearin.

Tristearin—$C_3H_5(O,C_{18}H_{35}O)_3$—890—is the most abundant constituent of the solid fatty substances. It is prepared in large quantities as an industrial product in the manufacture of stearin candles, etc., but is obtained in a state of purity only with great difficulty.

In as pure a form as readily obtainable, it forms a hard, brittle, crystalline mass; fusible at 68° (154°.4 F.), solidifiable at 61° (141°.8 F.); soluble in boiling alcohol, almost insoluble in cold alcohol, readily soluble in ether.

Triolein—$C_3H_5(O,C_{18}H_{33}O)_3$—884—exists in varying quantity in all fats, and is the predominant constituent of those which are liquid at ordinary temperatures; it may be obtained from animal fats by boiling with alcohol, filtering the solution, decanting after twenty-four hours' standing; freezing at 0° (32° F.), and expressing.

It is a colorless, odorless, tasteless oil; soluble in alcohol and ether, insoluble in water; sp. gr. 0.92.

Trinitro-glycerol — Nitro-glycerol—$C_3H_5(ONO_2)_3$—227—used as an explosive, both pure and mixed with other substances, in dynamite, giant powder, etc., is obtained by the combined action of H_2SO_4 and HNO_3 upon glycerol. Fuming HNO_3 is mixed with twice its weight of H_2SO_4 in a cooled earthen vessel; 33 parts by weight of the mixed acids are placed in a porcelain vessel, and 5 parts of glycerol, of 31° Beaumé, are gradually added with constant stirring, while the vessel is kept well cooled; after five minutes the whole is thrown into 5–6 volumes of cold water; the nitro-glycerol separates as a heavy oil, which is washed with cold water.

Nitro-glycerol is an odorless, yellowish oil; has a sweetish taste; sp. gr. 1.6; insoluble in water, soluble in alcohol and ether; not volatile; crystallizes in prismatic needles when kept for some time at 0° (32° F.); fuses again at 8° (46°.4 F.).

When pure nitro-glycerol is exposed to the air at 30° (86° F.) for some time, it decomposes, without explosion and with production of glyceric and oxalic acids. When heated to 100° (212° F.) it volatilizes without decomposition; at 185° (365° F.) it boils, giving off nitrous fumes; at 217° (422°.6 F.) it explodes violently; if quickly heated to 257° (494°.6 F.) it assumes the spheroidal form, and volatilizes without explosion. Upon the approach of flame at low temperatures it ignites and burns with slight decrepitations. When subjected to shock, it is suddenly decomposed into CO_2; N; vapor of H_2O, and O, the decomposition being attended with a violent explosion.

In order to render this explosive less dangerous to handle, it is now usually mixed with some inert substance, usually diatomaceous earth, in which form it is known as **dynamite,** etc.

When taken internally, nitro-glycerin is an active poison, producing effects somewhat similar to those of strychnin; in drop-doses, diluted, it causes violent headache, fever, intestinal pain, and nervous symptoms. It has been latterly used as a therapeutic agent, and has been used by the homœopaths under the name of **glonoin.**

NEUTRAL OILS AND FATS.

These are mixtures in varying proportions of **tripalmitin, tristearin,** and **triolein,** with small quantities of other glycerids, coloring and odorous principles, which are obtained from animal and vegetable bodies. The oils are fluid at ordinary temperatures, the solid glycerids being in solution in an excess of the liquid triolein. The fats, owing to a less proportion of the liquid glycerid, are solid or semi-solid at the ordinary temperature of the air. Members of both classes are fluid at sufficiently high temperatures, and solidify when exposed to a sufficiently low temperature. They are, when pure, nearly tasteless and odorless, unctuous to the touch, insoluble in and not miscible with H_2O, upon which they float; combustible, burning with a luminous flame. When rubbed upon paper they render it translucent. When heated with the caustic alkalies, or in a current of superheated steam, they are **saponified,** *i.e.*, decomposed into glycerin and a fatty acid. If the saponification be produced by an alkali, the fatty acid combines with the alkaline metal to form a soap.

Most of the fats and many of the oils, when exposed to the air, absorb O, are decomposed with liberation of volatile fatty acids, and acquire an acid taste and odor, and an acid reaction. A fat which has undergone these changes is said to have become **rancid.** Many of the vegetable oils are, however, not prone to this decomposition. Some of them, by oxidation on contact with the air, become thick, hard and dry, forming a kind of varnish over surfaces upon which they are spread; these are designated as **drying** or **siccative oils.** Others, although they become more dense on exposure to air, become neither dry nor gummy; these are known as **non-drying, greasy,** or **lubricating oils.**

Under ordinary conditions, oils and melted fats do not mix with water, and, if shaken with that fluid, form a *temporary* milky mixture, which, on standing for a short time, separates into two distinct layers, the oil floating on the water. In the presence, however, of small quantities of certain substances, such as albumen, pancreatin (*q.v.*), ptyalin, etc., the milky mixture obtained by shaking together oil and water does not separate into distinct layers on standing; such a mixture, in which the fat is held in a *permanent* state of suspension in small globules in a watery fluid, is called an **emulsion.** Good emulsions may be easily obtained by agitating an oil containing a trace of free oleic acid with a very dilute solution of sodium carbonate and borax.

Fixed oils.—These substances are designated as "fixed," to distinguish them from other vegetable products having an oily appearance, but which differ from the true oils in their chemical composition and in their physical properties, especially in that they are volatile without decomposition, and are obtained by distillation, while the fixed oils are obtained by expression, with or without the aid of a gentle heat.

Palm-oil is a reddish-yellow solid at ordinary temperatures, has a bland taste and an aromatic odor. It saponifies readily, and is usually acid and contains free glycerol liberated by spontaneous decomposition.

Rape-seed and **colza oils,** produced from various species of *Brassica*, are yellow, limpid oils having a strong odor and disagreeable taste.

Croton-oil—Oleum tiglii (U. S.)—Oleum crotonis (Br.)—varies much in color and activity, according to its source; that which is obtained from the East is yellowish, liquid, transparent, and much less active than that prepared in Europe from the imported seeds, which is darker, less fluid, caustic in taste, and wholly soluble in absolute alcohol. Croton-oil contains, besides the glycerids of oleic, crotonic and fatty acids, about four per cent. of a peculiar principle called **crotonol,** to which the oil owes its vesicating **properties.** It also contains an alkaloid-like substance, also existing in castor-oil, called **ricinin.** None of these bodies, however, are possessed of the drastic powers of the oil itself.

Peanut-oil—*Ground-nut-oil*—an almost colorless oil, very much resembling olive-oil, in place of which it is frequently used for culinary purposes, intentionally or otherwise. It is readily saponifiable, yielding two peculiar acids, **arachaic** and **hypogaic** (see Olive-oil).

Cotton-seed-oil—Oleum gossypii seminis (U. S.)—a pale yellow, bland oil, also resembling olive-oil, for which it is frequently substituted.

Almond-oil—Oleum amygdalæ expressum (U. S.)—Oleum amygdalæ (Br.)—a light yellow oil, very soluble in ether, soluble in alcohol; nearly inodorous; has a bland, sweetish taste. The pure oil has no odor of bitter almonds.

Olive-oil—Oleum olivæ (U. S., Br.)—a well-known oil of a yellow or greenish-yellow color, almost odorless, and of a bland and sweetish taste. The finest grades have a yellow tinge and a faint taste of the fruit; they are prepared by cold pressure; they are less subject to rancidity than the lower grades. Olive-oil is very frequently adulterated, chiefly with poppy-oil, sesame-oil, cotton-seed-oil and peanut-oil. The presence of the first is detected by Pontet's reagent (made by dissolving 6 parts Hg in 7.5 parts of HNO_3 of 36° in the cold), which converts pure olive-oil into a solid mass, while an oil adulterated with a drying oil remains semi-solid. A contamination with oil of sesame is indicated by the production of a green color, with a mixture of HNO_3 and H_2SO_4. Peanut-oil, an exceedingly common adulterant in this country, is recognized by the following method: ten grams of the oil are saponified; the soap is decomposed with HCl; the liberated fatty acids dissolved in 50 c.c. of strong alcohol; the solution precipitated with lead acetate; the precipitate washed with ether; the residue decomposed with hot dilute HCl; the oily layer separated and extracted with strong alcohol; the alcoholic fluid, on evaporation, yields crystals of **arachaic acid**, if the oil contains peanut-oil. The most usual adulteration is with cotton-seed-oil, which may be detected, if more than 5% be present, as follows: 10 c.c. each of the oil and of ethylic ether are agitated in a test-tube; add 5 c.c. strong solution of neutral lead acetate, and then 5 c.c. ammonium hydrate solution, and agitate again. In the presence of cotton-seed-oil an orange-red color is produced, particularly in the upper layer.

Cocoa-butter—Oleum theobromæ (U. S., Br.)—is, at ordinary temperatures, a whitish or yellowish solid of the consistency of tallow, and having an odor of chocolate and a pleasant taste; it does not easily become rancid. The most reliable test of its purity is its fusing-point, which should not be much below 33° (91°.4 F.).

Linseed-oil—Flaxseed-oil—Oleum lini (U. S., Br.)—is a dark, yellowish-brown oil of disagreeable odor and taste. In it oleic acid is, at least partially, replaced by **linoleic acid**, whose presence causes the oil, on exposure to air, to absorb oxygen and become thick and finally solid. This drying power is increased by boiling the oil with litharge (boiled oil).

Castor-oil—Oleum ricini (U. S., Br.)—is usually obtained by expression of the seeds, although in some countries it is prepared by decoction or by extraction with alcohol. It is a thick, viscid, yellowish oil, has a faint odor and a nauseous taste. It is more soluble in alcohol than any other fixed vegetable oil, and is also very soluble in ether. It saponifies very readily. Ammonia separates from it a crystalline solid, fusible at 66° (158°.8 F.), **ricinolamid.** Hot HNO_3 attacks it energetically, and finally converts it into *suberic acid.*

Whale-oil—*Train-oil*—obtained by *trying out* the fat or blubber of the "right whale" and of other species of *balænæ.* It is of sp. gr. 0.924 at 15° (59° F.); brownish in color; becomes solid at about 0°; has a very nauseous taste and odor. It is colored yellow by H_2SO_4; and is blackened by Cl.

Neat's-foot-oil—is obtained by the action of boiling H_2O upon the feet of neat cattle, horses, and sheep, deprived of the flesh and hoofs. It is straw-yellow or reddish-yellow, odorless, not disagreeable in taste, not prone to rancidity, does not solidify at quite low temperatures; sp. gr. at 15° (59° F.)=0.916. It is bleached, not colored, by chlorin.

Lard-oil—Oleum adipis (**U. S.**)—obtained in large quantities in the United States as a by-product in the manufacture of candles, etc., from pig's fat. A light yellow oil, used principally as a lubricant; is not colored by H_2SO_4, but is colored brown by a mixture of H_2SO_4 and HNO_3.

Tallow-oil—obtained by expression with a gentle heat from the fat of the ox and sheep. Sp. gr. 0.9003; light yellow in color. Colored brown by H_2SO_4. Formerly this oil, under the trade name of "oleic acid," was simply a by-product in the manufacture of stearin candles; of late years, however, it is specially prepared for the manufacture of oleomargarine.

Cod-liver-oil—Oleum morrhuæ (**U. S., Br.**)—is obtained from the livers of cod-fish, either by extraction with water heated to about 80° (176° F.), or by hanging the livers in the sun and collecting the oil which drips from them. There are three commercial varieties of this oil: (*a*) *Brown.*—Dark brown, with greenish reflections; has a disagreeable, irritating taste; faintly acid; does not solidify at −13° (8°.6 F.). (*b*) *Pale brown.*—Of the color of Sherry wine; has a peculiar odor and a fishy, irritating taste; strongly acid. (*c*) *Pale.*—Golden yellow; deposits a white fat at −13° (8°.6 F.); has a fresh odor, slightly fishy, and a not unpleasant taste, without after-taste.

Pure cod-liver-oil, with a drop of H_2SO_4, gives a bluish-violet aureole, which gradually changes to crimson, and later to brown. A drop of fuming HNO_3 dropped into the oil is surrounded by a pink aureole if the oil be pure. If the oil be largely adulterated with other fish-oils, the pink color is not observed, and the oil becomes slightly cloudy. Fresh cod-liver-oil is not colored by rosanilin.

Cod-liver-oil contains, besides the glycerids of oleic, palmitic and stearic acids, those of butyric and acetic acids; certain biliary principles (to whose presence the sulfuric acid reaction given above is probably due), a phosphorized fat of undetermined composition; small quantities of bromin and iodin, probably in the form of organic compounds; a peculiar fatty acid called **gadinic acid,** which solidifies at 60° (140° F.); and a brown substance called **gaduin** or **gadinin.** It also contains two alkaloids: **Asellin,** $\mathbf{C_{25}H_{32}N_4}$, and **morrhuin,** $\mathbf{C_{19}H_{27}N_3}$.

To which, if to any, of these substances cod-liver-oil owes its value as a therapeutic agent is still unknown, although many theories have been advanced. Certain it is, however, that one of the chief values of this oil is as a food in a readily assimilable form.

Solid Animal Fats.—The glycerids of stearic, palmitic, and oleic acids exist, in health, in nearly all parts of the body; in the fluids in solution or in suspension, in the form of minute oil-globules; incorporated in the solid or semi-solid tissues, or deposited in collections in certain locations, as under the skin, enclosed in cells of connective tissue.

The total amount of fat in the body of a healthy adult is from 2.5 to 5 per cent. of the body-weight, although it may vary considerably from that proportion in conditions not, strictly speaking, pathological. The approximate quantities of fat in 100 parts of the various tissues and fluids, in health, are the following:

Urine	?	Crystalline lens	2.0
Perspiration	0.001	Liver	2.4
Vitreous humor	0.002	Muscle	3.3
Saliva	0.02	Hair	4.2
Lymph	0.05	Milk	4.3
Synovial fluid	0.06	Cortex of brain	5.5
Amniotic fluid	0.2	Brain	8.0
Chyle	0.3	Hen's egg	11.6
Mucus	0.4	White matter of brain	20.0
Blood	0.4	Nerve-tissue	22.1
Cartilage	1.3	Spinal cord	23.6
Bone	1.4	Fat-tissue	82.7
Bile	1.4	Marrow	96.0

The amount of fat, under normal conditions, is usually greater in women and children than in men; generally greater in middle than in old age, although in some individuals the reverse is the case; greater in the inhabitants of cold climates than in those of hot countries.

In wasting from disease and from starvation the fats are rapidly absorbed, and are again as rapidly deposited when the normal condition of affairs is restored.

Besides, as a result of the tendency to corpulence, which in some individuals amounts to a pathological condition, fats may accumulate in certain tissues as a result of morbid changes. This accumulation may be due either to degeneration or to infiltration. In the former case, as when muscular tissue degenerates in consequence of long disuse, the natural tissue disappears and is replaced by fat; in the latter case, as in fatty infiltration of the heart, oil-globules are deposited between the natural morphological elements, whose change, however, may subsequently take place by true fatty degeneration, due to pressure. The greater part of the fat of the body enters it as such with the food. Not unimportant quantities are, however, formed in the body, and that from the albuminoid as well as from the starchy and saccharine constituents of the food. By what steps this transformation takes place is still uncertain, although there is abundant evidence that it does occur.

Those fats taken in with the food are unaltered by the digestive fluids, except in that they are freed from their enclosing membranes in the stomach, until they reach the duodenum. Here, under the influence of the pancreatic juice, the major part is converted into a fine emulsion, in which form it is absorbed by the lacteals. A smaller portion is saponified, and the products of the saponification, free fatty acids, soaps, and glycerol, subsequently absorbed by lacteals and blood-vessels.

The service of the fats in the economy is undoubtedly as a producer of heat and force by its oxidation; and by its low power of conducting heat, and the position in which it is deposited under the skin, as a retainer of heat produced in the body. The fats are not discharged from the system in health, except the excess contained in the food over that which the absorbents are capable of taking up, which passes out with the fæces; a small quantity distributed over the surface in the perspiration and sebaceous secretion (which can hardly be said to be eliminated); and a mere trace in the urine.

Butter.—The fat of milk, separated and made to agglomerate by agitation, and more or less salted to insure its keeping. It consists of the glycerids of stearic, palmitic, oleic, butyric, capric, caprylic, and caproic acids, with a small amount of coloring matter, more or less water and salt, and casein. Good, natural butter contains 80-90 per cent. of fat, 6-10 per cent. of water, 2-5 per cent. of curd, and 2-5 per cent. of salt; fuses at from 32°.8 to 34°.9 (91°-94°.8 F.).

Butter is adulterated with excess of water and salt, starch, animal fats other than those of butter, and artificial coloring matters.

Excess of salt and water are usually worked in together, the former up to 14 per cent. and the latter to 15 per cent. To determine the presence of an excess of water, about 4 grams (60 grains) of the butter, taken from the middle of the lump, are weighed in a porcelain capsule, in which it is heated over the water-bath, as long as it loses weight; it is then weighed again; the loss of weight is that of the quantity of water in the original weight of butter, less that of the capsule. The proportion of salt is determined by incinerating a weighed quantity of butter and determining the chlorin in the ash by the nitrate of silver method (see Sodium chlorid). Roughly, the weight of the ash may be taken as salt. Starch is detected by spreading out a thin layer of butter, adding solution of iodin, and examining under the microscope for purple spots.

The detection of foreign fats in butter, formerly a most unsatisfactory problem to the analyst, has now become one which may be answered with great certainty. All of the chemical processes used are based upon a peculiar difference in the composition of butter-fat from other animal and vegetable fats and oils. When butter-fat is saponified, it yields from 5 to 8 per cent. of butyric acid and its near homologues, which are soluble in H_2O, and may be distilled without suffering decomposition, and from 85.5 to 87.5 of stearic, palmitic, and oleic acids, which are neither soluble in water nor capable of being distilled. The other fats and oils, when saponified, yield mere traces of the volatile or soluble fatty acids, and much larger quantities (95.3 to 95.7 per cent.) of insoluble acids. These variations are utilized directly in some processes, such as those of Hehner and Reichert, in which the percentage of fixed and volatile acids are directly determined. In other processes, such as those of Koettstorfer and Hübl, advantage is taken of the different neutralizing power of the two groups of acids. Thus, as butyric acid, $C_4H_8O_2$, and stearic acid, $C_{18}H_{36}O_2$, are each capable of neutralizing KHO, molecule for molecule, it follows that their neutralizing power is in proportion to their molecular weights, and that 56 parts KHO will require for neutralization 88 parts of butyric acid, or 284 parts of stearic acid. For descriptions of processes the student is referred to Allen, "Commercial Organic Analysis," 2d ed., II., pp. 145-160.


FIG. 39.

Methods for detecting admixture of foreign fats by physical means are unreliable. One of the best, which may be of service for preliminary testing, is that of Angell and Hehner. A pear-shaped bulb of thin glass is made of such size as to displace 1 c.c. water, is weighted with mercury until it weighs 3.4 grams (52.5 grains), and the pointed end closed by fusion. The butter to be tested is fused in a beaker over the water-bath, and when quite fluid is poured out into a test-tube about ¾ inch diameter and 6 inches long, which is kept moderately warm and upright until the fat has separated in a clear layer above the water, and then immersed in water at 15° (59° F.) until the fat has solidified. The test-tube is then arranged as shown in Fig. 39, the bulb being laid upon the surface of the fat. The water in the beaker is now heated until the globular part of the bulb has just sunk below the surface of the fat, at which time the height of the thermometer is noted; this is the "sinking-point."

The sinking-point of pure butter is 34°.3 to 36°.3 (93°.7-97°.3 F.), that of oleomargarine is lower, that of butter adulterated with other fats is higher.

"Oleomargarine" is a product made in imitation of butter, which it resembles very closely in color, taste, odor, and general appearance. Under the original patent, it is made from beef-fat, which is hashed, steamed, and subjected to pressure at a carefully regulated temperature. Under this treatment it is separated into two fatty products, one a white solid, "stearine," the other a faintly yellow oil, "oleo-oil." This oil is then mixed with milk, the mixture colored and churned. The subsequent treatment of the product is the same as that of butter. "Butterine," "suine," etc., are products made, by modifications of the above process, from beef or mutton tallow, lard, and cotton-seed-oil.

Butter is frequently, and oleomargarine is always, colored with some foreign pigment, "butter color," which is usually a preparation of annoto.

Soaps—are the metallic salts of stearic, palmitic, and oleic acids: those of K, Na, and NH_4 are soluble, those of the other metals insoluble. Those of Na are hard, those of K soft.

Soap is made from almost any oil or fat, the best from olive-oil, or peanut, or palm-oil, and lard. The first step in the process of manufacture is the **saponification** of the fat, which consists in the decomposition of the glyceric ethers into glycerol and the fatty acids, and the combination of the latter with an alkaline metal. It is usually effected by gradually adding fluid fat to a weak boiling solution of caustic soda, or potassa, to saturation. From this weak solution the soap is separated by "salting," which consists in adding, during constant agitation, a solution of caustic alkali, heavily charged with common salt, until the soap separates in grumous masses, which float upon the surface and are separated. Finally the soap is pressed to separate adhering water, fused, and cast into moulds.

White Castile soap—Sapo (U. S.), Sapo durus (Br.)—is a Na soap made from olive-oil; strongly alkaline, hard, not greasy, very soluble; contains 21 per cent. H_2O. **Sapo mollis (Br.)** is a K soap made from olive-oil, and contains an excess of alkali and glycerol. **Yellow soap** is made from tallow or other animal fat, and contains about $\frac{1}{3}$ its weight of rosin. **Emplastrum plumbi (U. S., Br.)** is a lead soap, prepared by saponifying olive-oil with litharge.

The soaps are decomposed by weak acids, with liberation of the fatty acid; by compounds of the alkaline earths, with formation of an insoluble soap; and in the same way by most of the metallic salts.

LECITHINS—NERVE-TISSUE.

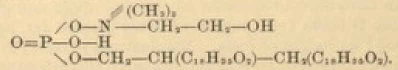
Lecithin—is a substance first obtained from the yolk of hens' eggs, and subsequently found to exist in brain-tissue, particularly the gray substance, nerve-tissue, semen, blood-corpuscles, blood-serum, milk, bile, and other animal tissues and fluids.

As obtained from brain-tissue lecithin is a colorless or faintly yellowish, imperfectly crystalline solid, or sometimes of a waxy consistency. It is very hygroscopic. It does not dissolve in H_2O, in which, however, it swells up and forms a mass like starch-paste. It dissolves in alcohol or ether, very sparingly in the cold, but readily under the influence of heat. It dissolves in chloroform and in benzene. Lecithin is very prone to decomposition, particularly at slightly elevated temperatures. Its chlorid combines with $PtCl_4$ to form an insoluble yellowish chloroplatinate.

When an alcoholic solution of lecithin is brought into contact with hot solution of barium hydroxid it yields **barium glycerophosphate, barium stearate,** and **cholin** (see p. 276). This decomposition indicates the constitution of lecithin and its relations to the fats. Glycerophosphoric acid is phosphoric acid in which an atom of hydrogen has been replaced by the univalent remainder $CH_2OH—CHOH—CH_2$—left by the removal of OH from glycerol:

$$O{=}P\begin{array}{l}\diagup OH\\ —OH\\ \diagdown O—CH_2—CHOH—CH_2OH.\end{array}$$

In lecithin the remaining oxhydryl groups of the glycerol remainder are removed by union with the basic hydrogen of two molecules of stearic acid, and one of the two remaining basic hydrogen atoms of the phosphoric acid is displaced by cholin. It is obvious that the number of lecithins is not limited to one, but that many may exist, and probably do, into whose composition any one, or any combination of two, of the acids of the same series as stearic acid may enter



$$O{=}P\begin{array}{l}\diagup O—\overset{\diagup\!\!\diagup (CH_3)_3}{N}——CH_2—CH_2—OH\\ —O—H\\ \diagdown O—CH_2—CH(C_{18}H_{35}O_2)—CH_2(C_{18}H_{35}O_2).\end{array}$$

Distearyl-lecithin.

Nerve-tissue, which is exceedingly complex in its chemical composition, and whose chemistry is still in a most rudimentary condition, seems to contain similar constituents in its different parts, which differ, however, materially in their quantitative composition.

The following substances have been obtained from cerebral tissue:

Mineral Substances

Water.
Phosphates of Na, K, Ca, Mg.
Ferric oxid.
Silicic oxid.
Traces of sulfates, chlorids, and fluorids.

Products of Decomposition.

Glycerophosphoric acid.
Oleophosphoric acid.
Volatile fatty acids.
Lactates.
Hypoxanthin.
Xanthin.
Creatin.

Albuminoids.

Substance related to myosin.
Soluble albuminoid, coagulable at 75° (167° F.).
Casein (?).

Organic Substances.

Elastin.
Neurokeratin.
Nuclein.
Cerebrin.
Lecithin.
Fats (?).
Inosite.
Cholesterin.

The composition of white and gray matter differs quantitatively, as shown below:

	Gray Matter.	White Matter.
Albuminoids	55.37	24.72
Lecithin	17.24	9.90
Cholesterin and fats	18.68	51.91
Cerebrin	0.53	9.55
Extractive matters, insoluble in ether	6.71	3.34
Salts	1.46	0.57

Cerebrin is a substance deposited in the crystalline form from hot ethero-alcoholic extracts of brain-tissue. It is white, very light, odorless, and tasteless; insoluble in water or in cold alcohol or ether. Its solutions are neutral. It does not contain phosphorus.

The substance known as **protagon**, described by Liebreich as having been obtained from brain-tissue, would seem to exist there notably in the white substance of Schwann. It appears to be a compound formed by the union of lecithin with cerebrin.

Neurokeratin is a substance occurring principally in the gray matter, which is insoluble in all solvents, and is not acted upon by digestive liquids.

Nuclein.—This name is applied to a phosphorized substance, or more probably several such substances, existing in the nuclei of animal and vegetable cells. The nucleins have been found in pus, in the yolk of eggs, spermatic fluid, liver, brain, and casein, in oleaginous seeds, and in many animal and vegetable tissues. The nucleins from pus, spermatic fluid, and brain, and that from yeast have been investigated.

The nucleins are, when freshly precipitated, white, amorphous, rather soluble in water, insoluble in acids and in the gastric juice. They are extremely unstable and when decomposed yield phosphoric acid, an albuminoid substance, xanthin, hypoxanthin, guanin, and adenin.

DIAMIDS OF THE TARTRONIC SERIES.

Corresponding to malic acid four amids are known:

Malamic acid—$C_4H_7NO_4$—is not known free, but exists as its ethylic ether in **malamethan.**

Aspartic acid—$C_4H_7NO_4$—occurs in the molasses from beet-sugar, and is produced by the decomposition of asparagin by acids or alkalies. It crystallizes in sparingly soluble prisms.

Malamid—$C_4H_8N_2O_3$—is produced in large crystals, by the action of excess of NH_3 on dry ethyl malate.

Asparagin—$C_4H_8N_2O_3$—is quite widely disseminated in vegetable nature, and is best obtained from asparagus, from the root of the marsh-mallow, or from vetches. It crystallizes in orthorhombic prisms with 1 Aq; sparingly soluble in water, odorless, faintly nauseous in taste, faintly acid in reaction. Its solutions are lævogyrous $[a]_j=35^\circ$–$38^\circ.8$. It enters into unstable combination with both acids and bases. It is converted into aspartic acid and ammonia by heating with dilute mineral acids or alkaline solutions. It is not oxidized by HNO_3 unless the acid contain nitrogen oxids, in which case it decomposes asparagin into malic acid, N, and H_2O.

THIRD SERIES OF HYDROCARBONS.

SERIES C_nH_{2n-2}.

The hydrocarbons of this series, above the first, form two isomeric series, designated as *alpha* and *Beta*. Those of the *alpha* series are produced by heating the dibromids or diiodids of the olefins with alcoholic solution of KHO. They have the general formula $HC{\equiv}C{-}C_nH_{2n+1}$. Those of the *Beta* series are produced by a variety of reactions, and have the general formula $H_2C{=}C{=}C_nH_{2n}$.

Acetylene—Ethine—C_2H_2—26—exists in coal-gas, and is formed in the decomposition, by heat or otherwise, of many organic substances. It is best prepared by passing a slow current of coal-gas through a narrow tube, traversed by induction sparks; directing the gas through a solution of cuprous chlorid; and collecting and decomposing the precipitate by HCl. It may be obtained by direct synthesis from H and C, by producing the electric arc between carbon points in a glass globe filled with hydrogen.

It is a colorless gas, rather soluble in H_2O; has a peculiar, disagreeable odor; such as is observed when a Bunsen burner burns within the tube. It forms explosive mixtures with O. It unites with N, under the influence of the electric discharge, to form hydrocyanic acid. Mixed with Cl, it detonates violently in diffuse daylight, without the aid of heat. It may be made to unite with itself to form its polymeres benzene, C_6H_6, styrolene, C_8H_8, and naphthydrene, $C_{10}H_{10}$.

Its presence may be detected by the formation in an ammoniacal solution of cuprous chlorid of a blood-red precipitate, which is explosive when dry. It is probable that explosions which sometimes occur in brass or copper pipes, through which illuminating gas is conducted, are due to the formation of this compound.

Illuminating gas—is now manufactured by a variety of processes; thus we have gas made from wood, from coal, from fats, from petroleum, and by the decomposition of H_2O and subsequent charging of the gas with the vapor of naphtha. The typical process is that in which the gas is produced by heating bituminous coal to bright redness in retorts. As it issues from the retorts the gas is charged with substances volatile only at high temperatures; these are deposited in the condensers or coolers, and form coal- or gas-tar. From the condensers the gas passes through what are known as "scrubbers" and "lime-purifiers," in which it is deprived of ammoniacal compounds and other impurities. As it comes from the condensers, coal-gas contains:

* Acetylene.
* Ethylene.
* Marsh-gas.
* Butylene.
* Propylene.
* Benzene.
* Styrolene.
* Naphthalene.
* Acenaphthalene.
* Fluorene.
* Propyl hydrid.
* Butyl hydrid.
‡ Hydrogen.
† Carbon monoxid.
† Carbon dioxid.
† Ammonia.
† Cyanogen.
† Sulfocyanogen.
† Hydrogen sulfid.
† Carbon disulfid.
† Sulfuretted hydrocarbons.
‡ Nitrogen.
‡ Aqueous vapor.

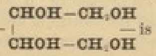
In passing through the purifiers the gas is freed of the impurities to a greater or less extent, and, as usually delivered to consumers, contains:

* Marsh-gas.
* Acetylene.
* Ethylene.
‡ Hydrogen.
‡ Nitrogen.
‡ Aqueous vapor.
† Carbon monoxid.
† Carbon dioxid.
* Vapors of hydrocarbons.

TETRATOMIC ALCOHOLS.

SERIES $C_nH_{2n+2}O_4$.

Very few of these compounds have yet been obtained. They may be regarded as the hydrates of the hydrocarbons C_nH_{2n-2}; as the glycols are the hydrates of the ethylene series.

Erythrite—Phycite— 

$$\begin{array}{l} CHOH-CH_2OH \\ | \\ CHOH-CH_2OH \end{array}$$

—is a product of decom-

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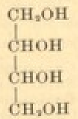
* Illuminating constituents. † Impurities. ‡ Diluent.

position of **erythrin, $C_{20}H_{22}O_{10}$**, which exists in the lichens of the genus *rocella*. It crystallizes in large, brilliant prisms; very soluble in H_2O and in hot alcohol, almost insoluble in ether; sweetish in taste; its solutions neither affect polarized light, nor reduce Fehling's solution, nor are capable of fermentation. Its watery solution, like that of sugar, is capable of dissolving a considerable quantity of lime, and from this solution alcohol precipitates a definite compound of erythrite and calcium. By oxidation with platinum-black it yields **erythroglucic acid, $C_4H_8O_5$**. With fuming HNO_3 it forms a tetranitro compound, which explodes under the hammer.

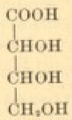
ACIDS DERIVABLE FROM ERYTHRITE.

Theoretically erythrite should, by simple oxidation, yield two acids; one of the series $C_nH_{2n}O_5$, and another of the series $C_nH_{2n-2}O_6$. Although both of these acids are known, only the first, *erythroglucic acid*, has been obtained by oxidation of erythrite:



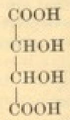
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Erythrite.



$$\begin{array}{l} COOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Erythroglucic acid.



$$\begin{array}{l} COOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ COOH \end{array}$$

Tartaric acid.

Tartaric acids—Acidum tartaricum (U. S., Br.)—$C_4H_6O_6$—150.—There exist four acids having the composition $C_4H_6O_6$, which differ from each other only in their physical properties, and are very readily converted into one another: they are designated as: 1st, **Right**; 2d, **Left**; 3d, **Inactive tartaric acid**; 4th, **Racemic acid**.

Right or **dextrotartaric acid** crystallizes in large, oblique, rhombic prisms, having hemihedral facettes. Solutions of the acid and its salts are dextrogyrous.

Lævotartaric acid crystallizes in the same form as dextrotartaric acid, only the hemihedral facettes are on the opposite sides, so that crystals of the two acids, when held facing each other, appear like the reflections one of the other. Its solutions and those of its salts are lævogyrous to the same degree that corresponding solutions of dextrotartaric acid are dextrogyrous. **Racemic acid** is a compound of the two preceding; it forms crystals having no hemihedral facettes, and its solutions are without action on polarized light. It is readily separated into its components. **Inactive tartaric acid,** although resembling racemic acid in its crystalline form and inactivity with respect to polarized light, differs essentially from that acid in that it cannot be decomposed into right and left acids, and in the method of its production.

The tartaric acid which exists in nature is the dextrotartaric. It occurs, both free and in combination, in the sap of the vine and in many other vegetable juices and fruits. Although this is probably the only tartaric acid existing in nature, all four varieties may and do occur in the commercial acid, being formed during the process of manufacture.

Tartaric acid is obtained in the arts from hydropotassic tartrate, or cream of tartar (*q.v.*). This salt is dissolved in H_2O and the solution boiled with chalk until its reaction is neutral; calcic and potassic tartrates are formed. The insoluble calcic salt is separated and the potassic salt decomposed by treating the solution with calcic chlorid. The united deposits of calcium tartrate are suspended in H_2O, decomposed with the proper quantity of H_2SO_4, the solution separated from the deposit of calcium sulfate, and evaporated to crystallization.

The ordinary tartaric acid crystallizes in large prisms; very soluble in H_2O and alcohol; acid in taste and reaction. It fuses at 170° (338° F.); at 180° (356° F.) it loses H_2O, and is gradually converted into an anhydrid; at 200°-210° (392°-410° F.) it is decomposed with formation of **pyruvic acid, $C_3H_4O_3$**, and **pyrotartaric acid, $C_5H_8O_4$**; at higher temperatures CO_2, CO, H_2O, hydrocarbons and charcoal are produced. If kept in fusion some time, two molecules unite, with loss of H_2O, to form **tartralic** or **ditartaric acid, $C_8H_{10}O_{11}$**.

Tartaric acid is attacked by oxidizing agents with formation of CO_2, H_2O, and, in some instances, formic and oxalic acids. Certain reducing agents convert it into malic and succinic acids. With fuming HNO_3 it forms a dinitro-compound, which is very unstable, and which, when decomposed below 36° (96°.8 F.), yields tartaric acid. It forms a precipitate with lime-water, soluble in an excess of H_2O. In not too dilute solution it forms a precipitate with potassium sulfate solution. It does not precipitate with the salts of Ca. When heated with a solution of auric chlorid it precipitates the gold in the metallic form. As its formula indicates (see above), tartaric acid is tetratomic and dibasic. It has a great tendency to the formation of double salts, such as tartar emetic (*q.v.*).

When taken into the economy, as it constantly is in the form of tartrates, the greater part is oxidized to carbonic acid (carbonates); but, if taken in sufficient quantity, a portion is excreted unchanged in the urine and perspiration. The free acid is poisonous in large doses.

HEXATOMIC ALCOHOLS.

The known terms of this series are isomeric; have the composition $C_6H_{14}O_6$. They are closely related to the carbohydrates.

Mannite—constitutes the greater part of *manna*, and also exists in a number of other plants. It is also produced during the so-called mucic fermentation of sugar, and during lactic fermentation. It crystallizes in long prisms, odorless, sweet, fuses at 166° (330°.8 F.) and crystallizes on cooling; boils at 200° (392° F.), at which temperature it is converted into **mannitan, $C_6H_{12}O_5$**; soluble in H_2O, very sparingly in alcohol. When oxidized it yields first mannitic, then saccharic acid (*q.v.*), and finally, oxalic acid. Organic acids combine with it to form compound ethers.

Dulcite—**Melampyrite**—*Dulcose*—*Dulcin*—exists in *Melampyrum nemorosum*. It forms colorless, transparent prisms, fuses at 182° (359°.6 F.), is odorless, faintly sweet, neutral in reaction, and optically inactive. It is subject to decompositions very similar to those to which mannite is subject, yielding **dulcitan,** $C_6H_{12}O_5$.

CARBOHYDRATES.

These substances are composed of C, H, and O; they all contain C_6, or some multiple thereof; and the H and O which they contain are always in the proportion of H_2 to O. Most of them exist in nature either in animal or vegetable organisms or as the products of fermentative processes.

Their constitution is still undetermined, although their reactions would indicate that some are aldehydes, others alcohols, and others ethers, while some are of mixed function. Indeed the synthesis of glucose has been recently accomplished in such manner as to indicate that it is partly aldehyde, partly secondary alcohol, and partly primary alcohol.

The carbohydrates are divisible into three groups, the members of each of which are isomeric with each other:

I. GLUCOSES.	II. SACCHAROSES.	III. AMYLOSES.
$n(C_6H_{12}O_6)$.	$n(C_{12}H_{22}O_{11})$.	$n(C_6H_{10}O_5)$.
+Glucose.	+Saccharose.	+Starch.
(Dextrose.)	+Lactose.	+Glycogen.
−Lævulose.	+Maltose.	+Dextrin.
Mannitose.	+Melitose.	−Inulin.
+Galactose.	+Melezitose.	Tunicin.
Inosite.	+Trehalose.	Cellulose.
−Sorbin.	+Mycose.	Gums.
−Eucalin.	Synanthrose.	
	+Parasaccharose.	

Glucoses, $C_6H_{12}O_6$—180.

Glucose—Grape-sugar—Dextrose—Liver-sugar—Diabetic sugar.—The substance from which this group takes its name exists in all sweet and acidulous fruits; in many vegetable juices; in honey; in the animal economy in the contents of the intestines, in the liver, bile, thymus, heart, lungs, blood, and in small quantity in the urine. Pathologically it is found in the saliva, perspiration, fæces, and largely increased in the blood and urine in diabetes mellitus (see below). It may also be obtained by decomposition of certain vegetable substances called **glucosids** (*q.v.*).

It is prepared artificially by heating starch or cellulose for 24 to 36 hours with a dilute mineral acid (H_2SO_4). Glucose obtained by this method is liable to contamination with traces of arsenic, which it receives from the H_2SO_4. Starch is also converted into glucose by the influence of **diastase,** formed during the germination of grain.

Glucose crystallizes with difficulty from its aqueous solution, in white, opaque, spheroidal masses containing 1 aq; from alcohol in fine, transparent, anhydrous prisms. At about 60° (140° F.) in dry air the hydrated variety loses H_2O. It is soluble in all proportions in hot H_2O; very soluble in cold H_2O; soluble in alcohol. It is less sweet and less soluble than cane-sugar. Its solutions are dextrogyrous: $[\alpha]_D=+52°.85$.

At 170° (338° F.) it loses H_2O and is converted into **glucosan,** $C_6H_{10}O_5$. Hot dilute mineral acids convert it into a brown substance, **ulmic acid,** and, in the presence of air, formic acid. It dissolves in concentrated H_2SO_4, without coloration, forming **sulfoglucic acid.** Cold concentrated HNO_3 converts it into **nitroglucose.** Hot dilute HNO_3 oxidizes it to a mixture of oxalic and oxysaccharic acids. With organic acids it forms ethers. Its solutions dissolve potash, soda, lime, baryta, and the oxids of Pb and Cu, with which it forms compounds. When its solutions are heated with an alkali they assume a yellow or brown color, and give off a molasses-like odor, from the formation of **glucic** and **melassic acids.** Glucose in alkaline solution exerts a strong reducing action, which is favored by heat; Ag, Bi, and Hg are precipitated from their salts; and cupric are reduced to cuprous compounds, with separation of cuprous oxid. In the presence of yeast, at suitable temperatures, glucose undergoes alcoholic fermentation.

Physiological.—The greater part of the glucose in the economy in health is introduced with the food, either in its own form or as other carbohydrates, which by digestion are converted into glucose. A certain quantity is also produced in the liver at the expense of glycogen, a formation which continues for some time after death. In some forms of diabetes the production of glucose in the liver is undoubtedly greatly increased. The quantity of sugar normally existing in the blood varies from 0.81 to 1.231 part per thousand; in diabetes it rises as high as 5.8 parts per thousand.

Under normal conditions, and with food not too rich in starch and saccharine materials, the quantity of sugar eliminated as such is exceedingly small. It is oxidized in the body, and the ultimate products of such oxidation eliminated as CO_2 and H_2O. Whether or no intermediate products are formed, is still uncertain; the probability, however, is that there are. The oxidation of sugar is impeded in diabetes.

Where this oxidation, or any of its steps, occurs, is at present a matter of conjecture merely. If, as is usually believed, glucose disappears to a marked extent in the passage of the blood through the lungs, the fact is a strong support of the view that its transformation into CO_2 and H_2O does not occur as a simple oxidation, as the notion that sugar or any other substance is "burned" in the lung, beyond the small amount required by the nutrition of the organ itself, is scarcely tenable at the present day.

So long as the quantity of glucose in the blood remains at or below the normal percentage, it is not eliminated in the urine in quantities appreciable by the tests usually employed. When, however, the amount of glucose in the blood surpasses this limit from any cause, the urine becomes saccharine, and that to an extent proportional to the increase of glucose in the circulating fluids. The causes which may bring about such an increase are numerous and varied. Many of them are entirely consistent with health, and the mere presence of increased quantities of sugar in the urine is no proof, taken by itself, of the existence of diabetes.

Sugar is detectable by the ordinary tests in the urine under the following circumstances:

Physiologically.—(1.) In the urine of pregnant women and during lactation. It appears in the latter stages of gestation and does not disappear entirely until the suppression of the lacteal secretion. (2.) In small quantities in sucking children from eight days to two and one-half months. (3.) In the urine of old persons (seventy to eighty years). (4.) In those whose food contains a large amount of starchy or saccharine material. To this cause is due the apparent prevalence of diabetes in certain-localities, as in districts where the different varieties of sugar are produced.

Pathologically.—(1.) In abnormally stout persons, especially in old persons and in women at the period of the menopause. The quantity does not exceed 8 to 12 grams per 1,000 c.c. (3.5–5.5 grains per ounce), and disappears when starchy and saccharine food is withheld. This form of glycosuria is liable to develop into true diabetes when it appears in young persons. (2.) In diseases attended with interference of the respiratory processes—lung diseases, etc. (3.) In diseases where there is interference with the hepatic circulation—hepatic congestion, compression of the portal vein by biliary calculi, cirrhosis, atrophy, fatty degeneration, etc. (4.) In many cerebral and cerebro-spinal disturbances—general paresis, dementia, epilepsy; by puncture of the fourth ventricle. (5.) In intermittent and typhus fevers. (6.) By the action of many poisons—carbon monoxid, arsenic, chloroform, curari; by injection into an artery of ether, ammonia, phosphoric acid, sodium chlorid, amyl nitrite, glycogen. (7.) In true diabetes the elimination of sugar in the urine is constant, unless arrested by suitable regulation of diet, and not temporary, as in the conditions previously mentioned. The quantity of urine is increased, sometimes enormously, and it is of high sp. gr. The elimination of urea is increased absolutely, although the quantity in 1,000 c.c. may be less than that normally existing in that bulk of urine. The quantity of sugar in diabetic urine is sometimes very large; an elimination of 200 grams (6.4 ounces) in twenty-four hours is by no means uncommon; instances in which the amount has reached 400 to 600 grams (12.9–19.3 ounces) are recorded, and one case in which no less than 1,376 grams (45 ounces) were discharged in one day. The elimination is not the same at all hours of the day; during the night less sugar is voided than during the day; the hourly elimination increases after meals, reaching its maximum in 4 hours, after which it diminishes to reach the minimum in 6 to 7 hours, when it may disappear entirely. This variation is more pronounced the more copious the meal. It is obvious from the above, that, in order that quantitative determinations of sugar in urine shall be of clinical value, it is necessary that the determination be made in a sample taken from the mixed urine of twenty-four hours.

Analytical Characters.—A saccharine urine is usually abundant in quantity, pale in color, of high sp. gr., covered with a persistent froth on being shaken, and exhales a peculiar odor; when evaporated it leaves a sticky residue. The presence of glucose in urine is indicated by the following tests:

If the urine be albuminous, it is indispensable that the albumen be separated before any of the tests for sugar are applied; this is done by adding one or two drops of dilute acetic acid, or, if the urine be alkaline, just enough acetic acid to turn the reaction to acid, *and no more*, heating over the water-bath until the albumen has separated in flocks, and filtering.

(1.) When examined by the polarimeter (see p. 25) it deviates the plane of polarization to the right.

(2.) When mixed with an equal volume of liquor potassæ and heated, it turns yellow, and, if sugar be abundant, brown. A molasses-like odor is observable on adding HNO_3 (Moore's test).

(3.) The urine, rendered faintly blue with indigo solution and faintly alkaline with sodium carbonate, and heated to boiling without agitation, turns violet and then yellow if sugar be present; on agitation the blue color is restored (Mulder-Neubauer test).

(4.) About 1 c.c. of the urine, diluted with twice its bulk of water, is treated with two or three drops of cupric sulfate solution and about 1 c.c. of caustic potassa solution; if sugar be present the bluish precipitate is dissolved on agitation, forming a blue solution. The clear blue fluid, when heated to near boiling, deposits a yellow, orange, or red precipitate of cuprous oxid if sugar be present (Trommer's test). In the application of this test an excess of cupric sulfate is to be avoided, lest the color be masked by the formation of the black cupric oxid. Sometimes no precipitate is formed, but the liquid changes in color from blue to yellow. This occurs in the presence of small quantities of cupric salt and large quantities of sugar, the cuprous oxid being held in solution by the excess of glucose. In this case the test is to be repeated, using a sample of urine more diluted with water. In some instances, also, the reaction is interfered with by excess of normal constituents of the urine, uric acid, creatinin, coloring matter, etc., and instead of a bright precipitate, a muddy deposit is formed. When this occurs the urine is heated with animal charcoal and filtered; the filtrate evaporated to dryness; the residue extracted with alcohol; the alcoholic extract evaporated; the residue redissolved in water, and tested as described above.

(5.) Four or five c.c. of Fehling's solution (see p. 380) are heated in a test-tube to boiling; it should remain unaltered. The urine is then added, and the mixture boiled after each addition of 4-5 drops; if it contain sugar, the mixture turns green, and a yellow or red precipitate of cuprous oxid is formed, usually darker in color than that obtained by Trommer's test. The absence of glucose is not to be inferred until a bulk of urine equal to that of the Fehling's solution used has been added, and the mixture boiled from time to time without the formation of a precipitate. This test is the most convenient and the most reliable for clinical purposes.

(6.) A few c.c. of the urine are mixed in a test-tube with an equal volume of solution of sodium carbonate (1 pt. crystal. carbonate and 3 pts. water), a few granules of bismuth subnitrate are added, and the mixture boiled for some time (until it begins to "bump," if necessary). If sugar be present, the bismuth powder turns brown or black by reduction to elementary bismuth

(Boettger's test). No other normal constituent of the urine reacts with this test; a fallacy is, however, possible from the presence of some compound, which, by giving up sulfur, may cause the formation of the black bismuth sulfid. To guard against this, when an affirmative result has been obtained, another sample of urine is rendered alkaline and boiled with pulverized litharge; the powder should not turn black.

Nylander's test is a mere modification of Boettger's, in which the Bi is used in solution. The test solution is made by dissolving 2.5 parts $Bi(NO_3)_3$ and 4 parts of Rochelle salt in 100 parts of a solution of NaHO of 8% strength. To use the reagent it is mixed with one-tenth its volume of the urine and boiled. In the presence of glucose a black ppt. is formed. The same precautions with regard to sulfur compounds are necessary.

(7.) A solution of sugar, mixed with good yeast and kept at 25° (77° F.) is decomposed into CO_2 and alcohol. To apply the fermentation-test to urine, take three test-tubes, A, B, and C, place in each some washed (or compressed) yeast, fill A completely with the urine to be tested, and place it in an inverted position, the mouth below the surface of some of the same urine in another vessel (the entrance of air being prevented, during the inversion, by closing the opening of the tube with the finger, or a cork on the end of a wire, until it has been brought below the surface of the urine). Fill B completely with some urine to which glucose has been added, and C with distilled water, and invert them in the same way as A; B in saccharine urine, and C in distilled water. Leave all three tubes in a place where the temperature is about 25° (77° F.) for twelve hours, and then examine them. If gas have collected in B over the surface of the liquid, and none in A, the urine is free from sugar; if gas have collected in both A and B, and not in C, the urine contains sugar; if no gas have collected in B, the yeast is worthless, and if any gas be found in C, the yeast itself has given off CO_2. In the last two cases the process must be repeated with a new sample of yeast.

Quantitative Determination of Glucose.—(1.) *By the polarimeter.*—The filtered urine is observed by the polariscope (see p. 25) and the mean of half a dozen readings taken as the angle of deviation. From this the percentage of sugar is determined by the formula $p=\frac{a}{52.85 \times l}$, in which p=the weight, in grams, of glucose in 1 c.c. of urine; a=the angle of deviation; l=the length of the tube in decimetres. The same formula may be used for other substances by substituting for 52.85 the value of $[a]_D$ for that substance. If the urine contain albumen, it must be removed before determining the value of a.

(2.) *By specific gravity; Robert's method.*—The sp. gr. of the urine is carefully determined at 25° (77° F.); yeast is then added, and the mixture kept at 25° (77° F.) until fermentation is complete; the sp. gr. is again observed, and will be found to be lower than before. Each degree of diminution represents 0.2196 gram of sugar in 100 c.c. (1 grain per ounce) of urine.

(3.) *By Fehling's solution.*—Of the many formulæ for Fehling's solutions, the one to which we give the preference is that of Dr. Piffard. Two solutions are required:

I.	Cupric sulfate (pure, crystals)........	51.98	grams.
	Water..................................	500.0	c.c.
II.	Rochelle salt (pure, crystals)...	259.9	grams.
	Sodium hydroxid solution, sp. gr. 1.12.	1000.0	c.c.

When required for use, one volume of No. I. is mixed with two volumes of No. II. The copper contained in 20 c.c. of this mixture is precipitated as cuprous oxid by 0.1 gram glucose.

To use the solution, 20 c.c. of the mixed solutions are placed in a flask of 250–300 c.c. capacity, 40 c.c. of distilled water are added, the whole thoroughly mixed and heated to boiling. On the other hand, the urine to be tested is diluted with four times its volume of water if poor in sugar, and with nine times its volume if highly saccharine (the degree of dilution required is, with a little practice, determined by the appearance of the deposit obtained in the qualitative testing); the water and urine are thoroughly mixed and a burette filled with the mixture. A few drops of aqua ammoniæ are added to the Fehling's solution and the diluted urine added, in small portions toward the end, until the blue color is entirely discharged—the contents of the flask being made to boil briskly between each addition from the burette. When the liquid in the flask shows no blue color, when looked through with a white background, the reading of the burette is taken. This reading, divided by five if the urine was diluted with four volumes of water, or by ten if with nine volumes, gives the number of c.c. of urine containing 0.1 gram of glucose; and consequently the elimination of glucose in twenty-four hours, in decigrams, is obtained by dividing the number of c.c. of urine in twenty-four hours by the result obtained above.

Example.—20 c.c. Fehling's solution used, and urine diluted with four volumes of water.

Reading of burette: 36.5 c.c. $\frac{36.5}{5}=7.3$ c.c. urine contain 0.1 gram glucose. Patient is passing 2,436 c.c. urine in twenty-four hours. $\frac{2,436}{7.3}=333.6$ decigr. $=33.36$ grams glucose in twenty-four hours.

The accuracy of the determination may be controlled by filtering off some of the fluid from the flask at the end of the reaction; a portion of the filtrate is acidulated with acetic acid and treated with potassium ferrocyanid solution; if it turn reddish-brown the reduction has not been complete, and the result is affected with a plus error. To another portion of the filtrate a few drops of cupric sulfate solution are added and the mixture boiled; if any precipitation of cuprous oxid be observed, an excess of urine has been added, and the result obtained is less than the true one.

This method, when carefully conducted with accurately prepared and undeteriorated solutions, is the best adapted to clinical uses. The copper solution should be kept in the dark, in a well-closed bottle, and the stopper and neck of the No. II. bottle should be well coated with paraffin.

(4.) *Gravimetric method.*—When more accurate results than are obtainable by Fehling's volumetric process are desired, recourse must be had to a determination of the weight of cuprous oxid obtained by reduction. A small quantity of freshly prepared Fehling's solution is heated to boiling in a small flask; to it is gradually added, with the precautions observed in the volumetric method, a known volume of urine, such that at the end of the reduction there shall remain an excess of unreduced copper salt. The flask is now completely filled with boiling H_2O, corked, and allowed to cool. The alkaline fluid is separated as rapidly as possible from the precipitated oxid, by decantation and filtration through a small double filter, and the precipitate and flask repeatedly washed with hot H_2O until the washings are no longer alkaline; a small portion of the precipitate remains adhering to the walls of the flask. The filter and its contents are dried and burned in a weighed porcelain crucible; when this has cooled, the flask is rinsed out with a small quantity of HNO_3; this is added to the contents of the crucible, evaporated over the water-bath, the crucible slowly heated to redness, cooled, and weighed. The difference between this last weight and that of the crucible + that of the filter-ash, is the weight of cupric oxid, of which 220 parts=100 parts of glucose.

Lævulose—*Uncrystallizable sugar*—forms the uncrystallizable portion of the sugar of fruits and of honey, in which it is associated with glucose; it is also produced artificially by the prolonged action of boiling water upon **inulin**; and as one of the constituents of inverted sugar.

Lævulose is not capable of crystallization, but may be obtained as a thick syrup; very soluble in water, insoluble in absolute alcohol; it is sweeter but less readily fermentable than glucose, which it equals in the readiness with which it reduces cupropotassic solutions. Its prominent physical property, and that to which it owes its name, is its strong left-handed polarization.

$[\alpha]_D = -106°$ at 15° (59° F.). At 170° (338° F.) it is converted into the solid, amorphous **lævulosan, $C_6H_{10}O_5$.**

Mannitose—is obtained by the oxidation of mannite. It is a yellow, uncrystallizable sugar, having many of the characters of glucose, but optically inactive.

Galactose—sometimes improperly called lactose—is formed by the action of dilute acids upon lactose (milk-sugar) as glucose is formed from saccharose. It differs from glucose in crystallizing more readily, in being very sparingly soluble in cold alcohol, in its action upon polarized light, $[\alpha]_D = +83°.33$, and in being oxidized to mucic acid by HNO_3. The substance called **cerebrose,** obtained by the action of H_2SO_4 on cerebrin and other constituents of nerve-tissue, is identical with galactose.

Inosite—*Muscle-sugar*—exists in the liquid of muscular tissue, in the lungs, kidneys, liver, spleen, brain, and blood; pathologically in the urine in Bright's, diabetes, and after the use of drastics in uræmia, and in the contents of hydatid cysts; also in the seeds and leaves of certain plants. What the source and function of inosite in the animal economy may be is still a matter of conjecture.

It forms long, colorless, monoclinic crystals, containing 2 Aq, usually arranged in groups having a cauliflower-like appearance. It effloresces in dry air; has a distinctly sweet taste; is easily soluble in water, difficultly in alcohol; insoluble in absolute alcohol and in ether; it is without action upon polarized light.

The position of inosite in this series is based entirely upon its chemical composition, as it does not possess the other characteristics of the group. It does not enter directly into alcoholic fermentation, although upon contact with putrefying animal matters it produces lactic and butyric acids; when boiled with barium or potassium hydroxid, it is not even colored; in the presence of inosite, potash precipitates with cupric sulfate solution, the precipitate being redissolved in an excess of potash; but no reduction takes place upon boiling the blue solution.

The presence of inosite is indicated by the following reactions: *Scherer's.*—Treated with HNO_3, the solution evaporated to near dryness, and the residue moistened with ammonium hydroxid and calcium chlorid, and again evaporated; a rose-pink color is produced. Succeeds only with nearly pure inosite. *Gallois'.*—Mercuric nitrate produces, in solutions of inosite, a yellow precipitate, which, on cautious heating, turns red; the color disappears on cooling, and reappears on heating.

Saccharoses, $C_{12}H_{22}O_{11}$—342.

Saccharose—Cane-sugar—Beet-sugar—Saccharum (U. S.)—the most important member of the group, exists in many roots, fruits, and grasses, and is produced from the sugar-cane, *Saccharum officinarum*, sorghum, *Sorghum saccharatum*, beet, *Beta vulgaris*, and sugar-maple, *Acer saccharinum*.

For the extraction of sugar the expressed juice is heated in large pans to about 100° (212° F.); milk of lime is added, which causes the precipitation of albumen, wax, calcic phosphate, etc.; the clear liquid is drawn off, and "delimed" by passing a current of CO_2 through it; the clear liquid is again drawn off and evaporated, during agitation, to the crystallizing-point; the product is drained, leaving what is termed **raw or muscovado sugar,** while the liquor which drains off is **molasses.** The sugar so obtained is purified by the process of "refining," which consists essentially in adding to the raw sugar, in solution, albumen in some form, which is then coagulated, filtering first through canvas, afterward through animal charcoal; the clear liquid is evaporated in "vacuum-pans," at a temperature not exceeding 72° (161°.6 F.), to the crystallizing-point. The product is allowed to crystallize in earthen moulds; a saturated solution of pure sugar is poured upon the crystalline mass in order to displace the uncrystallizable sugar which still remains, and the loaf is finally dried in an oven. The liquid displaced as above is what is known as **sugar-house syrup.**

Pure sugar should be entirely soluble in water; the solution should not turn brown when warmed with dilute potassium hydroxid solution; should not reduce Fehling's solution, and should give no precipitate with ammonium oxalate.

Beet-sugar is the same as cane-sugar, except that, as usually met with in commerce, it is lighter, bulk for bulk. **Sugar-candy,** or **rock-candy,** is cane-sugar allowed to crystallize slowly from a concentrated solution without agitation. **Maple-sugar** is a partially refined, but not decolorized variety of cane-sugar.

Saccharose crystallizes in small, white, monoclinic prisms; or, as sugar-candy, in large, yellowish, transparent crystals; sp. gr. 1.606. It is very soluble in water, dissolving in about one-third its weight of cold water, and more abundantly in hot water. It is insoluble in absolute alcohol or ether, and its solubility in water is progressively diminished by the addition of alcohol. Aqueous solutions of cane-sugar are dextrogyrous, $[\alpha]_D=+73^\circ.8$.

When saccharose is heated to 160° (320° F.) it fuses, and the liquid, on cooling, solidifies to a yellow, transparent, amorphous mass, known as **barley-sugar;** at a slightly higher temperature, it is decomposed into glucose and lævulosan; at a still higher temperature, H_2O is given off, and the glucose already formed is converted into glucosan; at 210° (410° F.) the evolution of H_2O is more abundant, and there remains a brown material known as **caramel,** or **burnt sugar;** a tasteless substance, insoluble in strong alcohol, but soluble in H_2O or aqueous alcohol, and used to communicate color to spirits; finally, at higher temperatures, methyl hydrid and the two oxids of carbon are given off; a brown oil, acetone, acetic acid, and aldehyde distil over; and a carbonaceous residue remains.

If saccharose be boiled for some time with H_2O, it is converted into **inverted sugar,** which is a mixture of glucose and lævulose: $C_{12}H_{22}O_{11}+H_2O=C_6H_{12}O_6+C_6H_{12}O_6$. With a solution of saccharose the polarization is dextrogyrous, but, after inversion, it becomes lævogyrous, because the left-handed action of the molecule of lævulose produced, $[\alpha]_D=-106°$, is only partly neutralized by the right-handed action of the glucose, $[\alpha]_D=+52°.85$. This inversion of cane-sugar is utilized in the testing of samples of sugar. On the other hand, it is to avoid its occurrence, and the consequent loss of sugar, that the vacuum-pan is used in refining—its object being to remove the H_2O at a low temperature.

Those acids which are not oxidizing agents act upon saccharose in three ways, according to circumstances: (1) if tartaric and other organic acids be heated for some time with saccharose to 100°–120° (212°–248° F.), compounds known as **saccharids,** and having the constitution of ethers, are formed; (2) heated with mineral acids, even dilute, and less rapidly with some organic acids, saccharose is quickly converted into inverted sugar; (3) concentrated acids decompose cane-sugar entirely, more rapidly when heated than in the cold; with HCl, formic acid and a brown, flocculent material (ulmic acid?) are formed; with H_2SO_4, SO_2 and H_2O are formed, and a voluminous mass of charcoal remains. Oxalic acid, aided by heat, produces CO_2, formic acid, and a brown substance (humin?).

Oxidizing agents act energetically upon cane-sugar, which is a good reducing agent. With potassium chlorate, sugar forms a mixture which detonates when subjected to shock, and which deflagrates when moistened with H_2SO_4. Dilute HNO_3, when heated with saccharose, oxidizes it to saccharic and oxalic acids. Concentrated HNO_3, alone or mixed with H_2SO_4, converts it into the explosive **nitro-saccharose.** Potassium permanganate, in acid solution, oxidizes it completely to CO_2 and H_2O.

Cane-sugar reduces the compounds of Ag, Hg, and Au, when heated with their solutions; it does not reduce the cupro-potassic solutions in the cold, but effects their reduction when heated with them, to an extent proportional to the amount of excess of alkali present.

When moderately heated with liquor potassæ, cane-sugar does not turn brown, as does glucose; but by long ebullition it is decomposed by the alkalies much less readily than glucose, with formation of acids of the fatty series and oxalic acid.

With the bases, saccharose forms definite compounds called **sucrates** (improperly saccharates, a name belonging to the salts of saccharic acid). With Ca it forms five compounds. Calcium hydroxid dissolves readily in solutions of sugar, with formation of a Ca compound, soluble in H_2O, containing an excess of sugar. A solution containing 100 parts of sugar in 600 parts of H_2O dissolves 32 parts of calcic oxid. These solutions have an alkaline taste; are decomposed, with formation of a gelatinous precipitate, when heated, and with deposition of calcium carbonate and regeneration of saccharose, when treated with CO_2. Quantities of calcium sucrates are frequently introduced into sugars to increase their weight—an adulteration the less readily detected, as the sucrate dissolves with the sugar. Calcium sucrates exist in the **liq. calcis saccharatus** (**Br.**).

Yeast causes fermentation of solutions of cane-sugar, but only after its conversion into glucose. Fermentation is also caused by exposing a solution of sugar containing ammonium phosphate to the air.

During the process of digestion, probably in the small intestine, cane-sugar is converted into glucose.

Lactose—Milk-sugar—*Lactine*—**Saccharum lactis** (**U. S., Br.**)—has hitherto been found only in the milk of the mammalia. It may be obtained from skim-milk by coagulating the casein with a small quantity of H_2SO_4, filtering, evaporating, redissolving, decolorizing with animal charcoal, and recrystallizing.

It forms prismatic crystals; sp. gr. 1.53; hard, transparent, faintly sweet, soluble in 6 parts of cold and in 2.5 parts of boiling H_2O; soluble in acetic acid; insoluble in alcohol and in ether; its solutions are dextrogyrous $[\alpha]_D = +59^\circ.3$. The crystals, dried at 100° (212° F.), contain 1 Aq, which they lose at 150° (302° F.).

Lactose is not altered by contact with air. Heated with dilute mineral or with strong organic acids, it is converted into galactose. HNO_3 oxidizes it to mucic and oxalic acids. A mixture of HNO_3 and H_2SO_4 converts it into an explosive nitro-compound. With organic acids it forms ethers. With soda, potash, and lime it forms compounds similar to those of saccharose, from which lactose may be recovered by neutralization, unless they have been heated to 100° (212° F.), at which temperature they are decomposed. It reduces Fehling's solution, and reacts with Trommer's test.

In the presence of yeast, lactose is capable of alcoholic fermentation, which takes place slowly, and, as it appears, without previous transformation of the lactose into either glucose or galactose. On contact with putrefying albuminoids it enters into lactic fermentation.

The average proportion of lactose in different milks is as follows: **Cow, 5.5 per cent.**; mare, 5.5; ass, 5.8; human, 5.3; sheep, 4.2; goat, 4.0. When taken internally, it is converted into galactose by the pancreatic secretion; when injected into the blood, it does not appear in the urine, which, however, contains glucose.

Maltose—a sugar closely resembling glucose in many of its properties, is formed along with dextrin during the conversion of starch into sugar by the action of diastase and of the cryptolytes of the saliva and pancreatic juice. It crystallizes as does glucose, but differs from that sugar in being less soluble in alcohol and in exerting a dextrogyratory power three times as great.

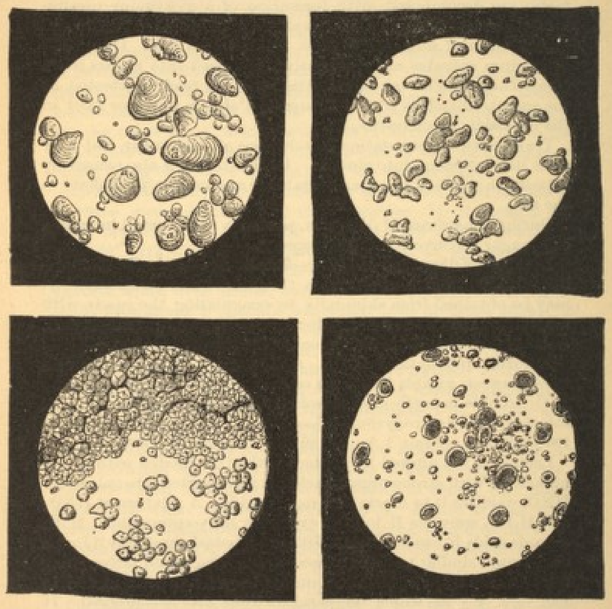


FIG. 40.

Amyloses, $n(C_6H_{10}O_5)$—$n162$.

Starch—Amylum (U. S.)—the most important member of the group, exists in the roots, stems, and seeds of all plants. It is prepared from rice, wheat, potatoes, maniot, beans, sago, arrowroot, etc. The comminuted vegetable tissue is steeped for a considerable time in H_2O rendered faintly alkaline with soda; the softened mass is then rubbed on a sieve under a current of water, which washes out the starch granules; the washings are allowed to deposit the starch, which, after washing by decantation, is dried at a low temperature.

Starch is a white powder, having a peculiar slippery feel, or it appears in short columnar masses. The granules of starch differ in size and appearance according to the kind of plant from which they have been obtained. They are rounded or egg-shaped masses, having at the centre or toward one end a spot, called the **hilum**, around which are a series of concentric lines more or less well marked. Differences in size, shape, and markings of starch granules are shown in Fig. 40.

Starch is not altered by exposure to air, except that it absorbs moisture. Commercial starch contains 18 per cent. of H_2O, of which it loses 8 per cent. in vacuo, and the remaining 10 per cent. at 145° (293° F.). It is insoluble in alcohol, ether and cold water.

If 15 to 20 parts of H_2O be gradually heated with 1 part of starch, the granules swell at about 55° (131° F.), and at 80° (176° F.) they have reached 30 times their original dimensions; their structure is no longer distinguishable, and they form a translucent, gelatinous mass, commonly known as starch-paste. In this state the starch is said to be hydrated, and, if boiled with much H_2O, and the liquid filtered, a solution of starch passes through, which is opalescent from the suspension in it of undissolved particles. Cold dilute solutions of the alkalies produce the same effects on starch as does hot water. Hydrated starch is dextrogyrous, $[\alpha]_D=+216°$. Dry heat causes the granules of starch to swell and burst; at 200° (392° F.) it is converted into **dextrin**; at 230° (446° F.) it forms a brownish-yellow, fused mass, composed principally of **pyrodextrin.** Hydrated starch is converted into dextrin by heating with H_2O at 160° (320° F.), and, if the action be prolonged, the new product is changed to glucose.

The amount of starch contained in food vegetables varies from about 5 per cent. in turnips to 89 per cent. in rice, as will be observed in the table on page 388.

If starch be ground up with dilute H_2SO_4, after about half an hour the mixture gives only a violet color with I (see below); if now the acid be neutralized with chalk and the filtered liquid evaporated, it yields a white, granular product, which differs from starch in being soluble in H_2O, especially at 50° (122° F.), and in having a lower rotary power, $[\alpha]_D=+211°$. If the action be prolonged, the value of $[\alpha]_D$ continues to sink until it reaches $+73°.7$, when the product consists of a mixture of dextrin and glucose. Concentrated HNO_3 dissolves starch in the cold, forming a nitro-product called **xylodin** or **pyroxam,** which is insoluble in H_2O, soluble in a mixture of alcohol and ether; explosive. HCl and oxalic acid convert starch into glucose. When starch is heated under pressure to 120° (248° F.) with stearic or acetic acid, compounds are formed which seem to be ethers, and to indicate that starch is the hydrate of a trivalent, oxygenated radical, $(C_6H_7O_2)'''$. Potash and soda in dilute solution convert starch into the soluble modification mentioned above.

COMPOSITION OF VEGETABLE FOODS.

	Nitrogenized matter.	Starch.	Dextrin, etc.	Cellulose.	Fat.	Mineral matter.	Carbohydrate.	Water.	Vegetable fibre, etc.	Authority.
Wheat, hard	22.75	58.62	9.50	3.50	2.61	3.02	.....	.....	....	Payen.
Wheat, hard	19.50	65.07	7.60	3.0	2.12	2.71	.....	.....	....	Payen.
Wheat, hard	20.0	63.80	8.0	3.10	2.25	2.85	.....	.....	....	Payen.
Wheat, semi-hard.	15.25	70.05	7.0	3.0	1.95	2.75	.....	.....	....	Payen.
Wheat, soft	12.65	76.51	6.05	2.80	1.87	2.12	.....	.....	....	Payen.
Rye	12.50	64.65	14.90	3.10	2.25	2.60	.....	.....	....	Payen.
Barley	12.96	66.43	10.0	4.75	2.76	3.10	.....	.....	....	Payen.
Oats	14.39	60.59	9.25	7.06	5.50	3.25	.....	.....	....	Payen.
Maize	12.50	67.55	4.0	5.90	8.80	1.25	.....	.....	....	Payen.
Rice	7.55	88.65	1.0	1.10	0.80	0.90	.....	.....	....	Payen.
Flour	14.45	.....	.....	....	1.25	1.60	68.48	14.22	....	Payen.
Flour	10.80	.....	.....	....	2.0	1.70	70.50	15.0	....	Letheby.
Bread	8.10	.....	.....	....	1.60	2.30	51.00	37.0	....	Letheby.
Oatmeal	12.60	.....	.....	....	5.60	3.0	63.80	15.0	....	Letheby.
Buckwheat	13.10	64.90	.....	3.50	3.0	2.50	.....	13.0	....	Payen.
Quinoa seeds	22.86	56.80	.....	....	5.74	5.05	.....	.....	9.53	Voelcker.
Quinoa flour	19.0	60.0	.....	....	5.0	....	.....	16.0	....	Voelcker.
Horse-bean	30.80	48.30	.....	3.0	1.90	3.50	.....	12.50	....	Payen.
Broad bean	29.63	55.85	.....	1.05	2.0	3.65	.....	8.40	....	Payen.
White bean	25.50	55.70	.....	2.09	2.80	3.20	.....	9.90	....	Payen.
Peas, dried	23.80	58.70	.....	3.50	2.10	2.10	.....	8.30	....	Payen.
Lentils	25.20	56.0	.....	2.40	2.60	2.30	.....	11.50	....	Payen.
Potato	2.50	20.0	1.09	1.04	0.11	1.26	.....	74.0	....	Payen.
Potato	2.10	18.80	3.20	....	0.20	0.70	.....	75.0	....	Letheby.
Sweet potato	1.50	16.05	10.20	0.45	0.30	2.60	.....	67.50	1.10	Payen.
Carrots	1.30	8.40	6.10	....	0.20	1.0	.....	83.0	....	Letheby.
Parsnip	1.10	9.60	5.80	....	0.50	1.0	.....	82.0	....	Letheby.
Turnip	1.20	5.10	2.10	....	....	0.60	.....	91.0	....	Letheby.

A dilute solution of I produces a more or less intense blue-violet color with starch, either dry, hydrated, or in solution, the color disappearing on the application of heat, and returning on cooling. If to a solution of starch, blued by I, a solution of a neutral salt be added, there separates a blue, flocculent deposit of the so-called **iodid of starch.** Iodin renders starch soluble in water, and a soluble iodized starch, **Amylum iodatum** (**U. S.**), is obtained by triturating together **19 pts.** starch, 2 pts. water, and **1 pt.** iodin, and drying below 40° (104° F.).

Starch has not been found in the animal economy outside of the alimentary canal, in which, as a prerequisite to its absorption, it must be converted into dextrin and glucose. This change is partially effected by the action of the saliva; more rapidly with hydrated than with dry starch, and more rapidly with the saliva of some animals than that of others; those of man and of the rabbit acting much more quickly than those of the horse and dog. A great part of the starch taken with the food passes into the small intestine unchanged; here, under the influence of a pancreatic cryptolyte, a further transformation into glucose, and of a portion into lactic and butyric acids, takes place.

During the germination of grain, as in the process of malting, a peculiar, nitrogenized substance is produced, which is known as **diastase.** Under the influence of this body the starch is more or less completely converted into glucose, in very much the same way as the conversion occurs in the body.

This "diastatic" action, whether produced by vegetable or animal processes, does not take place by a simple conversion of starch into glucose, by some such single reaction as that expressed by $C_6H_{10}O_5+H_2O=C_6H_{12}O_6$, but by successive stages in which "soluble starch" is first produced, then several bodies called **dextrins,** then maltose, and finally glucose. (See Dextrin, p. 390.)

Glycogen occurs in the liver, the placenta, white blood-corpuscles, pus-cells, young cartilage-cells, in many embryonic tissues, and in muscular tissue. During the activity of muscles the amount of glycogen which they contain is diminished, and that of sugar increased.

Pure glycogen is a snow-white, floury powder; amorphous, tasteless, and odorless; soluble in H_2O, insoluble in alcohol and ether. In H_2O it swells up at first, and forms an opalescent solution, which becomes clear on the addition of potash. Its solutions are dextrogyrous to about three times the extent of those of glucose.

Dilute acids, ptyalin, pancreatin, extract of liver-tissue, blood, diastase, and albuminoids convert glycogen into a sugar having all the properties of glucose Cold HNO_3 converts it into xyloidin; on boiling, into oxalic acid. Its solutions dissolve cupric hydroxid, which is, however, not reduced on boiling. Iodin colors glycogen wine-red.

Concerning the method of formation of glycogen in the economy, but little is known with certainty; there is little room for doubting, however, that while the bulk of the glycogen found in the liver results from modification of the carbohydrates, it may be and is produced from the albuminoids as well. The ultimate fate of glycogen is undoubtedly its transformation into sugar under the influence of the many substances existing in the body capable of provoking that change. This transformation is continuous in the liver during life, and is accomplished through the same series of intermediary changes into dextrins and maltose as in the case of the conversion of starch into sugar, except that possibly the structure of the dextrins may be different.

Dextrin—*British gum*—a substance resembling gum arabic in appearance and in many properties, is obtained by one of three methods: (1) by subjecting starch to a dry heat of 175° (347° F.); (2) by heating starch with dilute H_2SO_4 to 90° (194° F.) until a drop of the liquid gives only a wine-red color with iodin; neutralizing with chalk, filtering, concentrating, precipitating with alcohol; (3) by the action of diastase (infusion of malt) upon hydrated starch. As soon as the starch is dissolved the liquid must be rapidly heated to boiling to prevent saccharification.

Commercial dextrin is a colorless, or yellowish, amorphous powder, soluble in H_2O in all proportions, forming mucilaginous liquids. When obtained by evaporation of its solution, it forms masses resembling gum arabic in appearance. Its solutions are dextrogyrous, and reduce cupro-potassic solutions under the influence of heat, to amounts varying with the method of formation of the sample. It is colored wine-red by iodin. It is extensively used as a substitute for gum acacia.

By the action of diastase upon starch, four dextrins are produced: 1st, **Erythrodextrin**, which is colored red by iodin, and which is easily attacked by diastase; 2d, **Achroodextrin** α, not colored by iodin; partially converted into sugar by diastase; rotary power $[\alpha]_D = +210°$; reducing power (glucose=100)=12; 3d, **Achroodextrin** β, not colored by iodin, nor decomposable in 24 hours by diastase; rotary power $+190°$; reducing power=12; 4th, **Achroodextrin** γ, not colored by iodin, nor decomposed by diastase; slowly converted into glucose by dilute H_2SO_4; rotary power $= +150°$; reducing power=28.

An explanation of this series of transformations has been suggested in the supposition that the molecule of starch consists of $50(C_{12}H_{20}O_{10})$; that this is first converted into soluble starch $10(C_{12}H_{20}O_{10})$, and that this is then converted into the different forms of dextrin by a series of hydrations attended by simultaneous formation of maltose, of which the final result might be representd by the equation:

$$\underset{\text{Soluble starch.}}{10(C_{12}H_{20}O_{10})} + \underset{\text{Water.}}{8(H_2O)} = \underset{\text{Achroödextrin.}}{2(C_{12}H_{20}O_{10})} + \underset{\text{Maltose.}}{8(C_{12}H_{22}O_{11})}$$

Cellulose—*Cellulin*—forms the basis of all vegetable tissues. It exists, almost pure, in the pith of elder and of other plants, in the purer, unsized papers, in cotton, and in the silky appendages of certain seeds. Cotton, freed from extraneous matter by boiling with potash, and afterward with dilute HCl, yields pure cellulose, in which form it is now met with in commerce under the name "absorbent cotton."

It is a white material, having the shape of the vegetable structure from which it was obtained; insoluble in the usual neutral solvents, but soluble in the deep-blue liquid obtained by dissolving copper in ammonia in contact with air.

Vegetable parchment, or **parchment paper,** is a tough material, possessing many of the valuable properties of parchment, made by immersing unsized paper for an instant in moderately strong H_2SO_4, washing thoroughly, and drying.

Nitro-cellulose.—By the action of HNO_3 upon cellulose (cotton) three different products of substitution may be obtained: **mono-nitro-cellulose,** soluble in acetic acid, insoluble in a mixture of ether and alcohol; **dinitro-cellulose,** insoluble in acetic acid, soluble in a mixture of ether and alcohol; **trinitro-cellulose,** soluble in both the above solvents. **Gun-cotton** or **pyroxylin** is composed of varying proportions of these three derivatives. When gun-cotton is required as an explosive agent, the process is so managed that the product shall contain the greatest possible proportion of trinitro-cellulose, the most readily inflammable of the three. When required for the preparation of collodion, for use in medicine or in photography, dinitro-cellulose is the most valuable. To obtain this, a mixture is made of equal weights of HNO_3 and H_2SO_4 (of each about 5 times the weight of the cotton to be treated); in this the cotton is immersed and well stirred for about three minutes, after which it is well stirred in a large vessel of water, washed with fresh portions of water until the washings are no longer precipitated by barium chlorid, and dried. **Collodion** is a solution of dinitro-cellulose in a mixture of three volumes of ether and one volume of alcohol. **Celluloid** is gun-cotton and camphor compacted under pressure.

Lignin is an isomere of cellulose, which constitutes the greater part of the "incrusting substance" of wood.

Gums—are substances of unknown constitution, existing in plants; amorphous; soluble in water, insoluble in alcohol; converted into glucose by boiling with dilute H_2SO_4.

Lichenin is obtained from various lichens by extraction with boiling water, forming a jelly on cooling; it is oxidized to oxalic acid by HNO_3; is colored yellow by iodin; and is precipitated from its solutions by alcohol.

Arabin is the soluble portion of gum arabic and gum senegal—**Acacia (U. S.).** To separate it, gum arabic is dissolved in water acidulated with HCl, and precipitated by alcohol. It is a white, amorphous, tasteless substance, which is not colored by iodin; is oxidized by HNO_3 to mucic and saccharic acids; is converted by

H_2SO_4 into a non-fermentable sugar, **arabinose**; and has the composition, $C_{12}H_{20}O_{10}+1Aq$.

Bassorin constitutes the greater part of gum tragacanth; it is insoluble in water, but swells up to a jelly in that fluid.

Cerasin is an insoluble gum exuded by cherry- and plum-trees; water acts upon it as upon bassorin.

CYCLIC HYDROCARBONS AND THEIR DERIVATIVES.

AROMATIC SUBSTANCES.

It is among the compounds of this series that the most important products of synthetic chemistry are to be found; and it is in dealing with them that theoretic chemistry has received the widest applications.

Although many of these bodies occur in nature, by far the greater number, including all the hydrocarbons except the members of the paraffene and terebenthene groups, are artificial products.

Although the members of the acyclic and of the cyclic families are not readily converted into each other, acyclic compounds are frequently grafted upon cyclic, and cyclic compounds are frequently decomposed with formation of acyclic derivatives, but in the latter case cyclic derivatives are simultaneously produced.

Among the instances of conversion of acyclic into cyclic compounds is one of interest as bearing upon the constitution and relationships of the cyclic hydrocarbons, and as showing their pyrogenic origin.

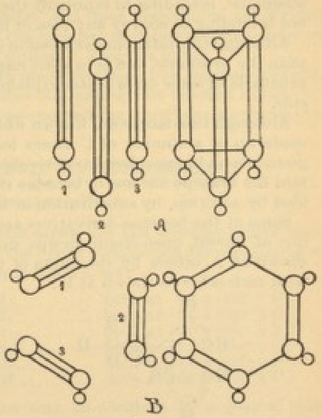
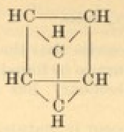


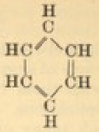
FIG. 41.

We have seen that one of the constituents of coal-gas is **acetylene, H—C≡C—H.** The central figure of the cyclic compounds is **benzene, C_6H_6,** which is obtained principally from gas-tar; and whose molecule may clearly be considered as produced by the union of three molecules of acetylene, $3C_2H_2 = C_6H_6$. If we represent three molecules of acetylene by 1, 2, 3, A or B, Fig. 41 (the larger circles representing the carbon, and the smaller the hydrogen atoms), it is easy to conceive that by the action of heat one of the three bonds uniting the two C atoms may be loosened, and that the neighboring C atoms will then attach themselves to each other, exchanging the valences thus liberated, and produce a molecule of benzene. The arrangement A produces the "pris-

matic formula," the arrangement B the **"hexagonal formula"** of benzene, usually represented in writing thus :



or

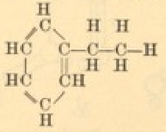


It is hardly necessary to mention that such formulæ are merely schematic, intending to represent the relations of the atoms, but not intending to convey any idea of the shape of the molecule.

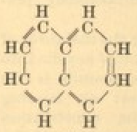
Although the hexagonal expression is more frequently met with than the prismatic, and is in some respects more manageable, the prismatic in some cases better explains the structure of the molecule.

Although substances are known which contain a cyclic nucleus made up of a number of C atoms less than six, all cyclic compounds may be considered as derivable from benzene, and all contain the **benzene nucleus** or **benzene ring**, C_6H_6, more or less modified by addition, by substitution or by subtraction.

Some of the benzene derivatives are produced by simple grafting of lateral, open-chain groups upon a benzene nucleus, as shown at A, others by the union of two or more benzene rings with each other as shown at B :



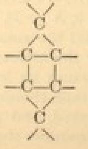
A.

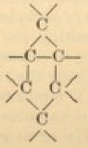


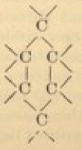
B.

and all the molecules so formed are capable of deeper modification by further substitution of atoms or groups for the remaining H atoms.

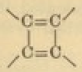
The prismatic formula given above may also be opened out, and the molecule thus gain two, four, or six valences, thus :

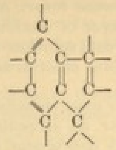


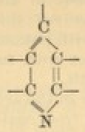




Condensation and substitution may also occur in the benzene ring itself, giving rise to compounds containing modified nuclei, such as :







The benzenic hydrocarbons (and their derivatives) are divided into groups according to the number of benzene nuclei, more or less modified, which they contain. Thus we have :

Monobenzenic hydrocarbons—containing one benzene nucleus.
Dibenzenic hydrocarbons—containing two benzene nuclei.
Tribenzenic hydrocarbons—containing three benzene nuclei, etc.

MONOBENZENIC HYDROCARBONS.

SERIES C_nH_{2n-6}

The hydrocarbons of this series are the starting-points from which the major part of the cyclic compounds are obtainable or derivable. Those at present known are :

Benzene	C_6H_6	boils at 80°.4 (176°.7 F.)
Toluene	C_7H_8	boils at 110°.3 (230°.5 F.)
Xylene	C_8H_{10}	boils at 142°.0 (287°.6 F.)
Cumene	C_9H_{12}	boils at 151°.4 (304°.5 F.)
Cymene	$C_{10}H_{14}$	boils at 175°.0 (347°.0 F.)
Laurene	$C_{11}H_{16}$	boils at 188°.0 (370°.4 F.)

The terms above benzene may be obtained by a general reaction, by treating a mixture of monobrombenzene, ether and the bromid or iodid of the corresponding alcoholic radical with sodium in excess :

$$\underset{\text{Monobrom-benzene.}}{C_6H_5Br} + \underset{\text{Methyl bromid.}}{CH_3Br} + \underset{\text{Sodium.}}{Na_2} = \underset{\text{Sodium bromid.}}{2\,NaBr} + \underset{\text{Methylbenzene. Toluene.}}{C_6H_5,CH_3}$$

The reaction is violent and small quantities only (30–40 grams) can be operated on.

Benzene—*Benzol—Phenyl hydrid*—$\mathbf{C_6H_6}$—78—(not to be confounded with the commercial *benzine*, a mixture of hydrocarbons of the series C_nH_{2n+2}, obtained from petroleum) does not exist in nature, but is produced in a number of reactions. It is obtained by one of two methods, according as it is required chemically pure or mixed with other substances.

To obtain it pure, recourse must be had to the decomposition of one of its derivatives, benzoic acid; this substance is intimately mixed with 3 pts. slacked lime, and the mixture heated to dull redness in an earthenware retort, connected with a well-cooled receiver; the upper layer of distilled liquid is separated, shaken with potassium hydroxid solution, again separated, dried by contact with fused calcium chlorid, and redistilled over the water-bath.

For use in the arts, and for most chemical purposes, benzene is obtained from coal- or gas-tar, an exceedingly complex mixture, containing some forty or fifty substances, among which are:

Hydrocarbons.

Benzene.
Toluene.
Xylene.
Cumene.
Cymene.
Naphthalene.
Acenaphthalene.
Fluorene.
Anthracene.
Retene.
Chrysene.
Pyrene.

Phenols.

Phenol.
Cresylol.
Phlorylic.
Corallin.
Catechol.

Bases.

Pyridin.
Anilin.
Picolin.
Lutidin.
Collidin.
Leucolin.
Iridolin.
Cryptidin.
Acridin.
Coridin.
Rubidin.
Viridin.

By a primary distillation of coal-tar the most volatile constituents, including benzene, are separated as **light oil**; this is washed, first with H_2SO_4, and then with caustic soda, and afterward redistilled; that portion being collected which passes between 80° and 85° (176°–185° F.). This is the commercial benzene, a product still contaminated with the higher homologues of the same series, from which it is almost impossible to separate it, but whose presence is necessary for the principal use to which benzene is put—the manufacture of anilin dyes.

Benzene is a colorless, mobile liquid, having, when pure, an agreeable odor; sp. gr. 0.86 at 15° (59° F.); crystallizing at +4°.5 (40°.1 F.); boiling at 80°.5 (176°.9 F.); very sparingly soluble in water, soluble in alcohol, ether, and acetone. It dissolves I, S, P, resins, caoutchouc, gutta-percha, and almost all the alkaloids. It is inflammable, and burns with a luminous, smoky flame.

Benzene unites with Cl or Br to form products of addition, or of substitution; the corresponding iodin compounds can only be obtained by indirect methods. Sulfuric acid combines with benzene to form a neutral substance, **sulfo-benzid**, when the anhydrous acid is used, and **phenyl-sulfurous acid** with the ordinary H_2SO_4.

If fuming HNO_3 of sp. gr. 1.52 be slowly added to benzene, a reddish liquid is formed; from which, on the addition of H_2O a reddish-yellow oil separates, and is purified by washing with H_2O and with sodium carbonate solution, drying and rectifying. This oily material is **mononitro-benzene** (see p. 417). If benzene be boiled with fuming HNO_3, or if it be dropped into a mixture of HNO_3 and H_2SO_4, so long as the fluids mix, a crystalline product, **dinitro-benzene**, is formed.

The superior homologues of benzene include many isomeres. As they are derivable from benzene by substitution of a hydrocarbon radical or radicals C_nH_{2n+1} for one or more atoms of hydrogen, the following isomeres may exist:

$$\left.\begin{array}{l} C_6H_4(CH_3)_2 = \text{Dimethylbenzene} \\ C_6H_5(C_2H_5) = \text{Ethylbenzene} \end{array}\right\} C_8H_{10}$$

$$\left.\begin{array}{l} C_6H_3(CH_3)_3 = \text{Trimethylbenzene} \\ C_6H_5(C_3H_7) = \text{Propylbenzene} \\ C_6H_4(CH_3)(C_2H_5) = \text{Methylethylbenzene} \end{array}\right\} = C_9H_{12}$$

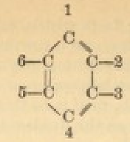
$$\left.\begin{array}{l} C_6H_2(CH_3)_4 = \text{Tetramethylbenzene} \\ C_6H_4(C_2H_5)_2 = \text{Diethylbenzene} \\ C_6H_5(C_4H_9) = \text{Butylbenzene} \\ C_6H_3(CH_3)_2(C_2H_5) = \text{Dimethylethylbenzene} \\ C_6H_4(CH_3)(C_3H_7) = \text{Methylpropylbenzene} \end{array}\right\} = C_{10}H_{14}$$

The number of isomeres among the higher terms of the series is further increased by the occurrence of increasing numbers of isomeres among the substituted radicals themselves, as $CH_2—CH_2—CH_3$ and $CH\begin{array}{l}\diagup CH_3\\ \diagdown CH_3\end{array}$, etc. Further, when the number of substituted groups is greater than one, different substances are produced by the substitution of the same groups in positions bearing different relations to each other in the benzene nucleus.

In the case of benzene itself there exist products of substitution containing 1, 2, 3, 4, 5, and 6 groups CH_3, C_2H_5, etc. (or other radicals or univalent atoms), or combinations of two or three of those radicals or elements. In the case of the unisubstituted derivatives, C_6H_5,CH_3; C_6H_5,C_2H_5, etc., but one of each exists. Of the bisubstituted, trisubstituted, and quadrisubstituted derivatives three of each are known.

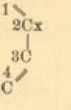
From the existence of but one unisubstituted derivative it is obvious that it is immaterial in which of the CH groups this substitution occurs, and hence these six groups are equal to each other in value. The existence of isomeres of the higher products of substitution depends upon differences in the **relative positions** of the substituted radicals or atoms to each other, their **orientation**, as it is called, and not to their absolute positions.

If we represent the molecule of benzene by a hexagon, leaving out the H atoms for the sake of brevity, we may start from any angle and number the angles, or positions, from 1 to 6:

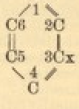


In such a hexagon there are three possible positions with relation to each other, in which two atoms or radicals may be placed.

They may be **consecutive**, *i.e.*, occupying two adjoining positions, as 1—2, 2—3, 3—4, 4—5, 5—6, or 6—1; as for instance in 1, in which x may be a radical C_nH_{2n+1}, a univalent atom, or any



1.

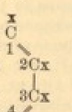


2.

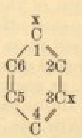
3.

univalent radical. Or the positions may be **unsymmetrical**, 1—3, 2—4, 3—5, 4—6, 5—1, as in 2. Or the substitution may be **symmetrical**, as in 3, occupying the diagonal positions 1—4, 2—5, 3—6.

In the case of trisubstituted derivatives in which the substituted radical or element is the same there may also be three positions, thus:



4.



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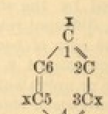


6.

either **consecutive** as in 4; **unsymmetrical** as in 5; or **symmetrical** as in 6.

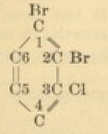
The three series of bi- and tri-substituted derivatives of benzene, whether the substitution be of a halogen or of any univalent element or radical, are designated by the prefixes **ortho, meta,** and **para.** Thus, in the figures above:

Nos. 1 and 4 = 1—2 = Ortho——benzene.
Nos. 2 and 5 = 1—3 = Meta——benzene.
Nos. 3 and 6 = 1—4 = Para——benzene.

The distinction between the three groups is best made by the relations between the bi- and tri-substituted derivatives. The consecutive or **ortho** bisubstituted derivatives can produce by further substitution two tri-derivatives, one consecutive, the other unsymmetrical; the unsymmetrical, or **meta,** can produce three trisubstituted derivatives; and the symmetrical, or **para,** can produce but one trisubstituted derivative, an unsymmetrical.

In expressing the constitution of substituted derivatives it is customary either to use the prefixes ortho, para, and meta, as explained above, or to designate the substance by the numerical positions of the substituted atoms or radicals, considering the substituted atom or group in the parent mono-substituted derivative as always occupying the position 1.

When, in a trisubstituted derivative, the substituted radicals or atoms are not the same in kind, the number of possible isomeres is further increased. Thus, there are six possible chloro-dibromobenzenes: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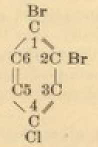
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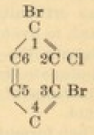
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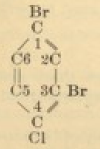
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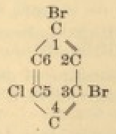
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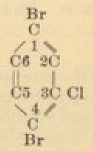
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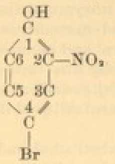
of which 1 and 2 are derivable from orthobibromobenzene, 3, 4, and 5 from metabibromobenzene, and 6 from parabibromobenzene. If, in place of two elements or radicals, we have three, the number of trisubstituted derivatives is increased to ten.

The naming of such polysubstituted derivatives presents many difficulties. Adherence to the principle that the name of a compound shall indicate its constitution, involves the construction of names which are frequently of unwieldy length. It is usual to consider the characterizing group as occupying the position 1 in the hexagon, and to prefix the term **ortho** to the name of that radical or atom occupying one of the ortho-positions 2 and 6 with relation to the characterizing group; **meta** to that occupying one of the meta-positions 3 and 5; and **para** to that occupying the para-position 4.

Thus the substance having the constitution indicated by the formula 1 is designated by the name **orthonitroparabromo-phe-**



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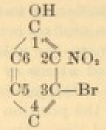

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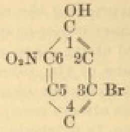


3.

nol. But even this is not always sufficiently definite, for to each of the substances 2 and 3, although differing in characters, the name **orthonitrometabromo-phenol** applies. It has been suggested, to avoid this difficulty, that the prefix **allortho** be used to designate the second ortho-position 6, and the prefix **allometa** to designate the second meta-position 5.

The name of No. 3 would thus become **metabromoallorthonitrophenol.**

When formulæ are used, all confusion may be readily avoided, even in the most complex substances, by the use of the numeral corresponding to the position in the benzene chain, enclosed in brackets. Thus, the formulæ of 2 and 3 above may be written:

$$C_6H_3(OH)(NO_2)_{(2)}Br_{(3)}\text{; and}$$
$$C_6H_3(OH)Br_{(3)}(NO_2)_{(6)}.$$

In the case of the tetrasubstituted derivatives there are also three possible positions: **consecutive**, 1, 2, 3, 4; **symmetrical**, 1, 3, 4, 6, and **unsymmetrical**, 1, 3, 4, 5.

In these hydrocarbons and in other derivatives of benzene the six atoms of carbon belonging to benzene constitute what is known as the **benzene nucleus, benzene ring,** or the **principal chain**; while the substituted groups are designated as the **lateral chains.**

Toluene—Toluol—Methyl-benzene—C_6H_5,CH_3—92—exists in the products of distillation of wood, coal, etc., and as one of the constituents of commercial benzene. It has been formed synthetically by acting upon a mixture of monobromo-benzene and methyl iodid with sodium.

It is a colorless liquid, having a peculiar odor, differing somewhat from that of benzene; boils at 110°.3 (230°.5 F.); does not solidify at −20° (−4° F.); sp. gr. 0.872 at 15° (59° F.); almost insoluble in water, soluble in alcohol, ether, carbon disulfid. It burns with a bright, but very smoky flame. It yields a number of derivatives similar to those of benzene, among which may be mentioned *nitro-toluene* and *toluidin*, the homologues of nitrobenzene and anilin, which accompany those substances in the commercial products; *cresylol*, the superior homologue of carbolic acid, and *benzylic alcohol*.

Xylenes—Xylols—C_8H_{10}.—Four isomeres are possible and are known: **ethyl-benzene, C_6H_5,C_2H_5**—and **ortho-** (1—2), **meta-** (1—3), and **para-** (1—4), **dimethyl-benzenes, $C_6H_4(CH_3)_2$.** **Ethylbenzene** is a colorless oil, boiling at 134° (273°.2 F.), obtained by fractional distillation of animal oil. The three **dimethyl benzenes** exist in coal-tar and in the commercial xylene, which boils at 139° (282°.2 F.), 70% consisting of metaxylene, and paraxylene being present in very small amount.

HALOID DERIVATIVES.

By the substitution of atoms of Cl, Br and I for the hydrogen of the principal and lateral chains in benzene and its superior homologues, a great number of substances are obtained, many of them forming isomeric groups.

The chlorin derivatives of benzene are :

Monochloro-benzene—C_6H_5Cl—liquid ; boils at 132° (269°.6 F.) ; sp. gr. 1.128 at 0° ; obtained by the action of Cl upon C_6H_6 in the cold, in the presence of a little I.

Orthodichloro-benzene—1—2—liquid ; boils at 179° (354°.2 F.); sp. gr. 1.328 at 0° ; obtained by the action of Cl on C_6H_6.

Metadichloro-benzene—1—3—liquid ; boils at 172° (341°.6 F.) ; sp. gr. 1.307 at 0° ; obtainable indirectly.

Paradichloro-benzene—1—4—crystalline ; fuses at 56°.4 (133°.5 F.) ; boils at 170° (343°.4 F.) ; is the principal product of the action of Cl on C_6H_6 in presence of I.

Metatrichloro-benzene—1—2—4—crystals ; fuses at 17° (62°.6 F.) ; boils at 213° (415°.4 F.).

Paratrichloro-benzene—1—3—5—crystals ; fuses at 63°.4 (146°.1 F.) ; boils at 208° (406°.4 F.).

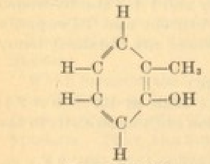
Tetrachloro-benzene—1—2—3—5—crystals ; fuses at 50° (122° F.) ; boils at 246° (474°.8 F.).

Tetrachloro-benzene—1—2—4—5—crystals ; fuses at 137° (278°.6 F.) ; boils between 243°-246° (469°.4-474°.8 F.).

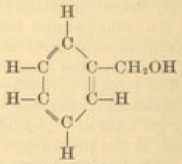
Benzoyl chlorid—$C_6H_5CH_2Cl$—is an example of the substitution of a halogen in the lateral chain of a superior homologue of benzene. It is obtained by the action of chlorin upon boiling toluene; or of PCl_5 on benzoic alcohol. It is a colorless liquid, boils at 176° (348°.8 F.), and gives off pungent vapors which excite the lachrymal secretion. It is readily oxidized to benzoic aldehyde or benzoic acid, and serves for the introduction of the radical **benzoyl, C_6H_5,CH_2** into other molecules.

PHENOLS.

The hydrocarbons of the benzene series, unlike those previously considered, form two distinct kinds of hydrates, differing from each other materially in their properties. The terms of one of these series exhibit all the functions of the alcohols, and are known as **aromatic alcohols.** The terms of the other series differ in function from any substance thus far considered, and are known as **phenols.** The difference between them and the aromatic alcohols is due to the fact that in the phenols the OH is directly attached to a C atom, while in the alcohols it forms part of the group of atoms CH_2OH, characteristic of the alcohols:



Benzylic phenol.



Benzylic alcohol.

The phenols differ from the alcohols in not furnishing by oxidation corresponding aldehydes and acids; in not dividing into water and hydrocarbon under the influence of dehydrating agents; in not reacting with acids to form ethers; in combining to form directly products of substitution with Cl and Br; and in forming with metallic elements compounds more stable than similar compounds of the true alcohols. In short, the phenols appear to have, besides an alcoholic function, more or less of the function of acids.

Phenol—Phenyl hydrate—Phenic acid—Carbolic acid—Acidum carbolicum (U. S., Br.)—C_6H_5OH—94—exists in considerable quantity in coal- and wood-tar, and in small quantity in castoreum, and possibly in urine.

It is formed: (1) by fusing sodium phenylsulfid with an excess of alkali; (2) by heating phenyl iodid with potassium hydroxid to 320° (608° F.); (3) by heating together salicylic acid and quicklime; (4) by total synthesis from acetylene; (5) by dry distillation of benzoin.

The source from which it is obtained is that portion of the product of distillation of coal-tar which passes over between 150° and 200° (302°–392° F.). This is treated with a saturated solution of potash, containing undissolved alkali; a solid phenate is formed, which is dissolved in hot H_2O; the liquid is allowed to separate into two layers, the lower of which is drawn off and neutralized with HCl; the phenol rises to the surface, is separated, washed with water, dried over calcium chlorid, redistilled, crystallized at −10° (14° F.), and the crystals drained. A "synthetic phenol" is now made from benzene and from anilin, and seems to be more nearly pure than the "natural" product.

Pure phenol crystallizes in long, colorless, prismatic needles, fusible at 40°–41° (104°–105°.8 F.), boiling at 181°.5 (258°.7 F.). It has a peculiar, well-known odor, and an acrid, burning taste; very sparingly soluble in water, readily soluble in alcohol and in ether; sp. gr. 1.065 at 18° (64°.4 F.); neutral in reaction. On contact with the skin or with mucous surfaces, it produces a white stain; it coagulates albuminoids, and is a powerful antiseptic.

It may be distilled without decomposition. It absorbs H_2O from damp air to form a hydrate, which crystallizes in six-sided prisms, fusible at 16° (60°.8 F.). Its vapor is reduced to benzene when heated with Zn. It combines with H_2SO_4 to form **phenylsulfuric acids.** It forms **trinitrophenic acid** (*q.v.*) with HNO_3 of 36° B. When heated with H_2SO_4 and oxalic acid it forms **rosolic acid** or **corallin**, which is a mixture from which the pigments **aurin, peonin, azulin**, and **phenicin** are obtained.

Analytical Characters.—(1.) Its peculiar odor. (2.) Mix with one-quarter volume of NH_4HO; add two drops sodium hypochlorite solution, and warm; a blue or green color. Add HCl to acid reaction; turns red. (3.) Add two drops of liquid to a little HCl, add one drop HNO_3; a purple red color. (4.) Boil with HNO_3 as long as red fumes are given off. Neutralize with KHO; a yellow, crystalline precipitate. (5.) With $FeSO_4$ solution; a lilac color. (6.) Float the liquid on H_2SO_4, add powdered KNO_3; violet color. (7.) With excess of Br water; a yellowish-white precipitate.

Toxicology.—When taken internally, phenol is an active poison, and one whose use by suicides has become quite common. When it has been taken the mouth is whitened by its caustic action, and there is a marked odor of carbolic acid in the breath. It is eliminated by the urine, partly unchanged, and partly in the form of colored derivatives, which color the urine greenish, brownish, or even black. The treatment consists in the administration of albumen (white of egg) and of emetics.

To detect phenol in the urine, that liquor must not be distilled with H_2SO_4, as sometimes recommended, as it contains normally substances which by such treatment yield carbolic acid. The best method consists in adding an excess of bromin water to about 500 c.c. of the urine; on standing some hours, a yellowish precipitate collects at the bottom of the vessel; this is removed, washed, and treated with sodium amalgam, when the characteristic odor of phenol is developed. From other parts of the body, phenol may be recovered by acidulating with tartaric acid; distilling; extracting the distillate by shaking with ether; evaporating the ethereal solution; extracting the residue with a small quantity of water, and applying to this solution the tests described above.

Phenates.—*Carbolates.*—The hydrogen of the oxhydryl group of phenol is replaceable by certain metals and by alcoholic radicals to form phenates. When phenol and KHO are heated together, **potassium phenate, C_6H_5OK,** is formed. This, when treated in alcoholic solution with $HgCl_2$, produces **mercuric phenate, $(C_6H_5O)_2Hg$,** a yellow, crystalline solid which has been used in medicine.

The **phenylic ethers** may be obtained by heating potassium phenate with the iodid of the alcoholic radical.

Methyl phenate—Anisol—C_6H_5,OCH_3—is a colorless, thin liquid, boils at 152° (305°.6 F.) without decomposition. Sulfuric acid dissolves it, with formation of methyl-phenol sulfonic acid.

Ethyl phenate—Phenetol—C_6H_5,OC_2H_5—is a colorless liquid, boils at 172° (341°.6 F.), having an aromatic odor.

Anisol and phenetol serve as the starting-points for the production of the **anisidins** and **phenetidins** (q.v.).

Cresols—Cresylols—Cresylic acids—Benzylic or cresylic phenols—$C_6H_4\left\langle\begin{matrix}CH_3\\OH\end{matrix}\right.$—108.—Of the three possible compounds, two, the para and ortho, accompany phenol in coal-tar, from which they may be separated by fractional distillation. They are more readily obtained pure from toluene.

Ortho-cresol (1—2) is a crystalline solid, fusible at 31°-31°.5 (87°.8-88°.7 F.), which assumes a blue color with ferric chlorid.

Metacresol (1—3) is obtainable by the action of P_2O_5 on thymol. It is a colorless liquid, whose odor resembles that of phenol, boils at 201° (393°.8 F.), does not solidify at −75° (−103° F.).

Paracresol (1—4) is a crystalline solid, fusible at 36° (96°.8 F.), boiling at 198° (388°.4 F.), having a phenol-like odor; colored blue by ferric chlorid.

Creasote—Creasotum (U. S.)—is a complex mixture containing phenol, cresol, **creasol, $C_8H_{10}O_2$, guaiacol, $C_7H_8O_2$** (see catechol), and other substances, obtained from wood-tar and formerly extensively used as an antiseptic. It is an oily liquid, colorless when freshly prepared, but becoming brownish on exposure to light; it has a burning taste and a strong, peculiar odor; it boils at 203° (397°.4 F.), and does not solidify at −27° (−16°.6 F.).

Crude phenol is often substituted for creasote; the two substances may be distinguished by the following characters: Phenol gives a brown color with ferric chlorid and alcohol, while creasote gives a green color; phenol dissolves in glycerin, in which creasote is insoluble; phenol precipitates nitro-cellulose from collodion, while creasote does not.

Xenols—Xylenols.—Theoretically there are six possible xenols which are **dimethyl phenols, $C_6H_3(CH_3)_2OH$**; two derivable from orthoxylene, three from metaxylene and one from paraxylene. They have all been produced synthetically. There are also three possible xenols which are **ethyl phenols, $C_6H_4(C_2H_5)OH$.**

Thymol — Methyl-parapropyl-metaphenol — *Cymylic phenol*— $C_6H_3(CH_3)_{(1)}(OH)_{(3)}(C_3H_7)_{(4)}$ — exists, accompanying cymene and thymene, $C_{10}H_{16}$, in essence of thyme, from which it is obtained. The essence contains about one-half its weight of thymol, which is separated by agitation with a concentrated solution of caustic soda; separation of the alkaline liquid, which is diluted and neutralized with HCl; thymol separates and is purified by rectification at 230° (446° F.). It is also prepared synthetically from cuminic aldehyde, $C_6H_4(CHO)_{(1)}(C_3H_7)_{(4)}$.

It crystallizes in large, transparent, rhombohedral tables; has a peppery taste, and an agreeable, aromatic odor; it fuses at 44° (111°.2 F.), and boils at 230° (446° F.); is sparingly soluble in water, very soluble in alcohol and ether. With the alkalies it forms definite compounds, which are very soluble in water. Its reactions are very similar to those of phenol.

Thymol is an excellent deodorizing and antiseptic agent, possessing the advantage over phenol of having itself a pleasant odor.

Aristol is a compound of thymol and iodin, properly belonging among the dibenzenic compounds, produced by the action of a solution of I in KI upon an aqueous solution of thymol in the presence of KHO. It is an inodorous, yellowish red powder, insoluble in H_2O, very sparingly soluble in alcohol, readily soluble in ether and in chloroform. It is decomposed by heat and by light and is said to be a non-poisonous antiseptic.

Carvacrol — Methyl-paraisopropyl-metaphenol — $C_6H_3(CH_3)_{(1)}(OH)_{(2)}(CH_3)_2CH_{(4)}$—an isomere of thymol, whose constitution differs in the position of the oxhydryl group, exists in many essential oils and is obtained by the action of iodin upon camphor; by the action of potash in fusion upon cymene sulfonic acid, $C_{10}H_{13}SO_3H$; or by a transposition of the atoms of another isomere, **carvol,** which exists in caraway oil. It is an oil, boiling at 233°–235° (451°.4–455° F.). Heated with P_2O_5, it yields orthocresol.

SUBSTITUTED PHENOLS.

We have seen above (p. 398) how three bi- and tri-substituted derivatives are derivable from benzene. Phenol is a unisubstituted derivative of the same substance and hence still contains five H atoms which may be replaced by other elements or radicals, to produce di- or tri- or poly-substituted derivatives of benzene, which will be ortho, meta or para, etc., according to the relations of the introduced groups to the OH, already existing in phenol, or to the C_nH_{2n+1} and OH groups in its superior homologues.

Chlorophenols.—The three monochlorinated compounds are obtainable from the corresponding chloranilins. **Orthochlorophenol** (1—2) is a colorless liquid, boils at 175°–176° (347°–348°.8 F.), converted into catechol by KHO. **Metachlorophenol** (1—3) is a liquid, boiling at 214° (417°.2 F.). KHO converts it into resorcin. **Parachlorophenol** (1—4) is a crystalline solid, fusible at 37° (98°.6 F.), converted into quinol by fusion with KHO. Di-, tri-, and penta-chlorophenols are also known.

Bromophenols correspond in method of formation and properties with the Cl derivatives.

Iodophenols are formed by the action of iodin and KS upon phenol in the presence of excess of alkali, or from the corresponding amidophenols. Like the chlorin and bromin derivatives, they yield the corresponding diphenol by the action of KHO in fusion. A tri-iodophenol, formed by the action of solution of I in KS upon an alkaline solution of phenol, has been proposed as a substitute for iodoform under the name **annidalin.**

Nitro-phenols—Mononitro-phenols—$C_6H_4(NO_2)OH$—(1—2), (1—3) and (1—4) are formed by the action of HNO_3 on C_6H_5OH. The **ortho** compound (1—2) crystallizes in large yellow needles, sparingly soluble, and capable of distillation with steam. The **meta** and **para** compounds are both colorless, non-volatile, crystalline bodies. Two **dinitro-phenols**, $C_6H_3OH(NO_2)_{2(1-4)}$ and $C_6H_3OH(NO_2)_{2(2-6)}$, are obtained by the action of strong nitric acid on phenol, or on ortho- or para-mononitro phenol. They are both solid, crystalline substances, converted by further nitration into picric acid.

Trinitro-phenols—$C_6H_2(NO_2)_3OH$.—Two are known: (1.) **Picric acid—Carbazotic acid—Trinitro-phenic acid**—(NO_2) in 2—4—6. It is formed by nitrification of phenol, or of 1—2—4 or 1—2—6 dinitro-phenols, and also by the action of HNO_3 on indigo, silk, wool, resins, etc. It crystallizes in brilliant, yellow, rectangular plates, or in six-sided prisms; it is odorless, and has an intensely bitter taste, whence its name (from *πικρὸς* = bitter); it is acid in reaction; sparingly soluble in water, very soluble in alcohol, ether, and benzene; it fuses at 122°.5 (252°.5 F.), and may, if heated with caution, be sublimed unchanged; but, if heated suddenly or in quantity, it explodes with violence. It behaves as a monobasic acid, forming salts, which are for the most part soluble, yellow, crystalline, and decomposed with explosion when heated.

Picric acid is valuable as a dye-stuff, coloring silk and wool yellow; as a staining medium in histological investigations; and as a reagent for the alkaloids, with many of which it forms crystalline precipitates. It is also sometimes fraudulently added to beer and to other food articles, to communicate to them either a bitter taste or a yellow color.

ANALYTICAL CHARACTERS.—(1.) Its intensely bitter taste. (2.) Its alcoholic solution, when shaken with a potassium salt, gives a yellow, crystalline ppt. (3.) An ammoniacal solution of cupric sulfate gives a green, crystalline ppt. (4.) Glucose, heated with a dilute alkaline solution of picric acid, communicates to it a blood-red color. (5.) Warmed with an alkaline solution of potassium cyanid, an intense red color is produced (the same effect is produced by ammonium sulfhydrate). (6.) Unbleached wool, immersed in boiling solution of picric acid, is dyed yellow.

Nos. 1, 3, 5, and 6 are quite delicate.

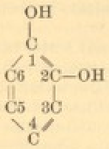
When taken internally in overdose, it acts as a poison; it may be separated from animal fluids or from beer by evaporation to a syrup, extracting with 95 per cent. alcohol, acidulated with H_2SO_4; filtering; evaporating; and applying the tests to a solution of the residue.

Amido-phenols—$\mathbf{C_6H_4,OH,NH_2}$.—Three are known, ortho-, meta- and para-, obtained by the action of reducing agents upon the corresponding nitro-compounds. Their methylic ethers, $\mathbf{C_6H_4,O(CH_3)NH_2}$, are known as **anisidins**; and their ethylic ethers, $\mathbf{C_6H_4,O(C_2H_5)NH_2}$, as **phenetidins.**

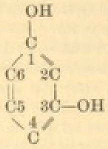
By the action of glacial acetic acid upon paraphenetidin, an aceto-derivative, **para-acetphenetidin,** $\mathbf{C_6H_4,O(C_2H_5)_{(1)},NH(C_2H_3O)_{(4)}}$, is formed. It has been recommended as an antipyretic, under the name **phenacetine,** and is a reddish, odorless, tasteless powder, sparingly soluble in H_2O, readily soluble in alcohol. Its hot aqueous solution is colored violet, changing to ruby-red, by chlorin water. The corresponding anisidin, **para-acetanisidin**; $\mathbf{C_6H_4,O(CH_3)_{(1)},NH(C_2H_3O)_{(4)}}$, has also been suggested as a therapeutic agent. It crystallizes in white, shining, tasteless, odorless scales, fuses at 127° (260°.6 F.), sparingly soluble in H_2O, readily soluble in alcohol.

DIATOMIC PHENOLS.

Diatomic phenols are derived from the benzene series of hydrocarbons by the substitution of two (OH) groups for two atoms of hydrogen. In obedience to the laws of substitution already discussed, three such compounds exist, corresponding to each hydrocarbon. Thus, in the case of benzene :



Ortho.
1—2
Catechol.



Meta.
1—3
Resorcinol.

Para.
1—4
Quinol.

Catechol—*Pyrocatechin—Oxyphenic acid—Orthodioxy-benzene*—$\mathbf{C_6H_4(OH)_2}$—1—2—is obtained from catechin or from morintannic acid by dry distillation; also by the action of KHO on orthochlor- or orthoiodo-phenol, or by decomposing its methyl ether, **guaiacol,** by HI at 200° (392° F.). It crystallizes in short, square prisms; fuses at 104° (219°.2 F.), and boils at 245°.5 (473°.9 F.). Readily soluble in water, alcohol, and ether. Its aqueous solution gives a dark green color with Fe_2Cl_6 solution, changing to violet on addition of NH_4HO, $NaHCO_3$, or tartaric acid.

Resorcinol—*Resorcin—Metadioxy-benzene*—$\mathbf{C_6H_4(OH)_2}$—1—3—is obtained by the action of fused KHO on parachlor- or iodophenol. It is usually prepared by dry distillation of extract of Brazil wood.

It forms short, thick, colorless and odorless, rhombic prisms. Fuses at 104° (219°.2 F.), and boils at 271° (519°.8 F.). It is very soluble in water, alcohol, and ether. Its aqueous solution is neutral in reaction, and intensely sweet. With Fe_2Cl_6 its solutions assume a dark violet color, which is discharged by NH_4HO. Its ammoniacal solution, by exposure to air, assumes a pink color, changing to brown and, on evaporation, green and dark blue. Heated with phthalic anhydrid at 195° (383° F.) it yields **fluorescein** (see page 410). It dissolves in fuming H_2SO_4, forming an orange-red solution, which becomes darker, changes to greenish-black, then to pure blue, and finally to purple on being warmed.

Resorcinol, heated with sodium nitrite and H_2O to about 150°

(302° F.) yields a blue pigment known as **lacmoid**, which behaves like litmus with acids and alkalies, but is more sensitive.

Resorcinol has been recently used in medical practice.

Quinol—*Hydroquinone*—*Paradioxy-benzene*—$\mathbf{C_6H_4(OH)_2}$—1—4—is formed by fusing paraiodo-phenol with KHO at 180° (356° F.), by dry distillation of oxysalicylic acid or of quinic acid, and by the action of reducing agents on *quinone*. It forms colorless, rhombic prisms, which fuse at 169° (336°.2 F.). Readily soluble in water, alcohol, or ether. Its aqueous solution is turned red-brown by NH_4HO. Oxidizing agents convert it into quinone.

Quinone—$\mathbf{C_6H_4(OO)''}$—is the representative of a number of similar compounds, derivable from the aromatic hydrocarbons. It is produced by the oxidizing action of $MnO_2+H_2SO_4$ or of dilute chromic acid, upon quite a number of para-benzene derivatives; but best by the limited oxidation of quinic acid.

It crystallizes in yellow prisms; fuses at 116° (240°.8 F.); sublimes at ordinary temperatures; is sparingly soluble in cold, but readily soluble in hot water and in alcohol or ether. It gives off a peculiar, pungent odor, and stimulates the lachrymal secretion. Reducing agents convert it into quinol.

There is no similar substance known corresponding either to catechol or to resorcinol.

Orsin—*Dimetadioxy-toluene*—$\mathbf{C_6H_3(CH_3)_{(1)}(OH_3)_{(3)}(OH)_{(5)}}$—exists in nature in those lichens which are used as sources of archil and litmus (*Rocella tinctoria*, etc.). It crystallizes in six-sided prisms; is sweet; readily soluble in water, alcohol, or ether; fuses at 58° (136°.4 F.). Its aqueous solution is colored violet-blue by Fe_2Cl_6. It unites with NH_3 to form a compound which absorbs O from the air, and is converted into **orcein**, $\mathbf{C_7H_7NO_3}$; a dark red or purple body, which is the chief constituent of the dye-stuff known as archil, cudbear, French purple, and litmus.

TRIATOMIC PHENOLS.

The only compounds of this class at present known with certainty are two isomeric triatomic phenols, which owe the differences in properties existing between them to a different placing of the OH groups. They are *phloroglucin* and *pyrogallol*.

Phloroglucin—$\mathbf{C_6H_3(OH)_3}$—126—is obtained by the action of potash upon phloretin, quercitrin, maclurin (see Glucosids), catechin, kino, etc. It crystallizes in rhombic prisms, containing 2 Aq; is very sweet; very soluble in water, alcohol, and ether.

Pyrogallol—*Pyrogallic acid*—$\mathbf{C_6H_3(OH)_3}$—126—is formed when gallic acid (*q.v.*) is heated to 200° (392° F.). It crystallizes in white needles; neutral in reaction; very soluble in water; very bitter; fuses at 115° (239° F.); boils at 210° (410° F.); poisonous. Its most valuable property is that of absorbing oxygen, for which purpose it is used in the laboratory in the form of a solution of potassium pyrogallate.

When pyrogallol is heated with half its weight of phthalic anhydrid for several hours at 190°–200° (374°–392° F.) it yields **pyrogallol phthalein**, or **gallein**, a brown-red powder (or green crystals) which dissolves with a brown color in neutral solutions, the color changing to red with a faint excess of alkali.

PHENOL DYES.

Aurin—$C_{19}H_{14}O_3$ and **Rosolic acid**—$C_{20}H_{16}O_3$—are substances existing in the dye obtained by the action of oxalic acid upon phenol in presence of H_2SO_4, known as **corallin** or **pœonin**, which communicates to silk or wool a fine yellow-red color.

Aurin crystallizes in fine, red needles from its solution in HCl. It is insoluble in H_2O, but soluble in HCl, alcohol, and glacial acetic acid. It forms a colorless compound with potassium bisulfite.

Phthaleins.—These substances are produced by heating the phenols with phthalic anhydrid, $C_8H_4O_3$, water being at the same time eliminated.

Their constitution is that of a benzene nucleus, two of whose H atoms have been replaced by two acetone groups (CO), whose remaining valences attach them to two phenol groups by exchange with an atom of hydrogen.

Thus **phenol-phthalein**, the simplest of the group, has the constitution

$$C_6H_4\left\langle\begin{matrix}CO-C_6H_4(OH).\\CO-C_6H_4(OH).\end{matrix}\right.$$

Phenol-phthalein is a yellow, crystalline powder, insoluble in water, but soluble in alcohol. Its alcoholic solution, perfectly colorless if neutral, assumes a brilliant magenta-red in the presence of an alkali. This property renders phenol-phthalein very valuable as an *indicator* of reaction.

Resorcin-phthalein—Fluorescein—$C_{20}H_{12}O_5$—bears the same relation to resorcin that phenol-phthalein does to phenol, and is obtained from resorcin by a corresponding method. It is a dark brown crystalline powder, which dissolves in ammonia to form a red solution, exhibiting a most brilliant green fluorescence. A tetrabromo-derivative of fluorescein is used as a dye under the name **eosin**.

AROMATIC ALCOHOLS.

The alcohols corresponding to this series of hydrocarbons have the same composition as the corresponding phenols, from which they differ in constitution, and in having the functions of true alcohols. They yield on oxidation, first an aldehyde and then an acid, and they contain the characterizing group of the primary alcohols, CH_2OH ; once if the alcohol be monoatomic, twice if diatomic, etc. Thus:

C_6H_5,CH_2OH = Benzylic alcohol.
C_6H_5,COH = Benzoic aldehyde.
$C_6H_5,COOH$ = Benzoic acid.

As they contain the benzene nucleus, they are capable of yielding isomeric products of further substitution, ortho, para, or meta, according to the position of the substituted atom or radical.

Benzylic alcohol—Benzoic alcohol—Benzyl hydrate—$C_6H_5(CH_2OH)$—108—does not exist in nature, and is of interest chiefly as corresponding to two important compounds, benzoic acid and benzoic aldehyde (oil of bitter almonds). It is obtained by the action of potassium hydroxid upon oil of bitter almonds, or by slowly adding sodium amalgam to a boiling solution of benzoic acid.

It is a colorless liquid; boils at 206°.5 (403°.7 F.); has an aromatic odor; is insoluble in water, soluble in all proportions in alcohol, ether, and carbon disulfid. By oxidation it yields, first, benzoic aldehyde, $C_6H_5(COH)$; and afterward, benzoic acid, $C_6H_5(COOH)$. By the same means it may be made to yield products similar to those obtained from the alcohols of the saturated hydrocarbons.

ALPHENOLS.

These substances are intermediate in function between the alcohols and the phenols, and contain both substituted groups (OH) and CH_2OH.

Saligenin,  $C_6H_4\left\langle\begin{matrix}CH_2OH\\OH\end{matrix}\right.$—124—is obtained from salicin (*q.v.*) in large, tabular crystals; quite soluble in alcohol, water, and ether. Oxidizing agents convert it into salicylic aldehyde, which by further oxidation yields salicylic acid. It is also formed by the action of nascent hydrogen on salicylic aldehyde.

ALDEHYDES.

Benzoic aldehyde—Benzoyl hydrid—$C_6H_5(COH)$—106—is the main constituent of oil of bitter almonds, although it does not exist in the almonds (see p. 460); it is formed, along with hydrocyanic acid and glucose, by the action of water upon amygdalin. It is also formed by a number of general methods of producing aldehydes; by the dehydration of benzylic alcohol; by the dry distillation of a mixture in molecular proportions of calcium benzoate and formate; by the action of nascent hydrogen upon benzoyl cyanid, etc.

It is obtained from bitter almonds. The crude oil contains, besides benzoic aldehyde, hydrocyanic and benzoic acids and cyanobenzoyl. To purify it, it is treated with three to four times its volume of a concentrated solution of sodium bisulfite; the crystalline mass is expressed, dissolved in a small quantity of water, and decomposed with a concentrated solution of sodium carbonate—the treatment being repeated, if necessary.

It is a colorless oil, having an acrid taste and the odor of bitter almonds; sp. gr. 1.043; boils at 179°.4 (354°.9 F.); soluble in 30 parts of water, and in all proportions in alcohol and ether. Oxidizing agents convert it into benzoic acid, a change which occurs by mere exposure to air. Nascent hydrogen converts it into benzylic alcohol. With Cl and Br it forms benzoyl chlorid or bromid. H_2SO_4 dissolves it when heated, forming a purple-red color, which turns black if more strongly heated.

When perfectly pure, benzoic aldehyde exerts no deleterious action when taken internally; owing, however, to the difficulty of completely removing the hydrocyanic acid, the substances usually sold as *oil of bitter almonds, ratafia*, and *almond flavor*, are almost always poisonous, if taken in sufficient quantity. They may contain as much as 10–15 per cent. of hydrocyanic acid, although said to be "purified." The presence of the poisonous substances may be detected by the tests given on page 292.

Salicylic aldehyde—*Salicyl hydrid—Salicylal—Salicylous acid* **—$C_6H_4(OH)COH$—**122—exists in the flowers of *Spiræa ulmaria*, and is the principal ingredient of the essential oil of that plant. It is best obtained by oxidizing salicin (*q.v.*).

It is a colorless oil; turns red on exposure to air; has an agreeable, aromatic odor, and a sharp, burning taste; sp. gr. 1.173 at 13°.5 (56°.3 F.); boils at 196°.5 (385°.7 F.); soluble in water, more so in alcohol and ether.

It is, as we should suspect from its origin, a substance of mixed function, possessing the characteristic properties of aldehyde and phenol. It produces a great number of derivatives, some of which have the characters of salts and ethers.

Methyl-protocatechuic aldehyde—Vanillin—$C_6H_3(OH)(OCH_3)COH$—is the odoriferous principle of vanilla. It is produced artificially by oxidation of **coniferin, $C_{16}H_{22}O_8$**, a glucosid occurring in coniferous plants. It crystallizes in needles, fuses at 80° (176° F.); is sparingly soluble in water, readily soluble in alcohol or ether. It has a pungent taste, and a faint odor of vanilla, the latter more marked, when the substance is heated. On exposure to air it becomes partially oxidized to **vanillic acid $C_8H_8O_4$**.

KETONES.

The ketones of this series are produced by the union of a benzene nucleus with an alcoholic radical through a group $(CO)''$ thus: C_6H_5,CO,CH_3. They are also called **phenones**.

Phenyl methyl ketone—Aceto-phenone—Hypnone—C_6H_5,CO,CH_3—is obtained by distilling a mixture of calcium benzoate and acetate; or by the action of zinc-methyl upon benzoyl chlorid. It forms large crystalline plates, fusible at 14° (57°.2 F.). It has been used as a hypnotic

ACIDS CORRESPONDING TO THE AROMATIC HYDRATES.

The acids possibly derivable from benzene by the substitution of (COOH), or of (COOH) and (OH), for atoms of hydrogen, would form, were they all known, a great number of series; there are, however, comparatively few of them which have been as yet obtained, although the number of acid series known is greater than that of corresponding alcohols. Each series of mono- and diatomic alcohols furnishes a corresponding series of acids, thus:

$C_6H_5—CH_2OH$	$C_6H_4\left\langle\begin{matrix}CH_2OH\\CH_2OH\end{matrix}\right.$	$C_6H_4\left\langle\begin{matrix}CH_2OH\\OH\end{matrix}\right.$
Benzoic alcohol.	Toluyl glycol.	Saligenin.
$C_6H_5—COOH$	$C_6H_4\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right.$	$C_6H_4\left\langle\begin{matrix}COOH\\OH\end{matrix}\right.$
Benzoic acid.	Terephthalic acid.	Salicylic acid.

By the progressive substitution of groups (COOH) for atoms of hydrogen in benzene, we may obtain six series of acids, five of which have been isolated:

$C_6H_5(COOH)$	$—C_nH_{2n-8}O_2$	Benzoic series.
$C_6H_4(COOH)_2$	$—C_nH_{2n-10}O_4$	Phthalic series.
$C_6H_3(COOH)_3$	$—C_nH_{2n-12}O_6$	Trimellitic series.
$C_6H_2(COOH)_4$	$—C_nH_{2n-14}O_8$	Prehnitic series.
$C_6H(COOH)_5$	$—C_nH_{2n-16}O_{10}$	Wanting.
$C_6(COOH)_6$	$—C_nK_{2n-18}O_{12}$	Mellitic series.

There may also be three distinct series of bi- tri- and tetra- acids produced by differences in orientation (see p. 397), according as the groups COOH occupy consecutive, symmetrical or unsymmetrical positions.

The alphenols, containing a single group (OH), are at present represented by a single series :

$$C_6H_4(OH)(COOH)—C_nH_{2n-8}O_3—\text{Salicylic series.}$$

Corresponding to unknown alphenols, containing a greater number of (OH) groups, there are at present two series of acids known :

$$C_6H_3(OH)_2(COOH)—C_nH_{2n-8}O_4—\text{Veratric series,}$$

and

$$C_6H_2(OH)_3(COOH)—C_nH_{2n-8}O_5—\text{Gallic series.}$$

In each of these series the basicity is, as usual, equal to the number of groups (COOH).

Benzoic acid—Acidum benzoicum (U. S.)—$C_6H_5(COOH)$—122—exists ready formed in benzoin, tolu balsam, castoreum, and several resins. It does not exist in animal nature, so far as is at present known ; in those situations in which it has been found, it has resulted from decomposition of hippuric acid (*q.v.*), or has been introduced from without. When taken in moderate doses, it does not pass out in its own form, but is converted into hippuric acid ; in excessive doses a portion is eliminated unchanged in the urine. It is obtained from benzoin, or from the urine of herbivorous animals ; and is formed in a variety of reactions.

It crystallizes in white, transparent plates ; odorless ; acid ; fuses at 122° (251°.6 F.) ; sublimes at 145° (293° F.); boils at 240° (464° F.) ; sparingly soluble in cold water ; soluble in hot water, alcohol, and ether. Dilute HNO_3 does not attack it. It dissolves in ordinary H_2SO_4, and is precipitated unchanged by H_2O. Its salts are all soluble.

From it are produced many derivatives by the further substitution of atoms or radicals for one or more of the atoms of H remaining in the C_6H_5 group.

Hippuric acid—Benzyl-glycocol—Benzyl-amido-acetic acid—$CH_2,[NH(C_6H_5CO)],COOH$—179—is a constant constituent of the urine of the herbivora, and of human urine to the extent of 0.29–2.84 grams (4.5–43.8 grains) in 24 hours. It is more abundant with a purely vegetable diet, after the administration of benzoic acid, and in diabetes mellitus and chorea.

It crystallizes in transparent, colorless, odorless, bitter prisms ; sparingly soluble in water ; fuses at 130° (266° F.). It dissolves unchanged in HCl ; but on boiling the solution it is decomposed into benzoic acid and glycocol. The same decomposition is effected by dilute H_2SO_4, HNO_3, and oxalic acid, and by a ferment developed in putrefying urine. Oxidizing agents convert it into benzoic acid, benzamid, and CO_2.

The characters of hippuric acid are : (1) when heated in a dry tube it fuses and gives off a sublimate of benzoic acid and an odor of hydrocyanic acid ; (2) it gives a brown ppt. with ferric chlorid ; (3) when heated with lime it gives off benzene and ammonia.

Salicylic acids—Oxybenzoic acids.—Three are known, ortho, meta and para. The **Acidum salicylicum (U. S.)**, $\mathbf{C_6H_4(OH)COOH}$, is the ortho acid (1, 2)—138. It was first obtained from essence of *spiræa*, which consists largely of salicylic aldehyde, and subsequently from oil of wintergreen (*gaultheria*), which contains methyl salicylate, and also from *salicin*, a glucosid ; yielding salicylic aldehyde. It is now obtained from phenol. This is fused, and, while a current of dry CO_2 is passed through it, small portions of Na are added ; the sodium salicylate thus formed is dissolved in H_2O and decomposed with HCl, when the liberated salicylic acid is precipitated.

It crystallizes in fine white needles ; very sparingly soluble in cold water, quite soluble in hot water, alcohol, and ether ; it fuses at 158° (316°.4 F.), and may be distilled with but slight decomposition, if it be pure. Cl and Br form with it products of substitution. Fuming HNO_3 forms with it a nitro-derivative and, if the action be prolonged, converts it into picric acid. With ferric chlorid, its aqueous solution assumes a fine violet color.

The meta- and para- acids are obtained by fusing meta- or para-chloro- bromo- or iodo-benzoic acid with KHO.

Salicylic acid and its salts (it is monobasic, although diatomic) are extensively used in medicine, both externally as antiseptics and internally in the treatment of rheumatism, etc. It is not without caustic properties, and hence, when taken internally, it should be largely diluted.

Phenyl salicylate—$\mathbf{C_6H_4,OH,COO,C_6H_5}$—has been used as an antiseptic and antipyretic under the name **salol.** It is a white crystalline powder, tasteless ; fusible at 42° (107°.4 F.) ; soluble in H_2O and in alcohol, ether and benzol. The corresponding β naphthol (*q.v.*) compound, $\mathbf{C_6H_4,OH,COO,C_{10}H_7}$, is a colorless, odorless, and tasteless substance, insoluble in H_2O. It has been used for the same purposes as salol under the names **napthalol** and **naphthol-salol.**

Gallic acid—*Acidum gallicum* (*U. S.*)—$\mathbf{C_6H_2(OH)_3COOH}$—170—exists in nature in certain leaves, seeds, and fruits. It is best obtained from gall-nuts, which contain its glucosid, gallotannic acid (*q.v.*). It can be obtained from salicylic acid.

It crystallizes in long silky needles with 1 Aq ; odorless ; acidulous in taste; sparingly soluble in cold water, very soluble in hot water and in alcohol; its solutions are acid. When heated to 210°-215° (410°-419° F.) it yields CO_2 and pyrogallol (*q. v.*). Its solution does not precipitate gelatin, nor the salts of the alkaloids, as does tannin. It forms four series of salts.

SULFONIC ACIDS.

The sulfonic acids corresponding to the series C_nH_{2n-6} are derived from the hydrocarbons by the substitution of one or more groups $(SO_3H)'$ for one or more H atoms of the hydrocarbons. They are produced by the action of fuming sulfuric acid upon the hydrocarbons, and are mono-, bi- or polysubstituted, according to the degree of concentration of the acid used, and the temperature at which the action takes place. They are strong acids, forming soluble and crystalline salts. Their basicity varies with the number of (SO_3H) groups which they contain.

Benzo-monosulfonic acid—$\mathbf{C_6H_5,SO_3H}$—is formed by dissolving benzene in weak fuming sulfuric acid at a slightly elevated temperature, and diluting with H_2O. It crystallizes in extremely soluble, deliquescent plates with 1½ Aq.

Three **benzo-disulfonic acids**—$\mathbf{C_6H_4(SO_3H)_2}$—ortho-, meta- and para-, are known, also one **benzo-trisulfonic acid**—$\mathbf{C_6H_3(SO_3H)_3}$.

Three **tolu-sulfonic acids**—$\mathbf{C_6H_4CH_3,SO_3H}$—ortho-, meta-, and para-, have been obtained. By the action of a mixture of ordinary and fuming sulfuric acids upon toluene at a temperature not exceeding 100° (212° F.), a mixture of the ortho- and para-acids is produced. When this is treated with PCl_5, it is converted into a mixture of **para-** and **ortho-toluene sulfonic chlorids**—$\mathbf{C_6H_4,CH_3,SO_2Cl}$. The ortho-chlorid, when acted on by dry ammonia and ammonium carbonate, is converted into **ortho-toluene sulfimid**—$\mathbf{C_6H_4,CH_3,SO_2NH_2}$. This product, when oxidized by potassium permanganate, is converted into **benzyl-sulfonic imid**—$\mathbf{C_6H_4,CO,SO_2NH}$—or **saccharin**—an odorless, crystalline powder, having great sweetening power, its sweet taste being still detectable in a dilution of 1-50,000. Sparingly soluble in water and in ether, readily in alcohol. Its solutions are acid in reaction. When heated with Na_2CO_3 it is carbonized and gives off an odor of benzene. It is not attacked by H_2SO_4.

Another series of sulfonic derivatives is obtained from the phenols. Among them is:

Ortho-phenol sulfonic acid—**Sozolic acid**—**Aseptol**—$\mathbf{C_6H_4,OH,SO_3H}$—which is prepared by the action of cold concentrated H_2SO_4 upon phenol. It is a reddish, syrupy liquid, soluble in H_2O in all proportions, has a faint and not disagreeable odor. It prevents fermentation and putrefaction, and is a non-poisonous, non-irritant antiseptic. The salts of this and the corresponding para- and meta-acids have been used as antiseptics and insecticides, under the name of **sulfo-carbolates**, *e.g.*, **Sodii sulfo-carbolas** (**U. S.**).

Salicyl sulfonic acid—$\mathbf{C_6H_4,OH,COOH,SO_3H}$—is a crystalline solid formed by the action of strong H_2SO_4 on salicylic acid. It is easily soluble in H_2O. It has been recommended as a test for albumin.

Diiodo phenol monosulfonic acid—$\mathbf{C_6H_2I_2,OH,SO_3H}$—is used as an antiseptic and astringent, in the form of its salts under the name **sozoiodol**; and **Diiodo resorcin monosulfonic acid**—$\mathbf{C_6HI_2,(OH)_{2(1-3)},SO_3H}$—is also used as an antiseptic having but slight poisonous qualities, under the name **picrol.**

NITRO-DERIVATIVES OF BENZENE.

By substitution of the univalent radical (NO_2) for the hydrogen of benzene a series of substitution products are obtainable, corresponding to the series of haloid derivatives, phenols, etc. (see pp. 397–402).

Mono-nitro-benzene—Nitro-benzol—Nitro-benzene—Essence of Mirbane—$\mathbf{C_6H_5(NO_2)}$—123—is obtained by the moderated action of fuming HNO_3, or of a mixture of HNO_3 and H_2SO_4 on benzene.

It is a yellow, sweet liquid, with an odor of bitter almonds; sp. gr. 1.209 at 15° (59° F.); boils at 213° (415°.4 F.); almost insoluble in water; very soluble in alcohol and ether. Concentrated H_2SO_4 dissolves, and, when boiling, decomposes it. Boiled with fuming HNO_3, it is converted into **binitro-benzene**. It is converted into *anilin* by reducing agents.

It has been used in perfumery as *artificial essence of bitter almonds;* but as inhalation of its vapor, even largely diluted with air, causes headache, drowsiness, difficulty of respiration, cardiac irregularity, loss of muscular power, convulsions, and coma, its use for that purpose is to be condemned. Taken internally it is an active poison.

Nitro-benzol may be distinguished from oil of bitter almonds (benzoic aldehyde) by H_2SO_4, which does not color the former; and by the action of acetic acid and iron filings, which convert nitro-benzene into anilin, whose presence is detected by the reactions for that substance (*q.v.*).

AMIDO-DERIVATIVES OF BENZENE.

These substances are derivable from benzene and its homologues by the substitution of one or more univalent groups (NH_2) (amidogen) for atoms of hydrogen. They may also be considered as **phenylamins**, produced by the substitution of the univalent radical **phenyl** ($\mathbf{C_6H_5}$), or its homologues, derivable from the benzene nucleus, for the hydrogen of ammonia. They all are strongly basic in character.

Anilin—**Amido-benzene**—*Amido-benzol*—**Phenylamin**—*Kyanol*—*Cristallin*—$\left.\begin{matrix}\mathbf{C_6H_5}\\\mathbf{H_2}\end{matrix}\right\}\mathbf{N}$—93—exists in small quantity in coal-tar and is one of the products of the destructive distillation of indigo. It is prepared by the reduction of nitro-benzene by hydrogen: $C_6H_5(NO_2)+3H_2=C_6H_5(NH_2)+2H_2O$; the hydrogen being liberated in the nascent state in contact with nitro-benzene by the action of iron filings on acetic acid.

Pure anilin is a colorless liquid; has a peculiar, aromatic odor, and an acrid, burning taste; sp. gr. 1.02 at 16° (60°.8 F.); boils at 184°.8 (364°.6 F.); crystallizes at −8° (17°.6 F.); soluble in 31 pts. of cold water, soluble in all proportions in alcohol, ether, carbon disulfid, etc. When exposed to air, it turns brown, the color of the commercial "oil," and, finally, resinifies. It is neutral in reaction. Oxidizing agents convert it into blue, violet, red, green, or black derivatives. Cl, Br, and I act upon it violently to produce products of substitution. Concentrated H_2SO_4 converts it, according to the conditions, into **sulfanilic** or **disulfanilic acid.** With acids it unites, after the manner of the ammonia, without liberation of H_2O or H, to form salts, most of which are crystallizable, soluble in water, and colorless, although by exposure to air, especially if moist, they turn red. The sulfate has been used medicinally. Potassium permanganate oxidizes it to nitro-benzene. Heated with H_2SO_4 and glycerol it produces quinolin, and substituted quinolins may be obtained by a similar reaction from substituted anilins.

Anilin itself, when taken in the liquid form or by inhalation, is an active poison, producing symptoms similar to those caused by nitro-benzene (*q.v.*). Its salts, if pure, seem to have but slight deleterious action.

Anilin may be recognized by the following reactions: (1.) With a nitrate and H_2SO_4, a red color. (2.) Cold H_2SO_4 does not color it alone; on addition of potassium dichromate, a fine blue color is produced, which, on dilution with water, passes to violet, and, if not diluted, to black. (3.) With calcium hypochlorite, a violet color. (4.) Heated with cupric chlorate, a black color. (5.) Heated with mercuric chlorid, a deep crimson color. (6.) In very dilute solution (1 : 250,000), anilin gives a rose color with chlorid of lime, followed by ammonium sulfhydrate.

Toluidins—$C_6H_4(CH_3)(NH_2)$.—Three toluidins, ortho-, meta- and para-, are known as the superior homologues of anilin. They occur in commercial anilin and play an important part in the production of anilin colors.

Xylidins—Amido-xylenes—$C_6H_3(CH_3)_2(NH_2)$.—Six compounds of this composition are known: two ortho-, derived from ortho-xylene, three meta-, derived from metaxylene, and one para-, derived from paraxylene. Five of them exist in commercial xylidin.

The toluidins and xylidins yield products of substitution and addition similar to those of anilin.

Carbodiimids are substances having the general formula $C\Big\langle\begin{matrix}NR\\NR'\end{matrix}$ in which R are two univalent radicals usually belonging to the aromatic series. They are prepared from the sulfureids, by loss of the elements of carbon oxysulfid, COS, by the action of heat or of oxydants.

DERIVATIVES OF ANILIN.

By the substitution of other radicals or elements for the remaining hydrogen atoms of the benzene nucleus, or for the hydrogen atoms of the amidogen group, NH_2, a great number of derivatives, including many isomeres, are produced.

In all of these derivatives the group (NH_2) is considered as occupying the position 1.

Chloranilins.—Three **monochloranilins** are known, of which two, ortho- (1—2) and meta- (1—3), are liquid. The other, para- (1—4), is solid and crystalline.

Four **dichloranilins**, 1—2—4, 1—2—5, 1—3—5, and 1—3—4, are known, all solid and crystalline.

Two **trichloranilins**, 1—2—4—6 and 1—2—4—5, are known, both solid and crystalline.

The corresponding **bromanilins** are also known; also a **tetrabromanilin**, 1—2—3—4—6, and a **pentabromanilin, $C_6(NH_2)Br_5$.**

Of the possible **iodanilins**, but four have been described: **Metamoniodanilin** (1—3); **paramoniodanilin** (1—4); the **diiodanilin** (1—2—4); and the **triiodanilin** (1—2—4—6).

Nitranilins.—The three isomeres, **ortho-, meta-,** and **paramononitranilins,** $C_6H_4(NH_2)(NO_2)$, are formed by imperfect reduction of the dinitro-benzenes.

Two **dinitranilins,** $C_6H_3(NH_2)(NO_2)_2$ (1—2—4) and (1—2—6), are known:

A single **trinitranilin,** $C_6H_2(NH_2)(NO_2)_3$ (1—2—4—6), has been obtained by the action of alcoholic ammonia upon the ethylic or methylic ether of picric acid. It is also called **picramid.**

Anilids.—These are compounds in which one of the H atoms of the amidogen group has been replaced by an acid radical. Or they may also be considered as amids, whose remaining hydrogen has been more or less replaced by phenyl, C_6H_5.

Acetanilid—Antifebrin—Phenyl-acetamid—$\mathbf{C_6H_5(NH,C_2H_3O)}$—is obtained either by heating together anilin and glacial acetic acid for several hours, or, better, by the action of acetyl chlorid on anilin. It forms colorless, shining, crystalline scales; fuses at 112°.5 (234°.5 F.), and volatilizes unchanged at 295° (563° F.). It is sparingly soluble in cold water, soluble in hot water and in alcohol.

When acetanilid is heated with an equal weight of $ZnCl_2$, **flavanilin,** a colored substance having a fine green fluorescence, and soluble in warm dilute HCl, is produced.

By herbivorous animals acetanilid is eliminated as **para-amido phenol,** $\mathbf{C_6H_4,OH_{(1)},NH_{2(4)}}$; by carnivorous animals partly in that form, but mostly as **orthoxy-carbanil,** $\mathbf{C_6H_4,NO,COH}$.

By the further substitution of a group (CH_3) in acetanilid, **methyl-acetanilid,** or **exalgine,** $\mathbf{C_6H_5,N,(CH_3)C_2H_3O}$ is produced. It is formed by the action of methyl iodid upon sodium acetanilid, C_6H_5,NNa,C_2H_3O. It is a crystalline solid, sparingly soluble in H_2O, readily in dilute alcohol. Its odor is faintly aromatic.

Three **acettoluids,** $\mathbf{C_6H_4,CH_3,NH,C_2H_3O}$, ortho, meta, and para, are also known. The para- and meta- compounds seem to be almost inert, while the ortho- compound is highly poisonous.

The "anilin dyes" now so extensively used, even those made from anilin, are not compounds of anilin, but are salts of bases formed from it, themselves colorless, called rosanilins (see p. 436).

Phenylamins—Phenylendiamins, etc.—Anilin is the simplest representative of a large class of substances. It may be considered as benzene in which H has been replaced by NH_2, thus: C_6H_5,NH_2. Its superior homologues, derivable from the superior homologues of benzene, each have at least three isomeres, ortho-, meta- and para-, according to the orientation of the groups NH_2 and C_nH_{2n+1}. Anilin may also be considered as ammonia in which H has been replaced by phenyl, C_6H_5, thus being a primary monamin (see p. 274), $\left.\begin{matrix}C_6H_5\\H_2\end{matrix}\right\}N$. The remaining two H atoms may be replaced by other radicals to form an almost infinite variety of **secondary** and **tertiary phenylamins,** precisely as in the case of the alcoholic monamins.

Again, it is clear that, considering anilin as **amido-benzene,** the substitution of NH_2 is not limited to the introduction of one such group. There may be three **phenylendiamins,** $\mathbf{C_6H_4(NH_2)_2}$, ortho-, meta- and para-, three **triamido benzenes,** $\mathbf{C_6H_3(NH_2)_3}$, etc.

When it is remembered that each one of these compounds is capable of forming a large number of derivatives by further substitution, and a series of salts, it is plain that the chemistry of these compounds would easily fill a volume.

HYDRAZINS.

The hydrazins are theoretically derivable from the group $H_2N-NH_2{}'$, diamidogen, by the substitution of acid, alcoholic, or phenylic radicals for one or more of the hydrogen atoms. They may be primary, secondary, tertiary, or quaternary, as the substitution removes are two, three, or four of the H atoms. The secondary hydrazins may be symmetrical or unsymmetrical, according to the formulæ $RHN-NHR$ and R_2N-NH_2. They also form compounds resembling the ammonium salts, known as **azonium** compounds. In short, they play the part of compound ammonias. The substituted groups may be acyclic as in ethyl-hydrazin, $C_2H_5HN-NH_2$, but in the majority it is a cyclic derivative as in phenyl hydrazin.

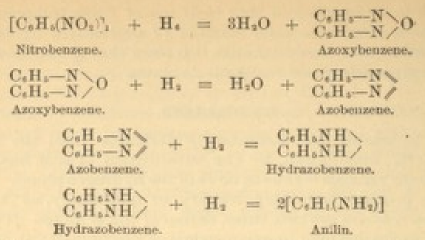
These compounds are valuable reagents in synthetic chemistry. With the chlorids of the acid radicals they form amids; they may produce compound ammonias; they form carbazic and sulfocarbazic acids with CO_2 and CS_2; by limited oxidation they form **tetrazones,** substances having the formula $R_2N-N=N-NR_2$, as the azo-compounds (see below) are produced from the amins, etc. They also combine with ketones to form products of condensation.

Phenyl hydrazin—$C_6H_5-HN-NH_2$—is obtained by the action of zinc-dust and acetic acid on diazo-amidobenzene. It is a yellow oil, sparingly soluble in water, soluble in alcohol and in ether, possessed of strong reducing power, and acting as a monacid base to form crystallized salts.

Phenyl-acetyl-hydrazin — Hydracetin—$C_6H_5.HN-NH-C_2H_3O$—is produced by the action of acetyl chlorid, or of acetic anhydrid, upon phenyl hydrazin. It is a white, tasteless, odorless, crystalline powder, sparingly soluble in H_2O, readily soluble in alcohol. It acts as a reducing agent. It is the active ingredient in the antipyretic known as **pyrodin.**

AZO AND DIAZO DERIVATIVES.

The azo compounds are derivable from the aromatic hydrocarbons by loss of two H atoms from two molecules of the hydrocarbon, and union of the remainders through the intermediary of a group $(-N=N-)''$. They are formed by the action of certain reducing agents upon the nitro-derivatives, and may be considered as intermediary products in the reduction of the nitro-derivatives to amins. Thus in the case of benzene :



$$\underset{\text{Nitrobenzene.}}{[C_6H_5(NO_2)]_2} + H_6 = 3H_2O + \underset{\text{Azoxybenzene.}}{\left.\begin{array}{l}C_6H_5-N\\C_6H_5-N\end{array}\right>O}$$

$$\underset{\text{Azoxybenzene.}}{\left.\begin{array}{l}C_6H_5-N\\C_6H_5-N\end{array}\right>O} + H_2 = H_2O + \underset{\text{Azobenzene.}}{\left.\begin{array}{l}C_6H_5-N\\C_6H_5-N\end{array}\right\rangle\!\!\rangle}$$

$$\underset{\text{Azobenzene.}}{\left.\begin{array}{l}C_6H_5-N\\C_6H_5-N\end{array}\right\rangle\!\!\rangle} + H_2 = \underset{\text{Hydrazobenzene.}}{\left.\begin{array}{l}C_6H_5NH\\C_6H_5NH\end{array}\right>}$$

$$\underset{\text{Hydrazobenzene.}}{\left.\begin{array}{l}C_6H_5NH\\C_6H_5NH\end{array}\right>} + H_2 = \underset{\text{Anilin.}}{2[C_6H_5(NH_2)]}$$

The diazo compounds consist of an univalent remainder of an aromatic hydrocarbon, united by the group ($-N=N-$) with a haloid atom, or an acid residue: $C_6H_5-N=N-Br$ = Diazobenzene bromid.

Phosphins, Stibins and Arsins.—As among the acyclic compounds (see p. 299), there exist substances in which P, Sb, or As takes the place of N, so among the cyclic derivatives there are similar derivatives. Thus **diphosphenyl—$C_6H_5P=PC_6H_5$**, corresponding to diazobenzene, $C_6H_5N=NC_6H_5$; **Phenylphosphin—$C_6H_5PH_2$**, corresponding to anilin, $C_6H_5NH_2$; **Triphenylstibin—$(C_6H_5)_3Sb$**, and **Triphenylarsin—$(C_6H_5)_3As$**, corresponding to trimethylamin, $(CH_3)_3N$.

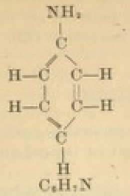
PYRIDIN BASES.

These interesting substances, closely related to the vegetable alkaloids, as well as to some of the alkaloids produced during purtrefactive decomposition of animal matters, were first discovered in 1846, as constituents of **oil of Dippel** = **oleum animale** = **oleum cornu cervi** = **bone-oil**, an oil produced during the dry distillation of bones, horns, etc., and as a by-product in the manufacture of ammoniacal compounds from those sources. They also occur in coal-tar, naphtha, and in commercial ammonia, methylic spirit, and fusel oil.

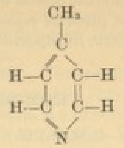
The pyridin bases at present known are:

	Formula.	Boiling-point.	Sp. gr. at 22°.
Pyridin	C_5H_5N	115°	0.924
Picolin	C_6H_7N	134°	0.933
Lutidin	C_7H_9N	154°	0.945
Collidin	$C_8H_{11}N$	170°	0.953
Parvolin	$C_9H_{13}N$	188°	0.966
Coridin	$C_{10}H_{15}N$	211°	0.974
Rubidin	$C_{11}H_{17}N$	230°	1.017
Viridin	$C_{12}H_{19}N$	251°	1.024

It will be observed that these compounds are metameric with the anilins, from which they differ in constitution, as shown by the structural formulæ of picolin and anilin :

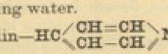


C_6H_7N
Anilin.



C_6H_7N
Picolin.

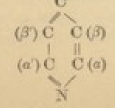
They are all liquid at the ordinary temperature, behave as tertiary monamins, react with several of the general reagents of the alkaloids, and form chloroplatinates which are decomposed by boiling water.

Pyridin— $HC\left\langle\begin{matrix}CH=CH\\CH-CH\end{matrix}\right\rangle N$—is obtained from oil of Dippel. It is obtainable synthetically from **piperidin,** which is itself a derivative of **piperin,** a constituent of black and white pepper (see below); and also by the action of sodium in the presence of methylene iodid, upon pyrrol (q. v.), as well as by other reactions.

It is a colorless, mobile liquid, having a peculiar, very penetrating odor. It boils at 115° (239° F.). It mixes with water in all proportions. It is strongly alkaline, and combines with acids as does NH_3. Like all the bases of this series, it is very stable, and withstands the action of such oxidizing agents as fuming HNO_3 and chromic acid. It forms crystalline salts.

PRODUCTS OF SUBSTITUTION OF PYRIDIN.

The products of substitution of pyridin, among which may be included its superior homologues, are very numerous, and, by reason of the introduction of the N atom in the benzene-chain, form a greater number of isomeres than are possible with the symmetrical unaltered benzene-chain. Thus, while there is but one monosubstituted derivative of the same univalent element or radical in the case of benzene, there are three possible in the case of pyridin, according as the substitution occurs in one of the α or in a β, or in the γ position with reference to the N atom, thus:



There are six each of bi- and tri-substituted derivatives, three tetra-substituted derivatives and one penta-substituted. Further, the double bonds with the chain may also be liberated, thus forming a nucleus possessed of eleven in place of six valences, such as exists in piperidin and its derivatives (see p. 425).

HOMOLOGUES OF PYRIDIN.

Picolins—$C_5H_4N(CH_3)$.—As pointed out above three picolins, α, β, and γ are known, all of which exist in oil of Dippel and have been produced synthetically.

Lutidins.—Theoretically there are three possible **ethyl-pyridins, $C_5H_4N(C_2H_5)$**, and six possible **dimethyl-pyridins, $C_5H_3N(CH_3)_2$**. The former are all known, and three of the latter.

Collidins—$C_8H_{11}N$.—There are twenty-two possible collidins, of which twelve are known. Of these several are the products of decomposition of vegetable alkaloids, or are basic substances existing in oil of Dippel, or formed during putrefactive changes.

Conyrin.—A basic substance produced by distilling coniïn with zinc chlorid, is α **propyl pyridin.** β **propyl pyridin** is produced from nicotin by passing its vapor through a red-hot tube. Two isomeric collidins, probably methyl ethyl pyridins, are formed by the action of fused KHO on cinchonin.

Aldehydin is a collidin of unknown constitution, formed by heating aldehyde-ammonia in alcoholic solution to 120° (248° F.), and by several other reactions, and exists also in the products of rectification of alcohol. An oily ptomain product during the putrefaction of gelatin in the presence of pancreas is a collidin of undetermined constitution.

Parvolins—$C_9H_{13}N$.—Theory indicates the existence of 57 parvolins, of which five are known. One of these is a ptomain produced during the decomposition of mackerel and of horse-flesh. It is an oily substance, slightly soluble in H_2O, which, when fresh, has an odor of hawthorn blossoms, but on exposure to air becomes brown and resinous.

One of the **coridins, $C_{10}H_{15}N$**, has been obtained as a product of putrefaction of fibrin and of jelly-fish during several months. It is an alkaline oil, which has a poisonous action resembling that of curara.

The pyridin bases exert a paralyzing action upon the central, and to a less degree upon the peripheral, nervous system. They are the antagonists of **strychnin.**

CARBOPYRIDIC ACIDS.

These acids are derived from pyridin, in the same manner as the benzoic and other series are derived from benzene (p. 413), by the substitution of COOH for H, but differ from those acids in presenting a greater number of isomeres.

Monocarbopyridic acids—**$C_5H_4N(COOH)$**.—Three isomeric acids having this composition corresponding to the three picolins (p. 424) are known. The α acid, **picolic acid,** is a crystalline solid, formed by oxidation of the corresponding picolin. The β acid, **nicotic acid,** is formed by the oxidation of nicotin, of pilocarpin, and of many artificial pyridin derivatives. The γ acid, **isonicotic acid,** is formed during the oxidation of many pyridin derivatives.

Dicarbopyridic acids—**$C_5H_3N(COOH)_2$**.—The six acids whose existence is indicated by theory are all known. Among them are **quinolinic acid,** formed by the oxidation of quinolin, and **cinchomeric acid,** produced by the oxidation of cinchonin, cinchonidin or quinin.

PIPERIDIN AND RELATED ALKALOIDS.

The researches made in recent years concerning the constitution of the vegetable alkaloids have proved that, with a few exceptions, they are derivatives either of a more or less modified pyridin, or of quinolin, itself an addition product of pyridin and benzene (see p. 447); and that many of the alkaloids may be considered as made up of a basic substance containing all the nitrogen of the alkaloid, a more or less modified pyridin or quinolin, with a substance which is either an acid or a neutral substance. The alkaloids of this class which are the most simple in constitution are those derived from:

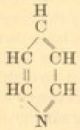
Piperidin—**$C_5H_{11}N$**—which is a product of the action of KHO on piperin (see below), and may also be obtained from pyridin by the action of reducing agents, such as Sn+HCl. It is a colorless liquid, having a strongly alkaline reaction and an ammoniacal odor. When heated with methyl iodid it is converted into **methyl-piperidin.** The composition of piperidin and its formation from pyridin by reduction, as well as the fact that, on treatment with silver oxid, it produces pyridin, prove it to be *hexa hydropyridin*, or pyridin whose bonds have been released and satisfied by hydrogen atoms (see below).

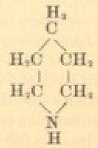
Coniin—**$C_8H_{17}N$**—is the most simply constituted of the natural vegetable alkaloids, and was the first to be produced by synthesis. It exists in *Conium maculatum*, in which it is accompanied by two other alkaloids, **methyl-coniin, $C_8H_{16}N(CH_3)$**, and **conhydrin, $C_8H_{17}NO$**—the former a volatile liquid, the second a crystalline solid.

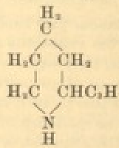
Coniïn is a colorless, oily liquid; has an acrid taste and a disagreeable penetrating odor; sp. gr. 0.878; can be distilled when protected from air; boils at 212° (413°.6 F.); exposed to air it resinifies; it is very sparingly soluble in water, but is more soluble in cold than in hot water; soluble in all proportions in alcohol, soluble in six volumes of ether, very soluble in fixed and volatile oils.

The vapor which it gives off at ordinary temperatures forms a white cloud when it comes in contact with a glass rod moistened with HCl, as does NH_3. It forms salts which crystallize with difficulty. Cl and Br combine with it to form crystallizable compounds; I in alcoholic solution forms a brown precipitate in alcoholic solutions of coniïn, which is soluble without color in an excess. Oxidizing agents attack it with production of butyric acid (see below). The iodids of ethyl and methyl combine with it to form iodids of ethyl- and methyl-coniïn.

It has been obtained synthetically from α picolin by reactions which show it to be α propyl piperidin. The relations of pyridin, piperidin, and coniïn are shown by the following formulæ:


Pyridin.


Piperidin.


Coniïn.

Analytical Characters.—(1.) With dry HCl gas it turns reddish-purple, and then dark blue. (2.) Aqueous HCl of sp. gr. 1.12 evaporated from coniïn leaves a green-blue, crystalline mass. (3.) With iodic acid a white ppt. from alcoholic solutions. (4.) With H_2SO_4 and evaporation of the acid: a red color, changing to green, and an odor of butyric acid. (5.) When mixed with commercial nitrobenzene a fine blue color is produced, changing to red and yellow.

Paraconiin—$\mathbf{C_8H_{15}N}$—is a synthetical product closely resembling coniïn, obtained by first allowing butyric aldehyde and an alcoholic solution of ammonia to remain some months in contact at 30° (86° F.), when dibutyraldin is formed:

$$\underset{\text{Butyric aldehyde.}}{2(C_4H_8O)} + \underset{\text{Ammonia.}}{NH_3} = \underset{\text{Dibutyraldin.}}{C_8H_{17}NO} + \underset{\text{Water.}}{H_2O}$$

The dibutyraldin thus obtained is then heated under pressure to 150°–180° (302°–356° F.), when it loses water:

$$\underset{\text{Dibutyraldin.}}{C_8H_{17}NO} = \underset{\text{Paraconiïn}}{C_8H_{15}N} + \underset{\text{Water.}}{H_2O}$$

A synthesis which, in connection with the decompositions of paraconiïn, shows its rational formula to be $\left.\begin{matrix}(C_4H_7)' \\ (C_4H_7)' \\ H\end{matrix}\right\} N$.

Atropin—Atropina (U. S.)—Atropia (Br.)—$C_{17}H_{23}NO_3$.—Belladonna, stramonium, hyoscyamus, and duboisia contain five alkaloids: *Atropin*, *hyoscyamin*, *hyoscin*, *belladonin*, and *daturin*. The first three are isomeric with each other and the first two possibly identical. The last two have been imperfectly studied.

Atropin forms colorless, silky needles, which are sparingly soluble in cold water, more readily soluble in hot water, very soluble in chloroform. It is odorless, but has a disagreeable, persistent, bitter taste. It is distinctly alkaline, and neutralizes acids with formation of salts. One of these, the sulfate—**Atropinæ sulphas, U. S.**—is a white, crystalline powder, readily soluble in water, which is the form in which atropin is usually administered.

TOXICOLOGY.—It is actively poisonous, producing drowsiness, dryness of the mouth and throat, dilatation of the pupils, loss of speech, diplopia, dizziness, delirium, coma.

The treatment should consist in the administration of emetics and the use of the stomach-pump.

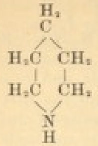
ANALYTICAL CHARACTERS.—(1.) If a fragment of potassium dichromate be dissolved in a few drops of H_2SO_4, the mixture warmed, a fragment of atropin and a drop or two of H_2O added, and the mixture stirred, an odor of orange-blossoms is developed. (2.) A solution of atropin dropped upon the eye of a cat produces dilatation of the pupil. (3.) The dry alkaloid (or salt) is moistened with fuming HNO_3 and the mixture dried on the water-bath. When cold it is moistened with an alcoholic solution of KHO—a violet color which changes to red (Vitali). (4.) If a saturated solution of Br in HBr be added to a solution of atropin a yellow precipitate is formed which rapidly becomes crystalline, and which is insoluble in acetic acid, sparingly soluble in H_2SO_4 and HCl.

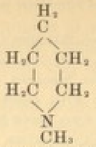
CONSTITUTION.—If atropin is acted upon by baryta at 60° (140° F.), or by caustic soda, or hydrochloric acid at 120°–130° (248°–266° F.) it is saponified, after the manner of an ether, into **tropin** and **tropic acid**, according to the equation:

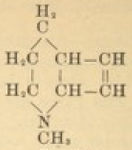
$$\underset{\text{Atropin.}}{C_{17}H_{23}NO_3} + H_2O = \underset{\text{Tropin.}}{C_8H_{15}NO} + \underset{\text{Tropic acid.}}{C_9H_{10}O_3}$$

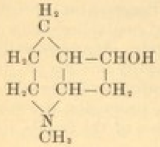
but if the action of the reagents be prolonged tropic acid loses H_2O and produces a mixture of **atropic acid, $C_9H_8O_2$**, and **isatropic acid, $C_{18}H_{16}O_4$**. And if, during the action of HCl, the temperature rises to 180° (356° F.) the tropin also loses H_2O and is converted into **tropidin, $C_8H_{13}N$.**

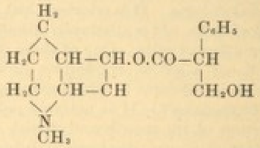
The relations of these bodies to each other and to piperidin are expressed by the following formulæ :


Piperidin.


Methyl-piperidin.


Tropidin.


Tropin.


Atropin.

and atropin may be considered as formed by the union of tropin with **tropic acid**, $C_6H_5-CH\left\langle\begin{matrix}CH_2OH\\COOH\end{matrix}\right.$, with loss of H_2O.

Tropin—$C_8H_{15}NO$—is a crystalline solid, fusible at 62° (143°.6 F.), very soluble in water. It reacts with methyl iodid to produce *a* **methyltropin.** Tropin has the poisonous qualities of atropin, but does not dilate the pupil.

Tropidin—$C_8H_{13}N$—is a liquid having the odor of coniïn, which it also resembles in being more soluble in cold than in hot H_2O. Its bromid heated with excess of Br produces **methyl dibromopyridin,** $C_5H_2N(Br)_2CH_3$, whose formation shows that it and its derivatives, tropin and atropin, are derivatives of pyridin.

Tropeins are substances produced synthetically, as **atropin** is produced from tropin and tropic acid, by the union of tropin with other organic acids, such as benzoic, salicylic, etc.

Piperin—$C_{17}H_{19}NO_3$—an alkaloid of black and white pepper, and isomeric with morphin, is constituted somewhat similarly to atropin. On saponification by alcoholic soda it yields piperidin (see above) and an acid, **piperic acid,** $C_{12}H_{10}O_4$, whose constitution, although partially known, is not completely established.

Piperin is a very feeble base, without alkaline reaction, insoluble in dilute acids and only forming very unstable salts with concentrated acids. It crystallizes in monoclinic prisms.

Cocain—$C_{17}H_{21}NO_4$—is another alkaloid of ethereal constitution, containing a modified methyl-piperidin nucleus, whose constitution is only partially known. It crystallizes in large, six-sided prisms. Its taste is at first bitter, producing paralysis of the sense of taste subsequently. It is strongly alkaline. Its chlorid, extensively used for the production of local anæsthesia, crystallizes in well-formed prismatic needles, readily soluble in water.

When boiled with H_2O it is saponified into **benzyl-ecgonin, $C_{16}H_{19}NO_4$**, and methylic alcohol. If the saponification be effected by baryta or by concentrated mineral acids the decomposition is more complete and **ecgonin, $C_9H_{15}NO_3$**, benzoic acid and methyl alcohol are formed. Cocain may also be regenerated by acting upon ecgonin with a mixture of methyl iodid and benzoic anhydrid, and, by substituting other alcoholic iodids for that of methyl, other alkaloids homologous with cocain may be obtained. Ecgonin not only combines with bases to form salts, but also with anhydrids to produce ethers. It is, therefore, both acid and basic in character, and yields numerous products of derivation besides cocain.

Besides cocain and benzyl-ecgonin, the leaves of erythroxylon coca contain another alkaloid, **hygrin**, a very alkaline liquid having an odor resembling that of trimethylamin.

ANALYTICAL CHARACTERS.—The reactions of cocain are not very marked. (1.) Picric acid forms a yellow ppt. in concentrated solutions. (2.) A solution of iodin in KI solution gives a fine red precipitate in a solution containing 1 to 10,000 of cocain. (3.) When cocain or one of its salts, dried at 100° (212° F.), is moistened with fuming HNO_3, evaporated to dryness, and the residue taken up with alcoholic solution of KHO, a strong odor resembling that of peppermint is developed, due to the formation of ethyl benzoate.

Pilocarpin—$C_{11}H_{16}N_2O_2$—occurs in jaborandi, along with two other alkaloids, **jaborin, $C_{22}H_{32}N_4O_4$** (?), and **pilocarpidin, $C_{10}H_{14}N_2O_2$**, and an essential oil, consisting principally of **pilocarpene, $C_{10}H_{16}$**.

Pilocarpin is colorless, crystalline, readily soluble in water, alcohol, ether, and chloroform. It is converted by heat into jaborin; and by HNO_3 or HCl into a mixture of jaborin and **jaborandin, $C_{10}H_{12}N_2O_3$**. Like atropin, piperin, etc., it is ethereal in constitution and is decomposed by KHO or NaHO into CO_2, methylamin, butyric acid, and pyridin bases.

COMPOUNDS OF OTHER SUBSTITUTED BENZENES.

Pyridin is the simplest product which may be considered as derived from benzene by the substitution of N for CH. Other substances are known in which a further substitution of N has more deeply modified the nucleus. Thus there exist three **diazins**, α, β, and γ, containing two nitrogen atoms in the nucleus, two **triazins,** *ββ'* and *αβ*, containing three, and one **tetrazin,** *αβγ*, containing four.

The benzene nucleus may also be modified by the substitution of oxygen, or of sulfur, producing compounds such as the following:

α Furane.

γ Furane.

γ Thiane.

Pyrone (γ)—*Pyrocomane*—$O\langle\begin{smallmatrix}CH=CH\\CH=CH\end{smallmatrix}\rangle CO$—is an oxidized derivative of γ furane, produced from comenic acid by the action of heat and constituting the nucleus of comanic, chelidonic, and meconic acids.

Comenic acid—$C_5H_3O_3$(COOH)—is produced by the action of hot H_2O, of dilute acids, or of bromin water upon meconic acid. It crystallizes in yellowish prisms, rather soluble in H_2O. It is monobasic. It is decomposed by heat into CO_2 and pyrone.

Chelidonic acid—$C_5H_2O_2$(OH)COOH—exists in chelidonium, in combination with the alkaloids **sanguinarin** and **chelidonin.** It is a crystalline solid, and a dibasic acid. Heat converts it into comenic acid, which in turn yields pyrone.

Meconic acid—C_5HO_2(OH)(COOH)$_2$—is peculiar to opium, in which it exists in combination with a part, at least, of the alkaloids. It crystallizes in small prismatic needles; acid and astringent in taste; loses its Aq at 120° (248° F.); quite soluble in water; soluble in alcohol; sparingly soluble in ether.

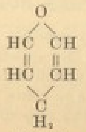
With ferric chlorid it forms a blood-red color, which is not discharged by dilute acids or by mercuric chlorid; but is discharged by stannous chlorid and by the alkaline hypochlorites.

COMPOUNDS WITH PENTAGONAL NUCLEI.

CONDENSATION PRODUCTS OF BENZENE.

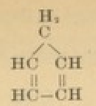
These compounds differ from the benzene derivatives in containing pentagonal in place of hexagonal nuclei; thus:

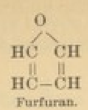
Benzene.

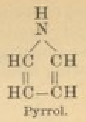


Furane.

Pyridin.

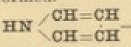

Valylene.


Furfuran.


Pyrrol.

Furfuran—C_4H_4O—is a product of the distillation of fir-wood, and is also formed from dehydrofurfuran, C_4H_6O, obtained from erythrite.

Furfurol — Furfuraldehyde — $C_4H_3O.CHO$ — was the earliest known of the series. It is produced by the dry distillation of sugar or of wood, or by the action of $ZnCl_2$ or dilute H_2SO_4 on bran. It is a colorless liquid, has an agreeable odor, boils at 162° (323°.6 F.), is soluble in water and in alcohol. Being an aldehyde it undergoes the reactions common to those substances. With urea and a trace of acid it develops a beautiful violet color, which disappears after a time, while an insoluble, black, flocculent precipitate is formed.

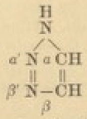


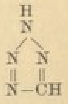
Pyrrol — $HN\left\langle\begin{matrix}CH=CH\\CH=CH\end{matrix}\right.$—accompanies the pyridin bases in oil of Dippel, and is formed in a variety of reactions; by the action of baryta at 150° (303° F.) upon albumen; by the dry distillation of gelatin or of ammonium saccharate, etc.

It is a colorless, oily liquid, having the odor of chloroform. By acting upon pyrrol with an ethereal solution of iodin, a quadri-substituted derivative, tetriodopyrrol, C_4HI_4N, is obtained as a brown powder, which has been used under the name **iodol** as a substitute for iodoform in surgical practice.

The molecule of pyrrol may be further modified by the introduction of further N atoms to produce:


α Pyrazol.

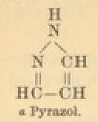

α β Pyrrodiazol.

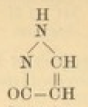

Pyrrotriazol.

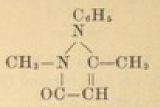
and there may be two pyrazols, α and β, and four pyrrodiazols, αβ, α′β, αα¹, ββ′, varying according to the position of the N atoms. As other substances may also be produced by substitution for the hydrogen atoms or by liberation of the double bonds, the pyrrol derivatives are very numerous. Among them is:

Antipyrin = Phenyl-dimethyl-pyrazolon — $C_{11}H_{12}N_2O$ — is obtained by heating phenyl-methyl-pyrazolon with methyl iodid and methyl alcohol in sealed vessels at 100° (212° F.); the first-named substance having been previously obtained by the action by acetylacetic ether upon phenyl hydrazin.

The constitution and relations of antipyrin are shown by the following formulæ:


a Pyrazol.


Pyrazolon.


Phenyl-dimethyl-pyrazolon, antipyrin.

It constitutes a voluminous, reddish, crystalline powder; readily soluble in water, ether, alcohol, and chloroform. With nitrous acid, or the nitrites (sp. æth. nitr.) in the presence of free acids, it forms a green, crystalline, sparingly soluble nitro-derivative which seems to be poisonous.

Its solution with Fe_2Cl_6 is colored deep red-brown, the color being discharged by H_2SO_4. Nitrous acid colors dilute solutions of antipyrin a bright green, which persists for several days at the ordinary temperature. If the mixture be heated, and a drop of fuming HNO_3 added, the color changes to light red, then blood-red, and the liquid deposits a purple oil on continued heating. Addition of a drop of fuming HNO_3 to a cold concentrated solution of antipyrin produces precipitation of small green crystals.

INCOMPLETE BENZENIC HYDROCARBONS.

SERIES C_nH_{2n-8} AND C_nH_{2n-10}.

These may be considered as benzenic compounds which have been rendered incomplete by loss of H_2, either in the benzene nucleus or in a lateral chain. Thus while ethylbenzene is produced by the addition of a molecule of ethylene to a molecule of benzene: $C_6H_5,H + CH_2,CH_2 = C_6H_5,CH_2,CH_3$; if acetylene be substituted for ethylene, ethylenbenzene is formed: $C_6H_5,H + CH,CH = C_6H_5,CH,CH_2$.

Styrolene—Cinnamene—Ethylenbenzene—Phenylethene—C_6H_5—$CH = CH_2$—104—exists ready formed in essential oil of styrax. It is also formed by decomposition of cinnamic acid (*q.v.*), or, synthetically, by the action of a red heat upon pure acetylene, a mixture of acetylene and benzene, or a mixture of benzene and ethylene. It is a colorless liquid, has a penetrating odor, recalling those of benzene and naphthalene, and a peppery taste; boils at 143° (289°.4 F.); soluble in all proportions in alcohol and water; neutral in reaction.

Phenyl-acetylene—Acetenyl-benzene—$C_6H_5,C{\equiv}CH$—is formed by heating acetophenone chlorid with KHO in alcoholic solution. It is a colorless liquid, of an aromatic odor, boils at 140° (284° F.).

ALCOHOLS.

SERIES $C_nH_{2n-8}O$.

Cholesteric alcohol—Cholesterin—$C_{26}H_{43}OH$—372—is an alcohol, although usually classed by physiologists among the fats, because it is greasy to the touch and soluble in ether.

It occurs in the animal economy, normally in the bile, blood (especially that coming from the brain), nerve-tissue, brain, spleen, sebum, contents of the intestines, meconium, and fæces; pathologically in biliary calculi, in the urine in diabetes and icterus, in the fluids of ascites, hydrocele, etc., in tubercular and cancerous deposits, in cataracts, in atheromatous degenerations, and sometimes in masses of considerable size, in cerebral tumors. It also exists in the vegetable world in peas, beans, olive-oil, wheat, etc. It is best obtained from biliary calculi, the lighter-colored varieties of which consist almost entirely of this substance.

Cholesterin crystallizes with or without Aq; from benzene, petroleum, chloroform or anhydrous ether, it separates in delicate, colorless, silky needles, having the composition $C_{26}H_{44}O$; from hot alcohol, or a mixture of alcohol and ether, it crystallizes in rhombic plates, usually with one obtuse angle wanting, having the composition $C_{26}H_{44}O + 1$ Aq; these crystals, transparent at first, become opaque on exposure to air, from loss of Aq. It is insoluble in water, in alkalies and dilute acids, difficultly soluble in cold alcohol, readily soluble in hot alcohol, ether, benzene, acetic acid, glycerol, and solutions of the biliary acids. It is odorless and tasteless. When anhydrous it fuses at 145° (293° F.) and solidifies at 137° (278°.6 F.); sp. gr. 1.046. It is lævogyrous, $[\alpha]_D = 31°.6$ in any solvent.

It combines readily with the volatile fatty acids. From its solution in glacial acetic acid a compound having the composition $C_{26}H_{44}O,C_2H_4O_2$ separates in fine curved crystals, which are decomposed on contact with water or alcohol; when heated with acids under pressure, it forms true ethers. Hot HNO_3 oxidizes it to **cholesteric acid, $C_8H_{10}O_5$**, which is also produced by the oxidation of biliary acids; a fact which indicates the probable existence of some relation between the methods of formation of cholesterin and of the biliary acids in the economy.

Cholesterin may be recognized by the following reactions: (1.) Moistened with HNO_3, and evaporated to dryness, a yellow residue remains, which turns brick-red on addition of NH_4HO. (2.) It is colored violet when a mixture of 2 vols. H_2SO_4 (or HCl) and

1 vol. ferric chlorid solution is evaporated upon it. (3.) When H_2SO_4 is added to a $CHCl_3$ solution of cholesterin the liquid is colored purple-red, changing during evaporation to blue, green and yellow.

Cholesterin is accompanied in wool fat by an isomere, **isocholesterin.**

Cholesterin combines with the fatty acids to form ethers, corresponding to the fats, and it probably exists in nature largely in such combination. **Lanolin** is a neutral, fatty body consisting of such **cholesterids**, or cholesterin ethers, obtained from suint, or wool fat. It is used as a vehicle in pharmacy, possessing two advantages over the fats and over vaseline: it is rapidly absorbed by the skin, and is miscible with water in all proportions.

BI- AND POLYBENZOIC HYDROCARBONS.

Among the compounds already considered are several containing more than one benzene nucleus, but in them the union of the two nuclei, as in the azo compounds, is through an element other than carbon. In the compounds now to be considered two or more benzene nuclei are united with each other, either directly, or through the carbon of a linking lateral chain.

HYDROCARBONS WITH INDIRECTLY UNITED BENZENE NUCLEI.

The simplest of the bi- and polybenzoic hydrocarbons are those in which two or more benzene nuclei are combined with a linking lateral chain. By the substitution of phenyl for the H of methane four compounds can be produced:

$$\begin{matrix} C_6H_5 \\ H \end{matrix} > C < \begin{matrix} H \\ H \end{matrix}$$

Monophenylmethane.
Toluene.

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} > C < \begin{matrix} C_6H_5 \\ H \end{matrix}$$

Triphenylmethane.

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} > C < \begin{matrix} H \\ H \end{matrix}$$

Diphenylmethane.

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} > C < \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}$$

Tetraphenylmethane.

Of these the first has been already considered, and the fourth has not been isolated, although the corresponding ethane is known.

Diphenylmethane—Benzyl-benzene—is produced by the action of aluminium chlorid upon a mixture of benzyl chlorid and benzene. It is a crystalline solid, fuses at 27° (80°.6 F.) and boils at 262° (503°.6 F.); soluble in alcohol, ether and chloroform; has an odor resembling that of the orange.

Triphenylmethane—is produced by the action of aluminium chlorid upon a mixture of benzene and chloroform. It is a crystalline solid, fuses at 92° (197°.6 F.); boils at 360° (680° F.); soluble in ether, and in chloroform. It is converted into a trinitro derivative by fuming HNO_3, and this, in turn, is converted by nascent H into **leuco-pararosanilin**, $CH,(C_6H_4,NH_2)_3$ (see below).

DERIVATIVES OF THE PHENYLMETHANES.

Ketones—$\mathbf{CO = (C_nH_{2n-7})_2}$.—These substances are similar to the phenones already described, but contain two benzene nuclei in place of one. They are produced by the oxidation of the hydrocarbons C_nH_{2n-14}; by the action of P_2O_5 on a mixture of a hydrocarbon C_nH_{2n-6} with an acid $C_nH_{2n-7}CO,OH$; and by the action of carbon oxychlorid upon a hydrocarbon C_nH_{2n-6} in the presence of Al_2Cl_6.

Benzophenone — Diphenyl-ketone — $\mathbf{CO = (C_6H_5)_2}$ — forms large rhombic prisms; fuses at 48° (118°.4 F.); boils at 305° (581° F.); insoluble in H_2O, soluble in alcohol and ether. It is decomposed by soda-lime into benzene and benzoic acid. Sodium amalgam converts it into **benzhydrol**, or **diphenylcarbinol**, $\mathbf{CH(OH) = (C_6H_5)_2}$, a secondary alcohol.

Amido-derivatives.—Among these substances are included some of great industrial interest. Many of the bases, whose salts are the brilliant pigments obtained from anilin and its homologues, are amido-derivatives of triphenylmethane.

Amido-triphenylmethane—$\mathbf{CH,(C_6H_5)_2(C_6H_4NH_2)}$—is formed by the action of benzhydrol upon anilin chlorid in the presence of $ZnCl_2$.

Diamido-triphenylmethane — $\mathbf{CH,(C_6H_5)(C_6H_4,NH_2)_2}$ — is produced by the action of anilin chlorid and benzoic aldehyde upon each other in the presence of $ZnCl_2$. The salts of this base are blue, and are decomposed by alkalies with liberation of the base, which is a yellow, imperfectly crystalline solid, insoluble in water, soluble in benzene and in alcohol.

The base is converted by $HgCl_2$ into the corresponding tertiary alcohol, **diamido-triphenyl carbinol**, $\mathbf{C(OH),(C_6H_5),(C_6H_4,NH_2)_2}$, whose oxalate or chloro-zincate is **malachite green**.

Triamido-triphenylmethane—$\mathbf{CH(C_6H_4,NH_2)_3}$—may be obtained by the reduction of para-nitrobenzoic aldehyde by nascent hydrogen, and is also known as **paraleucanilin**. By the action of oxidizing agents it is converted into a tertiary alcohol, **pararosanilin**, or **triamido-triphenyl carbinol**, which is the type of quite a number of important bodies, among which is **rosanilin**, or **di-**

phenyltoluyl carbinol, whose chlorid or acetate is the brilliant red dye known as **anilin red, magenta, fuchsine.** The relation of these bodies to each other is shown by the following formulæ:

$$H{-}C\begin{cases}C_6H_5\\C_6H_5\\C_6H_5\end{cases}$$

Triphenylmethane.

$$H{-}O{-}C\begin{cases}C_6H_4,NH_2\\C_6H_4,NH_2\\C_6H_4,NH_2\end{cases}$$

Triamidophenyl carbinol.
Pararosanilin.

$$H{-}C\begin{cases}C_6H_4,NH_2\\C_6H_4,NH_2\\C_6H_4,NH_2\end{cases}$$

Triamidophenylmethane.
Paraleucanilin.

$$H{-}O{-}C\begin{cases}C_6H_4,NH_2\\C_6H_4,NH_2\\C_6H_4,CH_3,NH_2\end{cases}$$

Diamidophenyl amidotoluyl carbinol.
Rosanilin.

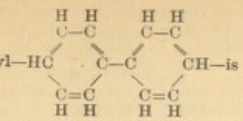
The **rosanilins** are powerful triacid bases, are colorless, but combine with acids to form brilliantly colored salts. Fuchsine is industrially obtained from "anilin oil," which contains both anilin and toluidin, neither of which in the pure state will produce a red color. The process consists essentially in heating the oil with a mixture of nitro-benzene, hydrochloric acid and iron filings. The product is a mixture of the chlorids of rosanilin and pararosanilin, is in hard, green crystals, soluble in water and alcohol, to which it communicates a brilliant red color.

The rosanilins are capable of further modification by the substitution of various radicals for the hydrogen atoms in the benzene nuclei, or in the groups NH_2, and by variations in the positions in which such substitution occurs.

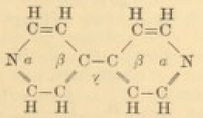
Hoffman's violet, obtained by heating rosanilin chlorid with methyl iodid, is **trimethylrosanilin chlorid.** By a further action of methyl iodid, a brilliant green, **iodin green, pentamethylrosanilin chlorid,** is produced. **Lyons blue** is **triphenylrosanilin chlorid,** formed by heating rosanilin chlorid with excess of anilin.

HYDROCARBONS WITH DIRECTLY UNITED BENZENE NUCLEI.

These hydrocarbons and their derivatives are divided into two classes: 1. Those in which two or more benzene nuclei, each retaining its six C atoms, are attached together by loss of H_2. 2. Those in which two or more benzene nuclei are united in such manner that each two possess two atoms of carbon in common, as shown in the formulæ of naphthalene and phenanthrene given below.

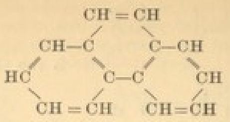
Diphenyl——is the simplest compound of the first class. It is obtained by the action of sodium upon monobromobenzene, or by passing benzene through a red-hot tube. It crystallizes in large plates, fusible at 70°.5 (159°.8 F.); boils at 254° (489°.2 F.). Diphenyl and its superior homologues, **ditoluyl, diphenylbenzene,** etc., constitute the nuclei of a great number of products of substitution, formed by the replacement of one or more of their H atoms by various radicals and elements, among them being many isomeres produced by differences of orientation.

Dipyridyls—$C_{10}H_8N_2$.—These substances bear the same relation to pyridin that diphenyl does to benzene; but, owing to the presence of the N atom in the nucleus there are six possible isomeres, varying with the position of the attachment, of which four are known. The earliest described is that in which the attachment is at the γ position (see p. 423).



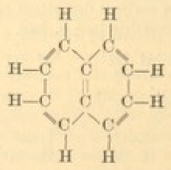
This substance is formed by the action of sodium upon pyridin. It is in crystalline needles, fusible at 114° (237° F.), which yield isonicotic acid on oxidation. The αβ and ββ dipyridyls are formed by the oxidation of phenanthrolins, and both yield nicotic acid on oxidation. The fourth, probably αα, is formed by passing vapor of pyridin through a red-hot tube. By the action of Zn+HCl the dipyridyls take up six H atoms to form substances, $C_{10}H_{14}N_2$, isomeric with nicotin (see nicotin below) and resembling that alkaloid closely in chemical properties and in physiological action. The one obtained from ββ dipyridyl is a very soluble and highly poisonous liquid, called **nicotidin.** That from γγ dipyridyl is a crystalline solid, soluble in H_2O, less actively poisonous than nicotin, and called **isonicotin.**

Phenanthrene—$C_{14}H_{10}$—isomeric with anthracene (*q.v.*), may be considered as a diortho-derivative of diphenyl, or as produced by the fusion of three benzene nuclei, the intermediate one of which has two C atoms in common with each of the extremes:



It crystallizes in brilliant, colorless plates, fusible at 99° (210°.2 F.), boils at 340° (644° F.), and sublimes readily at lower temperatures. Soluble in hot alcohol, and in cold benzene and ether, the solutions having a distinct blue fluorescence. It accompanies anthracene in the crude product. It is formed synthetically. Oxidizing agents convert it into **phenanthroquinone**, $(C_6H_4)_2(CO)_2$.

Naphthalene—$C_{10}H_8$—128—is the simplest compound of the second class (see above). It occurs in coal-tar. It has been formed by a synthesis which indicates its constitution. Benzene and ethylene, when heated together, unite to form, first, cinnamene and afterward naphthalene. It is constituted by the fusion of two benzol groups by two C atoms, thus:



It crystallizes in large, brilliant plates; has a burning taste and a faint aromatic odor; fuses at 80° (176° F.) and boils at 217° (422°.6 F.), subliming, however, at lower temperatures; burns with a bright, smoky flame; insoluble in water, soluble in alcohol, ether, and essences. It forms substitution compounds with Cl, Br, I, HNO_3, and H_2SO_4.

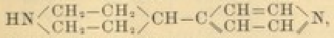
ALKALOIDS CONTAINING DIPYRIDYL OR PHENANTHRENE NUCLEI.

Although the constitution of nicotin and of morphin and its congeners is not definitely established, sufficient has already been determined to render it certain that nicotin contains a dipyridyl nucleus and morphin a phenanthrene nucleus.

Nicotin—$C_{10}H_{14}N_2$—162—exists in tobacco in the proportion of 2-8 per cent.

It is a colorless, oily liquid, which turns brown on exposure to light and air; has a burning, caustic taste and a disagreeable, penetrating odor; it distils at 250° (392° F.); it burns with a luminous flame; sp. gr. 1.027 at 15° (59° F.); it is very soluble in water, alcohol, the fatty oils, and ether; the last-named fluid removes it from its aqueous solution when the two are shaken together; it absorbs water rapidly from moist air. Its salts are deliquescent, and crystallize with difficulty.

The oxidation of nicotin produces nicotic or β monocarbopyridic acid (see p. 425). When distilled with $ZnCl_2+CaO$ it yields pyrrol, ammonia, methylamin, hydrogen, pyridic bases. When heated to 250° (482° F.) it yields a collidin (p. 424) along with other products. By limited oxidation it produces a substance, $C_{10}H_{10}N_2$, **isodipyridin.** These and other decompositions indicate that nicotin is a **piperidyl-pyridyl**, that is, a piperidin nucleus combined with a pyridyl, thus:



$HN\begin{array}{l}\diagup CH_2-CH_2\diagdown\\ \diagdown CH_2-CH_2\diagup\end{array}CH-C\begin{array}{l}\diagup CH=CH\diagdown\\ \diagdown CH-CH\diagup\end{array}N$, but the position of the attachment remains uncertain.

Analytical Characters.—(1.) Its ethereal solution, added to an ethereal solution of iodin, separates a reddish-brown, resinoid oil, which gradually becomes crystalline. (2.) With HCl, a violet color. (3.) With HNO_3, an orange color.

Toxicology.—Nicotin is a very active poison. The free alkaloid is probably capable of causing death in doses of two to three drops, and was the first alkaloid to be separated from the cadaver in a case of homicide. Most cases of poisoning from nicotin are due to tobacco, usually resulting from its use in enemata. When administered to dogs in doses of two to four drops, its effects begin within half a minute to two minutes, and death ensues within one to five minutes. In the human subject tobacco or its decoction causes nausea, vertigo, dilation of the pupils, vomiting, syncope, diminution of the rapidity and force of the heart. With large doses there are no subjective symptoms, the victim falls unconscious instantly and dies within five minutes, without convulsions, and with very few or only one deep sighing respiratory act.

OPIUM ALKALOIDS.

The alkaloids of opium are considered in this place on account of the relations of morphin and codein to phenanthrene, of which hydrocarbon they may be considered as derivatives (see constitution of morphin, p. 444).

Opium is the inspissated juice of the capsules of the poppy. It is of exceeding complex composition, and contains, besides a neutral body called **meconin** (probably a polyatomic alcohol, $C_{10}H_{10}O_4$), a peculiar acid, **meconic acid** (*q.v.*), lactic acid, gum, albumen, wax, and a volatile matter—no less than eighteen different alkaloids, one or two of which, however, are probably formed during the process of extraction, and do not pre-exist in opium.

The following is a list of the constituents of opium, those marked * being of medical interest:

Name.	Formula.	Per Cent. in Smyrna Opium.	Per Cent. in Constantinople Opium
* Meconic acid	$C_7H_4O_7$	4.70	4.38
Lactic acid	$C_3H_6O_3$	1.25	....
Meconin	$C_{10}H_{10}O_4$	0.08	0.30
* Morphin	$C_{17}H_{19}NO_3$	10.30	4.50
Pseudomorphin	$C_{17}H_{19}NO_4$	....	....
Hydrocotarnin	$C_{12}H_{15}NO_3$	....	....
* Codeïn	$C_{18}H_{21}NO_3$	0.25	1.52
* Thebaïn	$C_{19}H_{21}NO_3$	0.15	....
Protopin	$C_{20}H_{19}NO_5$	....	....
Rhœadin	$C_{21}H_{21}NO_6$	....	....
Codamin	$C_{20}H_{25}NO_4$	....	....
Laudanin	$C_{20}H_{25}NO_4$	....	....
Papaverin	$C_{21}H_{21}NO_4$	1.00	....
Opianin	$C_{21}H_{21}NO_7$	....	....
Meconidin	$C_{21}H_{23}NO_4$	....	....
Cryptopin	$C_{21}H_{23}NO_5$	....	....
Laudanosin	$C_{21}H_{27}NO_4$	....	....
* Narcotin	$C_{22}H_{23}NO_7$	1.30	3.47
Lanthopin	$C_{23}H_{25}NO_4$	....	....
* Narceïn	$C_{23}H_{29}NO_9$	0.71	0.42
Porphyroxin	....	....	....

Morphin—Morphina (U. S.)—$C_{17}H_{19}NO_3$+Aq—285+18—crystallizes in colorless prisms; odorless, but very bitter; it fuses at 120° (248° F.), losing its Aq. More strongly heated, it swells up, becomes carbonized, and finally burns. It is soluble in 1,000 pts. of cold water, in 400 pts. of boiling water; in 20 pts. of alcohol of 0.82, and in 13 pts. of boiling alcohol of the same strength; in 91 pts. of cold amyl alcohol, much more soluble in the same liquid warm; almost insoluble in aqueous ether; rather more soluble in alcoholic ether; almost insoluble in benzene; soluble in 860 pts. of chloroform. All the solvents dissolve morphin more readily and more copiously when it is freshly precipitated from solutions of its salts than when it has assumed the crystalline form.

Morphin combines with acids to form crystallizable salts, of which the chlorid, sulfate, and acetate are used in medicine. If morphin be heated for some hours with excess of HCl, under pressure, to 150° (302° F.), it loses water, and is converted into a new base—**apomorphin, $C_{17}H_{17}NO_2$.**

By heating together acetic anhydrid and morphin, three modifications, α, β, γ, of **acetyl-morphin, $C_{17}H_{18}(C_2H_3O)NO_3$**, are formed. Similarly substituted **butyryl-, benzoyl-, succinyl-, camphoryl-, methyl-**, and **ethyl-morphin** are also known.

Morphin is readily oxidized and is a strong reducing agent. It reduces the salts of Au and Ag in the cold. It is oxidized by atmospheric oxygen when it is in alkaline solution, as well as by nitrous acid, potassium permanganate, potassium ferricyanid or ammoniacal cupric sulfate, with the formation of a non-toxic compound which has received the names **oxymorphin, oxydimorphin, dehydromorphin,** and **pseudomorphin ($C_{17}H_{18}NO_3$)$_2$**, whose molecule consists of two morphin molecules, united with loss of H_2, and which is an inferior degree of condensation to **trimorphin** and **tetramorphin,** two amorphous, basic products of the action of H_2SO_4 on morphin at 100° (212° F.). When morphin is distilled with powdered Zn, the principal products of the reaction is phenanthrene, accompanied by ammonia, trimethylamin, pyrrol, pyridin, and a product having the formula $C_{17}H_{11}N$, probably phenanthrene-quinolin.

The salts of morphin are crystalline. The *acetate*—**Morphinæ acetas, U. S.—Morphiæ acetas, Br.**—is a white crystalline powder, soluble in 12 parts of water, which decomposes on exposure to air, with loss of acetic acid. The **chlorid—Morphinæ hydrochloras, U. S.**—is less soluble, but more permanent than the acetate. The **sulfate—Morphinæ sulfas, U. S.—Morphiæ sulfas, Br.** —is the form in which morphin is the most frequently used in medicine. It is a very light, crystalline, feathery powder; odorless, bitter, and neutral in reaction. It dissolves in 24 parts of water. Its solutions deposit morphin as a white precipitate on addition of an alkali. The crystals contain 5 Aq, which they lose at 130° (266° F.).

ANALYTICAL CHARACTERS.—(1.) It is colored orange, changing to yellow, by HNO_3. (2.) A neutral solution of a morphin salt gives a blue color with neutral solution of ferric chlorid. (3.) A solution of molybdic acid in H_2SO_4 (Fröhde's reagent) gives with morphin a violet color, changing to blue, dirty green, and faint pink. Water discharges the color. (4.) Take two test-tubes. Into one (*a*) put the solution of morphin, into the other (*b*) an equal bulk of H_2O. Add to each a granule of iodic acid and agitate: *a* becomes yellow or brown, *b* remains colorless. To each add a small drop of chloroform and agitate; the $CHCl_3$ in *a* is colored violet, that in *b* remains colorless. Float some very dilute ammonium hydroxid solution on the surface of the liquid in *a*; a brown band is formed at the junction of the layers. (5.) Moisten the solid material with HCl to which a small quantity of H_2SO_4 has been added, and evaporate on the water-bath until HCl is expelled: a violet-colored liquid residue remains. Moisten this with HCl and neutralize with solid sodium bicarbonate in slight excess: a pink or rose color is produced, most distinctly visible on the bubbles. Add a drop of H_2O and a drop or two of alcoholic solution of iodin: a green color is developed. This reaction, known as the Pellagri test, is based upon the conversion of morphin into apomorphin, and consequently reacts with that alkaloid. (6.) Moisten the solid with concentrated H_2SO_4 and heat cautiously until white fumes begin to be given off, cool and touch the liquid with a glass rod moistened with dilute HNO_3: a fine blue violet color, changing to red and then to orange. If the H_2SO_4 contains oxids of nitrogen, as it usually does, a violet tinge will be produced before addition of HNO_3, but then becomes much more intense. This reaction, known as the Husemann, may be applied by allowing the solid to remain in contact with H_2SO_4 for fifteen to eighteen hours in place of heating.

These are the most important tests for morphin, and affirmative results with all of them prove the presence of that alkaloid. Other tests have been suggested, among which are the following: (7.) Solution of morphin acetate produces a gray ppt. when warmed with ammoniacal silver nitrate solution; and the filtrate turns red or pink with HNO_3. (8.) Auric chlorid gives a yellow ppt., turning violet-blue, with solutions of morphin salts. (9.) Add solution of Fe_2Cl_6 (2–16) to solution of potassium ferricyanid (the mixture must not assume a blue color), add morphin solution—a deep blue color. (10.) Heat morphin with concentrated H_2SO_4 to 200° (392° F.) until green-black; add a drop of the liquid cautiously to water; the solution turns blue. Shake a portion with ether; the ether turns purple. Shake another portion with chloroform; the chloroform turns blue. (11.) Warm the solid alkaloid with concentrated H_2SO_4; add cautiously a few drops of alcoholic solution of KHO (30%); a yellow color is produced, changing to dirty red, then steel-blue, and sky-blue, and, with a further quantity of KHO solution, cherry-red. (12.) A mixture of morphin and cane-sugar (1 to 4) added to concentrated H_2SO_4 gives a dark red color, which is intensified by a drop of bromin-water.

Codein—Codeina (**U. S.**)—$\mathbf{C_{18}H_{21}NO_3+Aq}$—299+18—crystallizes in large rhombic prisms, or from ether, without Aq, in octahedra; bitter; soluble in 80 pts. cold water; 17 pts. boiling water; very soluble in alcohol, ether, chloroform, benzene; almost insoluble in petroleum-ether.

Codein is the methyl ether of morphin, or its superior homologue, and resembles that alkaloid in some of its reactions; thus under similar circumstances both form apomorphin, and morphin may be converted into codein by the action of methyl iodid in the presence of KHO. Codein, however, only contains one OH group and forms a monoacetylic derivative with acetyl chlorid, while morphin produces a diacetylic.

Analytical Characters.—(1.) Cold concentrated H_2SO_4 forms with it a coloress solution, which turns blue after some days, or when warmed. (2.) Fröhde's reagent dissolves it with a dirty green color, which after a time turns blue. (3.) Chlorin-water forms with it a colorless solution, which turns yellowish-red with NH_4HO.

Narcein—$C_{23}H_{29}NO_9+2Aq$—463+36—crystallizes in bitter, prismatic needles; sparingly soluble in water, alcohol, and amyl alcohol; insoluble in ether, benzene, and petroleum-ether.

Analytical Characters.—(1.) Concentrated H_2SO_4 dissolves it with a gray-brown color, which changes to red, slowly at ordinary temperatures, rapidly when heated. (2.) Fröhde's reagent colors it dark olive-green, passing to red after a time, or when heated. (3.) Iodin solution colors it blue-violet, like starch.

Narcotin—$C_{22}H_{23}NO_7$—413—crystallizes in transparent prisms, almost insoluble in water and in petroleum-ether; soluble in alcohol, ether, benzene, and chloroform. Its salts are mostly uncrystallizable, unstable, and readily soluble in water and alcohol.

Narcotin is decomposed by H_2O at 140° (284° F.), by dilute H_2SO_4 or by baryta, with formation of **opianic acid,** $C_{10}H_{10}O_5$, and **hydrocotarnin,** $C_{12}H_{15}NO_3$. Reducing agents decompose it into hydrocotarnin and **meconin,** $C_{10}H_{10}O_4$. Oxidizing agents convert it into opianic acid and **cotarnin,** $C_{12}H_{13}NO_3$.

Analytical Characters.—(1.) Concentrated H_2SO_4 forms with it a solution, at first colorless, in a few moments yellow, and after a day or two, red. (2.) Its solution in dilute H_2SO_4, if gradually evaporated until the acid volatilizes, turns orange-red, bluish-violet and reddish-violet. (3.) Fröhde's reagent dissolves it with a greenish color, passing to cherry-red.

Thebain—Paramorphin—$C_{19}H_{21}NO_3$—311—crystallizes in white plates; tasteless when pure; insoluble in water; soluble in alcohol, ether and benzene.

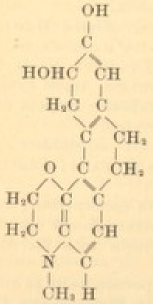
Analytical Characters.—(1.) With concentrated H_2SO_4 an immediate bright red color, turning to yellowish-red. (2.) Its solution in chlorin-water turns reddish-brown with NH_4HO. (3.) With Fröhde's reagent same as 1.

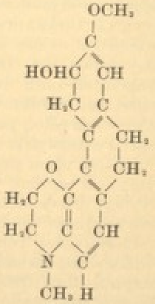
Apomorphin—$C_{17}H_{17}NO_2$—is used hypodermically as an emetic in the shape of the chlorid, **Apomorphinæ hydrochloras, U. S.** It is obtained by sealing morphin with an excess of strong HCl in a thick glass tube, and heating the whole to 140° (252° F.) for two to three hours. It is obtained also by the same process from codeïn. The free alkaloid is a white, amorphous solid, difficultly soluble in water. The chlorid forms colorless, shining crystals, which have a tendency to assume a green color on exposure to light and air. It is odorless, bitter and neutral; soluble in 6.8 parts of cold water.

Relations and Constitution of the Opium Alkaloids.—The alkaloids of opium may be arranged in two groups: I., including those which are strong bases, are highly poisonous and contain three or four atoms of oxygen; II., those which are weak bases and contain four to nine oxygen atoms. The six principal alkaloids are equally divided between the two groups:

I.		II.	
Morphin	$C_{17}H_{19}NO_3$	Papaverin	$C_{20}H_{21}NO_4$
Codein	$C_{18}H_{21}NO_3$	Narcotin	$C_{22}H_{23}NO_7$
Thebain	$C_{19}H_{21}NO_3$	Narcein	$C_{23}H_{29}NO_9$

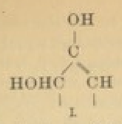
Although the syntheses of morphin and of codein have not been realized, and although their constitution has not been definitely determined in all details, enough has been learned from the products of decomposition of these complex molecules to indicate that morphin is a derivative of phenanthrene and oxypyridin, partly hydrogenated and containing two oxhydryl groups in the same terminal phenanthrene ring, one probably phenolic, the other alcoholic, and that codein is derivable from morphin by substitution of CH_3 for the hydrogen of one of the oxhydryl groups, probably the phenolic. The structural formulæ of morphin and codein may be thus expressed:


Morphin.

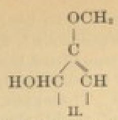

Codein.

the only points still remaining in doubt being the relative positions of the two OH groups in morphin, and the OH and OCH_3 groups in codein, in the upper phenanthrene ring, in which both exist.

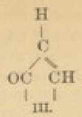
Apomorphin is derived from both morphin and codein, by loss of H_2O, or of CH_3HO, probably by a change of the superior terminal of the formulæ from I. or II. to III.:



I.



II.



III.

Toxicology of Opium and its Derivatives.—Opium, its preparations and the alkaloids obtained from it, are all active poisons. They produce drowsiness, stupor, slow and stertorous respiration, contraction of the pupils, small and irregular pulse, coma, and death. The symptoms set in from 10 minutes to 3 hours, sometimes immediately, sometimes only after 18 hours. Death has occurred in from 45 minutes to 3 days, usually in 5 to 18 hours. After 24 hours the prognosis is favorable. Death has been caused in an adult by one-half grain of acetate of morphia, while 30 grains a day have been taken by those accustomed to its use without ill effects.

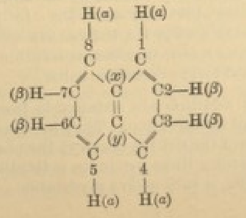
The alkaloids of opium have not the same action. In soporific action, beginning with the most powerful, they rank thus: Narceïn, morphin, codeïn; in tetanizing action: thebaïn, papaverin, narcotin, codeïn, morphin; in toxic action: thebaïn, codeïn, papaverin, narceïn, morphin, narcotin.

The treatment should consist in the removal of unabsorbed poison from the stomach by emesis and the stomach-pump, and washing out of the stomach after injection into it of powdered charcoal in suspension, or tea or coffee infusion. Cold affusions should be used, and the patient should be kept awake.

After death the reactions for meconic acid and narcotin permit of distinguishing whether the poisoning was by opium or its preparations, or by morphin.

SUBSTITUTION DERIVATIVES OF NAPHTHALENE.

By the replacement of the hydrogen atoms of naphthalene by other atoms or by radicals, substitution products are obtained somewhat in the same manner as in the case of benzene (see pp. 397–400). In the case of naphthalene, however, the number of



isomeres is much greater than with benzene. In the structural formula of naphthalene the positions 1, 4, 5, 8, although equal to each other, are of different value from the positions 2, 3, 6, 7, also equal to each other, as they are differently disposed with regard to the carbon atoms *x* and *y*. There exist, therefore, two possible unisubstituted derivatives of naphthalene for a single such derivative of benzene, etc. If the substituted group occupy the approximate positions 1, 4, 5, or 8, it is called an *α*-derivative; if it occupy the remote positions 2, 3, 6, or 7, it is a *β*-derivative.

Naphthols—$C_{10}H_7,OH$—of which there are two:

α-Naphthol has been obtained by heating phenyl-isocrotonic acid; also by boiling an aqueous solution of diazonaphthalene nitrate with nitrous acid, or by fusing *α*-naphthalene-sulfonic acid with KHO.

It crystallizes in colorless prisms; fuses at 94° (201°.2 F.); boils at 280° (536° F.); is nearly insoluble in water, but soluble in alcohol and in ether, and gives a transient violet color with Fe_2Cl_6 and a hypochlorite.

β-Naphthol=Isonaphthol—Hydronaphthol—is prepared industrially by fusion of *β*-naphthalene sulfonate of sodium with NaHO, for the manufacture of a number of coloring matters, among which are **Campobello yellow** and **tropeolin.** The commercial product is in reddish-gray, friable, light masses. The pure substance forms colorless, silky, crystalline plates, having a faint, phenol-like odor, and an evanescent, sharp, burning taste. It fuses at 123° (253°.4 F.), boils at 286° (514°.8 F.), and is sparingly soluble in water, but readily soluble in alcohol and ether. Its aqueous solutions are not colored violet by Fe_2Cl_6. The pure substance is a valuable antiseptic.

Naphthylamins — Amidonaphthalenes — $C_{10}H_7,NH_2$.—Two are known, corresponding in constitution to the naphthols. The *α* modification is formed by the reduction of *α*-nitronaphthalene. It crystallizes in flat needles, fuses at 50° (122° F.), boils at 300° (572° F.), insoluble in water, soluble in alcohol and ether. Has a disagreeable and persistent taste.

The *β*-naphthylamin is produced by the action of ammonia on *β*-naphthol at 150°–160° (302°–320° F.). It forms crystalline plates, fusible at 112° (233°.6 F.), boils at 294° (561°.2 F.); dissolves in hot H_2O, forming a blue fluorescent solution. Both forms are monacid bases, and form crystalline salts.

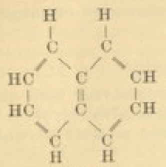
Compounds of addition are obtainable from naphthalene as well as products of substitution. They are produced by the freeing of one or more of the double bonds in the positions 1—2; 3—4; 5—6 and 7—8. Among these products is **tetrahydro *β*naphthylamin, $C_{10}H_7,H_4NH_2$**, a very active mydriatic.

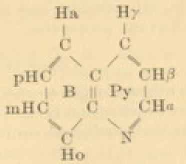
QUINOLIN BASES.

The bases of this group at present known are:

Quinolin	C_9H_7N	Pentahyrolin	$C_{13}H_{15}N$
Lepidin.	$C_{10}H_9N$	Isolin	$C_{14}H_{17}N$
Cryptidin	$C_{11}H_{11}N$	Ettidin.	$C_{15}H_{19}N$
Tetrahyrolin	$C_{12}H_{13}N$	Validin	$C_{16}H_{21}N$

These bodies, which are closely related to the vegetable alkaloids, bear the same relation to naphthalene that the pyridin bases do to benzene, as will be understood by comparison of the following formulæ:


Naphthalene.


Quinolin.

with those of anilin and picolin given on p. 423. As the molecule of naphthalene may be considered as produced by the fusion of two benzene nuclei, so quinolin may be regarded as resulting from the union of a benzene with a pyridin nucleus.

They are obtained by the destructive distillation of the cinchonin, quinin, and other natural alkaloids, to which they are closely related.

Quinolin—C_9H_7N—is a mobile liquid; boils at 238° (460°.4 F.); becomes rapidly colored on contact with air. It has an intensely bitter and acrid taste, and an odor somewhat like that of bitter almonds. It is sparingly soluble in water, readily soluble in alcohol and ether.

Quinolin is the nucleus of a vast number of products of substitution, among which are many isomeres, due to differences in orientation, according as the substitution occurs in the ortho, meta or para positions in the benzene group B (see formulæ above) or in the α, β, or γ positions in the pyridin group Py.

Among the derivatives of quinolin are several synthetic products used as medicines and some vegetable alkaloids. Among the synthetic products are:

Thallin=*Tetrahydroparachinanisol*—$C_{10}H_{11}NO$—is a derivative of the paramethyl ether of quinolin. It is met with in the form of sulfate and tartrate in the shape of crystalline powders. The odor of the sulfate is similar to that of anisol (methyl phenate);

that of the tartrate to that of coumarin. The taste of each is bitter, acrid, and salty. Both salts are readily soluble in H_2O, the sulfate the more readily. Solutions of thallin salts assume, even when very dilute, a magnificent emerald-green color with Fe_2Cl_6 solution. A similar color is produced by $AuCl_3$ and by $AgNO_3$.

Ethylthallin—$C_{12}H_{17}NO$—is a derivative of thallin, whose chlorid is hygroscopic; readily forming solutions which are acid in reaction, bitter in taste, and assume a red-brown color with Fe_2Cl_6.

Kairin—*Methyloxyquinolin hydrid*—$C_{10}H_{13}NO$—is more nearly derived from quinolin than the substances previously mentioned. Its chlorid is a crystalline, nearly white, easily soluble powder, whose taste is at once bitter, aromatic, and salty.

Thallin, ethylthallin, and kairin are possessed of antiperiodic and antipyretic properties.

CINCHONA ALKALOIDS.

The synthesis of the cinchona alkaloids has not been effected, and their constitution is far from being established, yet it is certain that their molecules contain one and possibly two quinolin groups.

Although by no means so complex as opium, cinchona bark contains a great number of substances: *quinin, cinchonin, quinidin, cinchonidin, aricin; quinic, quinotannic, and quinovic acids; cinchona red*, etc. Of these the most important are quinin and cinchonin.

Quinin—Quinina (U. S.)—$C_{20}H_{24}N_2O_2+n$ Aq—$324+n18$—exists in the bark of a variety of trees of the genera *Cinchona* and *China*, indigenous in the mountainous regions of the north of South America, which vary considerably in their richness in this alkaloid, and consequently in value; the best samples of calisaya bark contain from 30 to 32 parts per 1,000 of the sulfate; the poorer grades 4 to 20 parts per 1,000; inferior grades of bark contain from mere traces to 6 parts per 1,000.

It is known in three different states of hydration, with 1, 2, and 3 Aq, and anhydrous. The anhydrous form is an amorphous, resinous substance, obtained by evaporation of solutions in anhydrous alcohol or ether. The first hydrate is obtained in crystals by exposing to air recently precipitated and well-washed quinin. The second by precipitating by ammonia a solution of quinin sulfate, in which H has been previously liberated by the action of Zn upon H_2SO_4; it is a greenish, resinous body, which loses H_2O at 150° (302° F.). The third, that to which the following remarks apply, is formed by precipitating solution of quinin salts with ammonia.

It crystallizes in hexagonal prisms; very bitter; fuses at 57° (134°.6 F.); loses Aq at 100° (212° F.) and the remainder at 125°

(257° F.); becomes colored, swells up, and, finally, burns with a smoky flame. It does not sublime. It dissolves in 2,200 pts. of cold H_2O, in 760 of hot H_2O; very soluble in alcohol and chloroform; soluble in amyl alcohol, benzene, fatty and essential oils, and ether. Its alcoholic solution is powerfully lævogyrous, $[\alpha]_D = -270^\circ.7$ at 18° (64°.4 F.), which is diminished by increase of temperature, but increased by the presence of acids.

ANALYTICAL CHARACTERS.—(1.) Dilute H_2SO_4 dissolves quinin in colorless but fluorescent solution (see below). (2.) Solutions of quinin salts turn green when treated with Cl and then with NH_3. (3.) Cl passed through H_2O holding quinin in suspension forms a red solution. (4.) Solution of quinin treated with Cl water and then with fragments of potassium ferrocyanid becomes pink, passing to red.

SULFATE—*Disulfate*—**Quininæ sulfas (U. S.)—Quiniæ sulfas (Br.)**—$\mathbf{SO_4(C_{20}H_{24}N_2O_2)_2}+7$ **Aq**—746+126—crystallizes in prismatic needles; very light; intensely bitter; phosphorescent at 100° (212° F.); fuses readily; loses its Aq at 120° (248° F.), turns red, and finally carbonizes; effloresces in air, losing 6 Aq; soluble in 740 pts. H_2O at 13° (55°.4 F.), in 30 pts. boiling H_2O, and 60 pts. alcohol. Its solution with alcoholic solution of I deposits brilliant green crystals of **iodoquinin sulfate.**

HYDROSULFATE—**Quininæ bisulfas (U. S.)**—$\mathbf{SO_4H(C_{20}H_{24}N_2O_2)}$ $+7$ **Aq**—422+126—is formed when the sulfate is dissolved in excess of dilute H_2SO_4. It crystallizes in long, silky needles, or in short, rectangular prisms; soluble in 10 pts. H_2O at 15° (59° F.). Its solutions exhibit a marked fluorescence, being colorless, but showing a fine pale blue color when illuminated by a bright light against a dark background.

IMPURITIES.—Quinin sulfate should respond to the following tests: (1.) When 1 gram (15.4 grains) is shaken in a test-tube with 15 c.c. (4 fl ʒ) of ether, and 2 c.c. (32 ♏) of NH_4HO; the liquids should separate into two clear layers, without any milky zone between them (cinchonin). (2.) Dissolved in hot H_2O, the solution precipitated with an alkaline oxalate, the filtrate should not ppt. with NH_4HO (quinidin). (3.) It should dissolve completely in dilute H_2SO_4 (fats, resins). (4.) It should dissolve completely in boiling, dilute alcohol (gum, starch, salts). (5.) It should not blacken with H_2SO_4 (cane-sugar). (6.) It should not turn red or yellow with H_2SO_4 (salicin and phlorizin). (7.) It should leave no residue when burnt on platinum foil (mineral substances).

By the action of alkaline hydroxids upon quinin, formic acid, quinolin (see p. 447), and pyridin bases (see p. 422) are produced.

Concentrated HCl at 140°–150° (284°–302° F.) decomposes quinin, with separation of methyl chlorid and formation of **apoquinin,** $\mathbf{C_{19}H_{22}N_2O_2}$, an amorphous base.

Oxidizing agents produce from quinin oxalic acid and acids related to pyridin, notably **pyridindicarbonic** or **cinchomeric acid, $C_5H_3N(COOH)_2$**, which are also formed by oxidation of cinchonin.

Although cinchonin (see below) differs from quinin in composition by +O, and although the decompositions of the two bases show them both to be related to the chinolin and pyridin bases, attempts to convert cinchonin into quinin have resulted only in the formation of other products, among which is an isomere of quinin, **oxycinchonin.**

Methylquinin, $C_{20}H_{24}N_2O_2CH_3$, is a base which has a curare-like action.

Cinchonin—Cinchonina (U. S.)—$C_{19}H_{22}N_2O$—294—occurs in Peruvian bark in from 2 to 30 pts. per 1,000. It crystallizes without Aq in colorless prisms; fuses at 150° (302° F.); soluble in 3,810 pts. H_2O at 10° (50° F.), in 2,500 pts. boiling H_2O; in 140 pts. alcohol and in 40 pts. chloroform. The salts of cinchonin resemble those of quinin in composition; are quite soluble in H_2O and alcohol; are not fluorescent; permanent in air; phosphorescent at 100° (212° F.).

Quinidin and Quinicin—are bases isomeric with quinin; the former occurring in cinchona bark, and distinguishable from quinin by its strong dextrorotary power; the second a product of the action of heat on quinin, not existing in cinchona.

Cinchonidin—a base, isomeric with cinchonin, occurring in certain varieties of bark; lævogyrous. At 130° (266° F.) H_2SO_4 converts it into another isomere, **cinchonicin.**

INDIGO GROUP.

In this group are included a number of substances, derivable from indigo-blue, which are evidently closely related to the benzene group, as is shown by the number of benzene derivatives which are obtained by their decomposition, but whose constitution is not yet definitely established. They are classified here because some of the most perfectly studied seem to contain a nucleus consisting of a hexagonal benzene ring attached to a pentagonal pyrrol ring.

Indigotin—*Indigo-blue*—**$C_{16}H_{10}N_2O_2$**—constitutes the greater part of the commercial *indigo.* It does not exist preformed in the plants from which it is obtained, whose juice is naturally colorless, but is produced by decomposition of a glucosid contained in them (see Indican, p. 451).

Indigotin may be obtained by the action of phosphorus trichlorid on **isatin**; or, in a nearly pure form, by cautiously subliming commercial indigo. It forms purple-red, somewhat metallic, orthorhombic prisms or plates, odorless, tasteless, neutral, insoluble in water, ether, or dilute acids or alkalies. By dry distillation it yields anilin and other products. By moderate heating with dilute HNO_3 it gives off gas and is converted into isatin.

Indigo sulfonic Acids.—When indigo is heated for some time with fuming H_2SO_4 it dissolves. If the solution be diluted with H_2O, a blue powder, soluble in H_2O, but insoluble in dilute acids, is precipitated. This is **indigo-monosulfonic** or **phœnicin-sulfonic acid**—$C_{16}H_9N_2O_2SO_3H$.

The filtrate from the last-mentioned precipitate contains **indigo-disulfonic, sulfindylic,** or **sulfindigotic acid**—$C_{16}H_8N_2O_2(SO_3H)_2$—whose K and Na salts constitute soluble pastes known in the arts as **soluble indigo**, or **indigocarmine.**

Isatin—$C_8H_5NO_2$—obtained by oxidation of indigo-blue, forms shining, transparent, red-brown prisms. It is odorless, sparingly soluble in water, readily soluble in alcohol.

Dioxindol—*Hydrindic acid*—$C_8H_7NO_2$—is formed by the action of Na on isatin suspended in H_2O. It forms yellow prisms, soluble in H_2O, and combines with both bases and acids.

Oxindol—C_8H_7NO—is obtained from dioxindol by reduction with Na amalgam in acid solution. It crystallizes in easily soluble, colorless needles, and combines with acids and bases.

Indol—C_8H_7N—is produced by distilling oxindol over zinc-dust, or by heating orthonitrocinnamic acid with KHO and Fe filings.

It crystallizes in large, shining, colorless plates, having the odor of naphthylamin. It is a weak base, forming salts with acids, which are, however, decomposed by boiling water. Its aqueous solution, acidulated with HCl, is colored rose-red by KNO_2. It is converted into anilin by fused KHO.

It is one of the products of putrefaction of albuminoid substances, and is formed during the action of the pancreatic secretion upon albuminoids. It is partly eliminated with the fæces and partly reabsorbed.

In the intestine and fæces indol is invariably accompanied by **Skatol**, C_9H_9N, its superior homologue, which may also be obtained by the action of Sn and HCl on indigo. It crystallizes in brilliant plates, and is less soluble than indigo. The product obtained from indigo has a penetrating but not disagreeable odor, while that obtained from putrid albumin and from fæcal or intestinal matter has a disgusting odor, probably due to the presence of foreign substances.

Indican—$C_{26}H_{31}N_{17}$—is a glucosid existing in the different varieties of indigo-producing plants, and also in the urine and blood of man and the herbivora.

It is a yellow or light brown syrup, which cannot be dried without decomposition, bitter and disagreeable to the taste, acid in reaction, and soluble in water, alcohol, and ether.

It is very prone to decomposition. Even slight heating decomposes it into leucin, **indicanin, $C_{20}H_{23}NO_{12}$**, and **indiglucin, $C_6H_{10}O_6$**. A characteristic decomposition is that when heated in acid solution, or under the influence of certain ferments (?), it is decomposed into indigo-blue and indiglucin, the latter a glucose :

$$\underset{\text{Indican.}}{2C_{26}H_{31}NO_{17}} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Indigotin.}}{C_{16}H_{10}N_2O_2} + \underset{\text{Indiglucin.}}{6C_6H_{10}O_6}$$

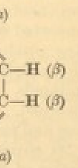
ANTHRACENE GROUP.

SERIES C_nH_{2n-18}.

Anthracene—$C_{14}H_{10}$—178—exists as a constituent of coal-tar, and is obtained by expression from the substance remaining in the still after the distillation of naphthalene, etc. The commercial product thus obtained is a yellowish mass containing 50-80 per cent. of anthracene, the purification of which is a matter of considerable difficulty. It has also been obtained synthetically, by the action of the heat on benzyl toluene, and in other ways.

When pure, anthracene crystallizes in rhombic tables having a bluish fluorescence; fusible at 210° (410° F.) and boiling above 360° (680° F.); its best solvents are benzene and carbon disulfid, in which, however, it is only sparingly soluble.

The constitution of anthracene is that of two benzene nuclei united through two of their C atoms by the group=CH—CH= :



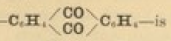
Oxidizing agents convert anthracene into anthraquinone. Reducing agents decompose it into three hydrocarbons, $C_{14}H_{16}$, C_7H_{16}, and an oily hydrocarbon boiling above 360° (648° F.). Br and Cl attack it violently, I more slowly, forming products of addition.

DERIVATIVES OF ANTHRACENE.

As may be inferred from the complex molecule of anthracene, the number of possible derivatives of substitution and of addition, including many isomeres, is very great.

Anthraphenols—$C_{14}H_9(OH)$.—Three are known, α and β **anthrol,**

and **anthranol.** The two former are produced by the substitution of OH for one of the H atoms *α* or *β* (see formula above) in anthracene, the latter by the substitution of the same group in the positions *x* or *y*.



$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_4$

Anthraquinone—$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_4$—is formed by oxidation of anthracene. It forms yellow needles, which fuse at 273° (523°.4 F.). It is not easily oxidized, but is converted into anthracene by sufficiently active reducing agents.

$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_2\left<\begin{matrix}OH\\OH\end{matrix}\right.$

Dioxyanthraquinone—Alizarin—$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_2\left<\begin{matrix}OH\\OH\end{matrix}\right.$—is the red pigment of the madder root (*Rubia tinctoria*). Artificial alizarin has now almost completely displaced the natural product in dyeing. It is obtained by the action of fused KHO on many anthracene derivatives, the one generally used being **anthraquinone-disulfonic acid,** $C_{14}H_6O_2(SO_3H)_2$.

Methylanthracene—$C_{14}H_9,CH_3$—is obtainable by synthesis, and also by heating chrysophanic acid, emodin, or aloin with zinc-dust.

Crysophanic Acid—*Parietic Acid*—*Rheic acid*—*Rhein*—$C_{15}H_{10}O_4$—is a derivative of methylanthracene, which exists in the lichens *Parmelia parietina* and *Squamaria elegans*, in senna, and in rhubarb, and obtainable to the extent of 80 per cent. from *Goa powder*=**Chrysarobin,** $C_{30}H_{26}O_7$.

Chrysophanic acid crystallizes in golden, orange-yellow, interlaced needles. It is almost tasteless and odorless; fuses at 162° (291°. F.); almost insoluble in cold water, sparingly soluble in hot water, alcohol, and ether, readily soluble in benzene. It forms a red solution with H_2SO_4, from which it is deposited unchanged by water. It also forms red solutions with alkalies. Reducing agents convert it into methylanthracene.

Trioxymethylanthraquinone—*Emodin*—$C_{14}H_4(CH_3)(OH)_3O_2$—occurs in the bark of *Rhamnus frangula*, and accompanies chrysophanic acid in rhubarb. It crystallizes in long, orange-red prisms which fuse at 250° (482° F.), and yield methylanthracene when heated with zinc-dust.

TEREBENTHIC SERIES.

In this series are included a number of isomeric hydrocarbons, having the formula $C_{10}H_{16}$, or a simple multiple thereof, and their products of derivation. The hydrocarbons are in some cases artificial products, but for the most part exist in nature in the different **turpentines,** and **volatile oils,** or **essences.** When liquid they are called **terpenes,** when solid **camphenes.**

Turpentine—Terebenthina (U. S.)—is the common *American*

turpentine, obtained from incisions in bark of *Pinus palustris* and *P. tæda*, and may be taken as the type of many similar products obtained from other plants. It is a yellowish-white semi-solid, having a balsamic odor, which is divided by distillation into two products. One a liquid, an **elœoptene: oil,** or **essence of turpentine**; the other a solid, a **stearoptene: rosin,** or **colophony.**

The liquid product so obtained, oil of turpentine, in the case of the American product consists chiefly of a hydrocarbon, $C_{10}H_{16}$, called **australene,** and in the case of the French turpentine of an isomeric body, called **terebenthene.**

These two bodies are obtained from the oils of turpentine by mixing with an alkaline carbonate and subjecting them to fractional distillation in vacuo over the water-bath. The differences between them are principally in their physical properties. Australene is dextrogyrous, $(\alpha)_D = 17°$, boils at about 155° (311° F.). Terebenthene is lævogyrous, $(\alpha)_D = -40°.32$, boils at 156°.5 (313°.7 F.), sp. gr. 0.864 at 16° (60°.8 F.). They are colorless, mobile liquids; have the peculiar odor of turpentine; burn with a smoky, luminous flame. They absorb oxygen rapidly from the air, whether pure or in the commercial essence, becoming thick, and finally gummy. Oxidizing agents, such as HNO_3, attack them energetically, causing them to ignite and burn suddenly, with separation of a large volume of carbon. HCl unites with them to form a number of compounds, as do also HI and HBr—all the compounds having the odor of camphor. When mixed with HNO_3, diluted with alcohol, and exposed to the air, they form terpin hydrate. Cl, Br and I form compounds of substitution or of addition.

Oil of turpentine may be boiled without suffering decomposition, but if heated under pressure at 250°–300° (482°–572° F.) the terpene is converted into two products, one liquid, boiling at 177° (350°.6 F.), isomeric with the terpene, called **isoterebenthene**; the other viscous, boiling at about 400° (752° F.), polymeric with the first, $C_{20}H_{32}$, called **metaterebenthene.**

Sulfuric acid acts violently upon oil of turpentine when the two liquids are agitated together, and the latter yields a number of isomeric and polymeric derivatives. After standing 24 hours the mixture separates into two layers. If the upper layer be distilled at about 250° (482° F.) it yields a mobile liquid, which, when purified by contact with dilute H_2SO_4 and then with solution of NaHO, and dried and subjected to fractional distillation, may be separated into (1) **Terebene,** $C_{10}H_{16}$, a colorless, mobile liquid, having a faint odor, optically inactive, boiling at 156° (312°.8 F.); (2) cymene; (3) a number of polymeres of terebenthene, among which is **Colophene,** or **Diterebene,** $C_{20}H_{32}$, a colorless oil, having a brilliant, indigo-blue fluorescence; boils at 300°–315° (572°–599° F.); sp. gr. 0.91 at 4° (39°.2 F.).

There exist a number of hydrates of the terpenes: **Terpinol—$2(C_{10}H_{16}),H_2O$**—produced by distilling terpin (see below) with very dilute H_2SO_4, or terpene monochlorhydrate with H_2O, or alcohol. It is a colorless liquid, having the odor of hyacinth, boiling at 168° (234°.4 F.); sp. gr. 0.852.

Terpene hydrate—$C_{10}H_{16},H_2O$—formed by distilling terpin with HCl; or by allowing French oil of turpentine to remain for some days in contact with alcohol and H_2SO_4. It is an oily liquid, boils at 210°–214° (410°–417°.2 F.), suffering partial decomposition.

Terpin—$C_{10}H_{16},2H_2O$—is formed by the dehydration of terpin hydrate (q.v.). It is crystalline, fusing at 103° (217°.4 F.), capable of sublimation, and boils at about 250° (482° F.). It absorbs H_2O eagerly to form terpin hydrate. It behaves like a diatomic alcohol, and is converted into **terebenthene dichlorhydrate**, by gaseous HCl, or by PCl_5. It is dehydrated by P_2O_5, and converted into terebene and colophene.

Terpin hydrate—$C_{10}H_{16},3H_2O$—formed when oil of turpentine remains for a long time in contact with H_2O, the formation being favored by the presence of a mixture of alcohol and dilute HNO_3. It exists in large, colorless, prismatic crystals, odorless, fuses at about 100° (212° F.), sparingly soluble in H_2O, soluble in alcohol and in ether. It readily gives up H_2O in dry air at 100° (212° F.), and is then converted into terpin.

The **Camphenes** are solid, crystalline bodies, having odors resembling that of camphor, formed by the action of the Na salts of weak acids, at 200°–220° (392°–428° F.) upon the monochlorhydrates of the corresponding terebenes.

Isomeres of Terebenthene.—There exist a great number of bodies, the products of distillation of vegetable substances, which are known as **essences, essential oils, volatile oils or distilled oils.** They resemble each other in being odorous, oily, sparingly soluble in water, more or less soluble in alcohol and ether; colorless or yellowish, inflammable, and prone to become resinous on exposure to air. **They are not simple chemical compounds**, but mixtures, and in many of them the principal ingredient is a hydrocarbon, isomeric with terebenthene, and consequently having the composition $_nC_{10}H_{16}$. Some contain hydrocarbons, others aldehydes, acetones, phenols, and ethers.

Of the numerous other hydrocarbons closely related to terebenthene, but two require further consideration as being the principal constituents of *caoutchouc* and *gutta-percha*.

Caoutchouc—India-rubber—is a peculiar substance existing in suspension in the milky juice of quite a number of trees growing in warm climates. It is, when pure, a mixture of two hydrocarbons—**caoutchene, $C_{10}H_{16}$**, and **isoprene, C_5H_8**.

The commercial article is yellowish-brown; sp. gr. 0.919 to 0.942; soft, flexible; almost impermeable, but still capable of acting as a dialyzing membrane when used in sufficiently thin layers. It is insoluble in H_2O and alcohol, both of which, however, it absorbs by long immersion, the former to the extent of 25 per cent., and the latter of 20 per cent., of its own weight; it is soluble in ether, petroleum, fatty and essential oils; its best solvent is carbon disulfid, either alone, or, better, mixed with 5 parts of absolute alcohol.

It is not acted upon by dilute mineral acids, but is attacked by concentrated HNO_3 and H_2SO_4, and especially by a mixture of the two. Alkalies tend to render it tougher, although a solution of soda of 40° B. renders it soft after an immersion of a few hours. Cl attacks it after a time, depriving it of its elasticity, and rendering it hard and brittle. When heated it becomes viscous at 145° (293° F.), and fuses at 170°–180° (347°–356° F.) to a thick liquid, which, on cooling, remains sticky, and only regains its primitive character after a long time. On contact with flame it ignites, burning with a reddish, smoky flame, which is extinguished with difficulty.

The most valuable property of india-rubber, apart from its elasticity, is that which it possesses of entering into combination with S to form what is known as **vulcanized rubber**, which is produced by heating together the normal caoutchouc and S to 130°–150° (266°–302° F.). Ordinary vulcanized rubber differs materially from the natural gum in its properties; its elasticity and flexibility are much increased; it does not harden when exposed to cold; it only fuses at 200° (392° F.); finally, it resists the action of reagents, of solvents, and of the atmosphere much better than does the natural gum.

Frequently rubber tubing is too heavily charged with sulfur for certain chemical uses, in which case it may be desulfurized by boiling with dilute caustic soda solution.

Hard rubber, vulcanite, or **ebonite,** is a hard, tough variety of vulcanized rubber, susceptible of a good polish, and a non-conductor of electricity. It contains 20 to 35 per cent. of S (the ordinary vulcanized rubber contains 7 to 10 per cent.).

Gutta-percha—is the concrete juice of *Isonandra gutta*. It is a tough, inelastic, brownish substance, having an odor similar to that of caoutchouc; when warmed it becomes soft and may be moulded, or even cast, so as to assume any form, which it retains on cooling; it may be welded at slightly elevated temperatures, is a good insulating and waterproofing material. It is insoluble in water, alkaline solutions, dilute acids, including hydrofluoric, and in fatty oils; it is soluble in benzene, oil of turpentine, essential oils, chloroform, and especially in carbon disulfid. A solution in chloroform is known as **traumaticine,** or **Liq. gutta-perchæ** (**U. S.**), and is used to obtain, by its evaporation, a thin film of gutta-percha over parts which it is desired to protect from the air. It is attacked by HNO_3 and H_2SO_4.

When exposed to air and light, it is gradually changed from the surface inward, assuming a sharp, acid odor, becoming hard and cracked, and even a conductor of electricity.

Gutta-percha seems to be made up of three substances: **Gutta,** $\mathbf{C_{20}H_{32}}$, 75–82 per cent., a white, tough substance, fusing at 150° (302° F.), soluble in the ordinary solvents of gutta-percha, but insoluble in alcohol and ether. **Albane,** $\mathbf{C_{20}H_{32}O_2}$, 14–19 per cent., a white, crystalline resin, heavier than water, fusible at 160° (320° F.); soluble in benzene, essence of turpentine, carbon disulfid, ether, chloroform, and hot absolute alcohol; not attacked by HCl. **Fluviale,** 4–6 per cent., $C_{20}H_{32}O$, a yellowish resin, slightly heavier than water, hard and brittle at 0° (32° F.), soft at 50° (122° F.), liquid at 100° (212° F.); soluble in the solvents of gutta-percha.

Camphors and Resins.—The **camphors** are probably aldehydes or alcohols corresponding to hydrocarbons related to terebenthene, although their constitution is still uncertain.

Common camphor—*Japan camphor*—*Laurel camphor*—**Campholic aldehyde**—**Camphora** (**U. S., Br.**)—$\mathbf{C_{10}H_{16}O}$—152.—Three modifications are known, which seem to differ from each other only in their action upon polarized light: (1.) **Dextro camphor**=*Camphora officinarum*; obtained from *Laurus camphora*—$[\alpha]_D = +47°.4$. (2.) **Lævo camphor,** obtained from *Matricaria postlanium*—$[\alpha]_D = -47°.4$. (3.) **Inactive camphor,** obtained from the essential oils of rosemary, sage, lavender, and origanum.

The first is the ordinary camphor of the shops. It is a white, translucent, crystalline solid; sp. gr. 0.986–0.996, hot and bitter in taste; aromatic; sparingly soluble in H_2O; quite soluble in ether, acetic acid, methylic and ethylic alcohols, and the oils; fuses at 175° (347° F.); boils at 204° (399°.2 F.); sublimes at all temperatures.

It ignites readily and burns with a luminous flame. Cold HNO_3 dissolves it, and from the solution H_2O precipitates it unchanged. Boiling HNO_3, or potassium permanganate, oxidizes it to **dextro camphoric acid,** $\mathbf{C_{10}H_{16}O_4}$. Concentrated H_2SO_4 forms with it a black solution, from which H_2O precipitates *camphene.* Distilled with P_2O_5, it yields *cymene,* $C_{10}H_{14}$. Alkaline solutions, by long heating under pressure, convert it into **camphic acid,** $\mathbf{C_{10}H_{16}O_2}$, and **borneol.** Cl attacks it with difficulty. Br unites with it to form an unstable compound, which forms ruby-red crystals, having the composition $C_{10}H_{16}OBr_2$. These crystals, when heated to 80°–90° (176°–194° F.), fuse and give off HBr, there remaining an amber-colored liquid, which solidifies on cooling, and yields, by recrystallization from boiling alcohol, long, hard, rectangular crystals of **monobromo camphor**—**Camphora monobromata** (**U. S.**)—$C_{10}H_{15}OBr$. When vapor of camphor is passed over a mixture of fused potash and lime, heated to 300°–400° (572°–752° F.), it unites directly with the potash to form the K salt of **campholic acid**, $C_{10}H_{18}O_2$.

Borneol—**Borneo camphor**—*Camphol*—**Camphyl alcohol**—$C_{10}H_{18}O$—154—is usually obtained from *Dryobalanops camphora*, although it may be obtained from other plants, and even artificially by the hydrogenation of laurel camphor. The product from these different sources is the same chemically, so far as we can determine, but varies, like the modifications of camphor, in its action on polarized light.

It forms small, white, transparent, friable crystals; has an odor which recalls at the same time those of laurel camphor and of pepper; has a hot taste; is insoluble in water, readily soluble in alcohol, ether and acetic acid; fuses at 198° (388°.4 F.), boils at 212° (413°.6 F.).

It is a true alcohol, and enters into double decomposition with acids to form ethers. When heated with P_2O_5, it yields a hydrocarbon, **borneene**, $C_{10}H_{16}$. Oxidized by HNO_3, it is converted into laurel camphor.

Menthol—**Menthyl alcohol**—$C_{10}H_{20}O$—156—exists in essential oil of peppermint. It crystallizes in colorless prisms; fusible at 36° (96°.8 F.); sparingly soluble in water; readily soluble in alcohol, ether, carbon disulfid, and in acids. Corresponding to it are a series of *menthyl* ethers.

Eucalyptol—$C_{12}H_{20}O$—180—is contained in the leaves of *Eucalyptus globulus*; it is liquid at ordinary temperatures, and boils at 175° (347° F.); by distillation with phosphoric anhydrid it yields **eucalyptene**, $C_{12}H_{18}$.

Resins—are generally the products of oxidation of the hydrocarbons allied to terebenthene; are amorphous (rarely crystalline); insoluble in water; soluble in alcohol, ether, and essences. Many of them contain acids.

They may be divided into several groups, according to the nature of their constituents: (1.) **Balsams**, which are usually soft or liquid, and are distinguished by containing free *cinnamic* or *benzoic acid* (*q.v.*). The principal members of this group are *benzoin*, *liquidambar*, *Peru balsam*, *styrax*, and *balsam tolu*. (2.) **Oleo-resins** consist of a true resin mixed with an oil, and usually with an oxidized product other than cinnamic or benzoic acid. The principal members of this group are *Burgundy* and *Canada pitch*, *Mecca balsam*, and the resins of *capsicum*, *copaiva*, *cubebs*, *elemi*, *labdanum*, and *lupulin*. (3.) **Gum-resins** are mixtures of true resins and gums. Many of them are possessed of medicinal qualities; *aloes*, *ammoniac*, *asafœtida*, *bdellium*, *euphorbium*, *galbanum*, *gamboge*, *guaiac*, *myrrh*, *olibanum*, *opoponax*, and *scammony*. (4.) **True resins** are hard substances obtainable from the members of the three previous classes, and containing neither essences, gums, nor aromatic acids. Such are *colophony* or *rosin*, *copal*, *dammar*, *dragon's blood*, *jalap*, *lac*, *mastic*, and *sandarac*. (5.) **Fossil resins,** such as *amber*, *asphalt*, and *ozocerite*.

COMPOUNDS OF UNKNOWN CONSTITUTION.

GLUCOSIDS.

Under this head are classed a number of substances, some of them important medicinal agents, which are the products of vegetable or animal nature. Their characteristic property is that, under the influence of a dilute mineral acid, they yield glucose, phloroglucin or mannite, together with some other substance. Under the supposition that glucose and its congeners are alcohols, it is quite probable that the glucosids are their corresponding ethers.

Amygdalin, $C_{20}H_{27}NO_{11}$—457—exists in cherry-laurel and in bitter almonds, but not in sweet almonds. Its characteristic reaction is that, in the presence of **emulsin,** which exists in sweet as well as in bitter almonds, and of water, it is decomposed into glucose, benzoic aldehyde, and hydrocyanic acid. The same reaction is brought about by boiling with dilute H_2SO_4 or HCl. Bitter almonds contain about 2 per cent. of amygdalin.

Digitalin.—The pharmaceutical products sold under the above name, and obtained from *digitalis*, are mixtures in varying proportions of several glucosids. **Digitonin, $C_{31}H_{52}O_{17}$,** an amorphous, yellowish substance, very soluble in aqueous alcohol. **Digitalin, $C_5H_8O_2$,** the principal constituent of the French digitalin, is a colorless, very bitter, crystalline solid, insoluble in water, soluble in alcohol. **Digitalein,** a white, intensely bitter, amorphous solid, very soluble in water, soluble in alcohol. **Digitoxin, $C_{21}H_{32}O_7$,** a colorless, crystalline solid, insoluble in water, sparingly soluble in alcohol. It is not a glucosid, and is converted into **toxiresin** by dilute acids.

The **Abstractum digitalis** (**U. S.**) probably contains all the above, the extraction of the first being more complete with weak alcohol, that of the others with strong alcohol.

Glycyrrhizin.—A non-crystallizable, yellowish, pulverulent principle, obtained from liquorice; soluble with difficulty in cold water, soluble in hot water, alcohol, and ether; bitter-sweet in taste. By long boiling with dilute acids it is decomposed into glucose and **glycyrrhetin, $C_{18}H_{26}O_4$.**

Jalapin—$C_{34}H_{56}O_{16}$—720—is the active principle of scammony, and exists also to a limited extent in jalap (see below). It is an insipid, colorless, amorphous substance, which is decomposed by dilute acids into glucose and **jalapinol.** The active ingredient of jalap is not, as the name would imply, jalapin, but a resinous substance called **convolvulin,** which is insoluble in ether, odorless, and insipid. It is not attacked by dilute H_2SO_4, although the concentrated acid dissolves it with a carmine-red color, slowly turning to brown; in alcoholic solution it is decomposed by gaseous HCl into glucose and **convolvulinic acid.**

Quinovin—Quinovatic acid.—A bitter principle, possessed of acid functions, obtained from the false bark, known as *Cinchona nova;* it is a glucosid, being decomposed by dilute acids into a sugar resembling mannitan and **quinovic acid.**

Salicin—Salicinum (U. S.)—$C_{13}H_{18}O_7$—286—occurs in the bark of the willow (*salix*). It is a white, crystalline substance; insoluble in ether, soluble in water and in alcohol; very bitter, its solutions are dextrogyrous, $[\alpha]_D = +55°.8$. Dilute acids decompose it into glucose and *saligenin* (*q.v.*). Concentrated H_2SO_4 colors it red, the color being discharged on the addition of water. When taken into the economy it is converted into salicylic aldehyde and acid, which are eliminated in the urine.

Santonin—*Santonic acid*—**Santoninum (U. S., Br.)—$C_{15}H_{18}O_3$**—246.—A glucosid having distinct acid properties; obtained from various species of *Artemisia*. It crystallizes in colorless, rectangular prisms, which turn yellow on exposure to light; odorless and tasteless; insoluble in cold water, sparingly soluble in hot water, alcohol, and ether; its solutions are faintly acid in reaction. Santonin, in solution, gives a chamois-colored precipitate with the ferric salts, and a white precipitate with silver, zinc, and mercurous salts; no precipitate with mercuric salts.

Patients taking santonin pass urine having the appearance of that containing bile, which, when treated with potash, turns cherry-red or crimson, the color being discharged by an acid, and regenerated on neutralization.

Solanin.—A glucosid, having basic properties, existing in different plants of the genus *Solanum*. It crystallizes in fine, white, silky needles; having an acrid, bitter taste; insoluble in water, and but sparingly soluble in ether and in alcohol. By the action of hot dilute acids it is decomposed into glucose and a basic substance, **solanidin.** When not heated, solanin combines with acids to form uncrystallizable salts. Cold concentrated H_2SO_4 colors it orange-yellow, and finally forms with it a brown solution; HNO_3 dissolves it, the solution being at first colorless, afterward rose-pink.

Strophanthin—$C_{20}H_{34}O_{10}$—a glucosid from *Strophanthus Kombé*, forms white, crystalline plates, bitter in taste, slightly soluble in water, more soluble in alcohol, insoluble in ether, carbon disulfid and benzene.

Tannins—Tannic acid—$C_{14}H_{10}O_9$—322.—Quite a number of different substances of vegetable origin, principally derived from barks, leaves, and seeds. They are amorphous, soluble in water, astringent, capable of precipitating albumen, and of forming imputrescible compounds with the gelatinoids. They are, with one possible exception, glucosids.

Gallo-tannic acid—**Acidum tannicum** (**U. S., Br.**)—is the best known of the tannins, and is obtained from nut-galls, **galla** (**U. S., Br.**), which are excrescences produced upon oak trees by the puncture of minute insects. It appears as a yellowish, amorphous, odorless, friable mass; has an astringent taste; very soluble in water, less so in alcohol, almost insoluble in ether; its solutions are acid in reaction, and on contact with animal tissues give up the dissolved tannin, which becomes fixed by the tissue to form a tough, insoluble, and non-putrescible material (leather).

A freshly prepared solution of pure gallo-tannic acid gives a dark blue precipitate with ferric salts, but not with ferrous salts. If, however, the solution have been exposed to the air, it is altered by oxidation, and gives, with ferrous salts, a black color (in whose production gallic acid probably plays an important part), which is the coloring material of ordinary writing-ink.

Caffetannic acid—exists in saline combination in coffee and in Paraguay tea. It colors the ferric salts green, and does not affect the ferrous salts, except in the presence of ammonia; it precipitates the salts of quinin and of cinchonin, but does not precipitate tartar emetic or gelatin. It is a glucosid, being decomposed by suitable means into **caffeic acid** and mannitan.

Cachoutannic acid—obtained from catechu, is soluble in water, alcohol, and ether. Its solutions precipitate gelatin, but not tartar emetic; they color the ferric salts grayish-green.

Morintannic acid—**Maclurin**—a yellow, crystalline substance, obtained from fustic; more soluble in alcohol than in water. Its solutions precipitate green with ferroso-ferric solutions; yellow with lead acetate; brown with tartar emetic; yellowish-brown with cupric sulfate. It is decomposable into phoroglucin and **protocatechuic acid.**

Quercitannic acid—is the active tanning principle of oak-bark; it differs from gallo-tannic acid in not being capable of conversion into gallic acid, and in not furnishing pyrogallol on dry distillation. It forms a violet-black precipitate with ferric salts. The tannin existing in black tea seems to be quercitannic acid.

Quinotannic acid—a tannin existing in cinchona barks, probably in combination with the alkaloids. It is a light yellow substance; soluble in water, alcohol, and ether; its taste is astringent, but not bitter. Dilute H_2SO_4 decomposes it, at a boiling temperature, into glucose and a red substance—**quinova red.**

ALKALOIDS.

The constitution of some of the substances belonging to this class has been more or less definitely established, yet there remain many of whose chemical relations little is known. Those whose constitution has been determined have been already considered.

The alkaloids are organic, nitrogenized substances, alkaline in reaction, and capable of combining with acids to form salts in the same way as does ammonia. They are also known as **vegetable** or **organic bases** or **alkalies.** The similarity between the relation of the free alkaloids to their salts and that of ammonia to the ammoniacal salts is shown in the following equations:

$$\underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Sulfuric acid.}}{H_2SO_4} = \underset{\text{Ammonium sulfate.}}{(NH_4)_2SO_4}$$

$$\underset{\text{Morphin.}}{2C_{17}H_{19}NO_3} + \underset{\text{Sulfuric acid.}}{H_2SO_4} = \underset{\text{Morphium sulfate.}}{(C_{17}H_{20}NO_3)_2SO_4}$$

Classification.—The natural alkaloids are temporarily arranged in two groups:

(1.) Those which are liquid and volatile, and consist of carbon, hydrogen and nitrogen.

(2.) Those which are solid, crystalline, volatile with difficulty, if at all, and consist of C, H, N and O.

General Physical Characters.—As a rule they are insoluble, or nearly so, in water; more soluble in alcohol, chloroform, petroleum-ether, and benzene. Their salts are, for the most part, soluble in water and insoluble or sparingly soluble in petroleum-ether, benzene, ether, chloroform, and amyl alcohol. All exert a rotary action on polarized light:

Quinin..........	$[a] = -126^\circ.7$	Codein..........	$[a] = -118^\circ.2$
Quinidin........	$[a] = +250^\circ.75$	Narcein.........	$[a] = -\ 6^\circ.7$
Cinchonin	$[a] = +190^\circ.4$	Strychnin......	$[a] = -132^\circ.07$
Cinchonidin	$[a] \doteq -144^\circ.61$	Brucin..........	$[a] = -\ 61^\circ.27$
Morphin..	$[a] = -\ 88^\circ.4$	Nicotin	$[a] = -\ 93^\circ.5$
Narcotin........	$[a] = -103^\circ.5$		

Generally, combination with an acid diminishes their rotary power; with quinin the reverse is the case. Free narcotin is lævogyrous; its salts are dextrogyrous. They are all bitter in taste.

General Chemical Reactions.—*Potash, soda, ammonia, lime, baryta, and magnesia* precipitate the alkaloids from solutions of their salts.

Phosphomolybdic acid forms a precipitate which is bright yellow, with anilin, morphin, veratrin, aconitin, emetin, atropin, hyoscyamin, thein, theobromin, coniin, and nicotin; brownish-yellow with narcotin, codein, and piperin; yellowish-white with quinin, cinchonin and strychnin; yolk-yellow with brucin.

The reagent is prepared as follows: Ammonium molybdate is dissolved in H_2O, the solution filtered, and a quantity of hydrodisodic phosphate ½ in weight of the molybdate used is added, and then HNO_3 to strong acid reaction. The mixture is warmed; set aside for a day; the yellow ppt. collected on a filter; washed with H_2O acidulated with HNO_3; and while still moist transferred to a porcelain capsule, to which the liquid obtained by exhausting the remainder on the filter with NH_4HO is added. The fluid is warmed and gradually treated with pulverized sodium carbonate until a colorless solution is obtained. This is evaporated to dryness; a small quantity of sodium nitrate is added, and the whole gradually heated to quiet fusion and until all NH_3 is expelled. The residue is dissolved in warm H_2O (1 to 10), acidulated with HNO_3, and decanted.

To use the reagent, a drop of the suspected liquid is placed on a glass plate with a black background, and near it a drop of the reagent; and the two drops are made to mix slowly by a pointed glass rod.

Potassium iodhydrargyrate gives a yellowish precipitate with alkaloidal solutions which are acid, neutral, or faintly alkaline in reaction.

The reagent is obtained by dissolving 13.546 grams of mercuric chlorid and 49.8 grams of potassium iodid in a litre of water.

The solution may be used for quantitative determinations. The reagent is added from a burette to the solution of alkaloid until a drop, filtered from the solution which is being tested, and placed upon a black surface, gives no precipitate with a drop of the reagent. Each c.c. of reagent used indicates the presence in the volume of liquid tested of the following quantities of alkaloids, in grams:

Aconitin	0.0267	Morphin	0.0200
Atropin	0.0145	Coniïn	0.00416
Narcotin	0.0213	Nicotin	0.00405
Strychnin	0.0167	Quinin	0.0108
Brucin	0.0233	Cinchonin	0.0102
Veratrin	0.0269	Quinidin	0.0120

Of course, the process can be used only in a solution containing a single alkaloid.

Separation of Alkaloids from Organic Mixtures and from Each Other.—One of the most difficult of the toxicologist's tasks is the separation from a mixture of organic material (contents of stomach, viscera) of an alkaloid in such a state of purity as to render its identification perfect. The difficulty is the greater if the amount present be small, as is usually the case; and if the search be not confined to a single alkaloid, as frequently occurs. Some of these substances, as strychnin, are detectable with much greater facility and certainty than others.

Of the processes hitherto suggested, the best is that of Dragendorff, devised for the detection of any alkaloid or poisonous organic principle present in the substances examined. It is very exhaustive, and well adapted to cases frequently arising in chemico-legal practice; but, on the other hand, is too intricate to be serviceable to the general practitioner.

An abridgement of this process may be of use to detect the presence of the more commonly used alkaloids in a mixture of organic material. *The physician should, however, bear in mind that, in cases liable to give rise to legal proceedings, these may become seriously complicated by the analysis of any parts of the body, dejecta, or suspected articles of food, etc., by any process open to attack by the most searching cross-examination.*

The substances to be examined are reduced to a fine state of subdivision, and are digested for an hour or more in water acidulated with H_2SO_4, at a temperature of 40° to 50° (104°–122° F.); this is repeated three times, the liquid being filtered and the solid material expressed. The united extracts are evaporated at the temperature of the water-bath to a *thin* syrup; this is mixed with three or four volumes of alcohol, the mixture kept at about 35° (95° F.) for 24 hours, cooled well and filtered; the residue being washed with seventy per cent. alcohol. The alcohol is distilled from the filtrate, and the watery residue diluted with H_2O and filtered.

The filtrate so obtained contains the sulfates of the alkaloids, and from it the alkaloids themselves are separated by the following steps:

A. The acid watery liquid is shaken with freshly rectified petroleum-ether (which should boil at about 65°–70° (149°–158° F.), and should be used with caution, as it is very inflammable); after several agitations the ether layer is allowed to separate and is removed; this treatment is repeated so long as the ether dissolves anything. The residue obtained by the evaporation of the ether —*Residue* I.—is mostly composed of coloring matters, etc., which it is desirable to remove.

B. The same treatment of the watery liquid is repeated with benzene, which on evaporation yields *Residue* II., which is, if crystalline, to be tested for cantharidin, santonin, and digitalin (*q.v.*); if amorphous, for elaterin and colchicin.

C. The acid, aqueous fluid is then treated in the same way with chloroform to obtain *Residue* III., which is examined for cinchonin, digitalin, and picrotoxin by the proper tests.

D. The watery fluid, after one more shaking with petroleum-ether and removal of the ethereal layer, is rendered alkaline with ammonium hydroxid and shaken with petroleum-ether at 40° (104° F.), the ethereal layer being removed as quickly as possible while still warm; this is repeated two or three times, and repeated with *cold* petroleum-ether, which is removed after a time. The warm ethereal layers yield *Residue* IV. *a;* the cold ones *Residue* IV. *b.* The former is tested for strychnin, quinin, brucin, veratrin; the latter for coniin and nicotin.

E. The alkaline, watery fluid is shaken with benzene, which, on evaporation, yields *Residue* V., which may contain strychnin, brucein, quinin, cinchonin, atropin, hyoscyamin, physostigmin, aconitin, codeïn, thebaïn, and narceïn.

F. A similar treatment with chloroform yields *Residue* VI., which may contain a trace of morphin.

G. The alkaline liquid is then shaken with amyl alcohol, which is separated and evaporated; *Residue* VII. is tested for morphin, solanin, and salicin.

H. Finally, the watery liquid is itself evaporated with pounded glass, the residue extracted with chloroform, and *Residue* VIII., left by the evaporation of the chloroform, tested for curarin.

Volatile Alkaloids.

The most important alkaloids of this class are nicotin (see p. 438), coniïn (see p. 425), and sparteïn.

Spartein—$C_{15}H_{26}N_2$—a colorless oil, whose odor resembles that of anilin; extremely bitter in taste; sparingly soluble in water, forming an alkaline solution. On exposure to air becomes brown and resinous.

Fixed Alkaloids.

These are much more numerous than those which are volatile, and form the active principles of a great number of poisonous plants. The classification adopted for such of these alkaloids as must still be included among the substances of unknown constitution is a temporary one, based upon the botanic character of the plants from which they are derived.

Alkaloids of the Loganiaceæ.—**Strychnin**—**Strychnina (U. S.)**—$C_{21}H_{22}N_2O_2$—334—exists in the seeds and bark of different varieties of *strychnos.*

It crystallizes on slow evaporation of its solutions in orthorhombic prisms, by rapid evaporation as a crystalline powder; very sparingly soluble in H_2O and in strong alcohol; soluble in 5 pts. chloroform. Its aqueous solution is intensely bitter, the taste being perceptible in a solution containing 1 pt. in 600,000.

It is a powerful base; neutralizes and dissolves in concentrated H_2SO_4 without coloration; and precipitates many metallic oxids from solutions of their salts. Its salts are mostly crystallizable, soluble in H_2O and alcohol, and intensely bitter. The *acetate* is the most soluble. The *neutral sulfate* crystallizes, with 7 Aq, in rectangular prisms. The iodids of methyl and ethyl react with strychnin to produce the iodids of **methyl** or **ethylstrychnium,** white, crystalline, basic substances, producing an action on the economy similar to that of curare. When acted on by H_2SO_4 and potassium chlorate, with proper precautions, **strychnic** or **igasuric acid** is formed.

ANALYTICAL CHARACTERS.—(1.) Dissolves in concentrated H_2SO_4 without color. The solution deposits strychnin when diluted w th H_2O, or when neutralized with magnesia or an alkali. (2.) If a fragment of potassium dichromate (or other substance capable of yielding nascent O) is drawn through a solution of strychnin in H_2SO_4, it is followed by a streak of color; at first blue (very transitory and frequently not observed), then a brilliant violet, which slowly passes to rose-pink, and finally to yellow. Reacts with $\frac{1}{50000}$ grain of strychnin. (3.) A dilute solution of potassium dichromate forms a yellow, crystalline ppt. in strychnin solutions; which, when washed and treated with concentrated H_2SO_4, gives the play of colors indicated in 2. (4.) If a solution of strychnin be evaporated on a bit of platinum foil, the residue moistened with concentrated H_2SO_4, the foil connected with the + pole of a single Grove cell, and a platinum wire from the − pole brought in contact with the surface of the acid, a violet color appears upon the surface of the foil. (5.) Strychnin and its salts are intensely bitter. (6.) A solution of strychnin introduced under the skin of the back of a frog causes difficulty of respiration and tetanic spasms, which are aggravated by the slightest irritation, and twitching of the muscles during the intervals between the convulsions. With a small frog, whose surface has been dried before injection of the solution, $\frac{1}{10000}$ grain of acetate of strychnin will produce tetanic spasms in 10 minutes. (7.) Solid strychnin, moistened with a solution of iodic acid in H_2SO_4, produces a yellow color, changing to brick-red and then to violet-red. (8.) Moderately concentrated HNO_3 colors strychnin yellow in the cold. A pink or red color indicates the presence of brucin.

TOXICOLOGY.—Strychnin is one of the most active and most frequently used of poisons. It produces a sense of suffocation, thirst, *tetanic spasms*, usually opisthotonos, sometimes emprosthotonos, occasionally vomiting, contraction of the pupils during the spasms, and death, either by asphyxia during a paroxysm, or by exhaustion during a remission. The symptoms appear in from a few minutes to an hour after taking the poison, usually in about 20 minutes; and death in from 5 minutes to 6 hours, usually within 2 hours. Death has been caused by ½ grain, and recovery has followed the taking of 20 grains.

The treatment should consist of the removal of the unabsorbed poison by the stomach-pump, injecting charcoal, and pumping it out after about 5 minutes; under the influence of chloroform if necessary. Chloral hydrate should be given.

Strychnin is one of the most stable of the alkaloids, and may remain for a long time in contact with putrefying organic matter without suffering decomposition.

Brucin—$C_{23}H_{26}N_2O_4$+4Aq—394+72—accompanies strychnin. It forms oblique rhomboidal prisms, which lose their Aq in dry air.

Sparingly soluble in H_2O; readily soluble in alcohol, chloroform, and amyl alcohol; intensely bitter. It is a powerful base and most of its salts are soluble and crystalline. Its action on the economy is similar to that of strychnin, but much less energetic.

ANALYTICAL CHARACTERS.—(1.) Concentrated HNO_3 colors it bright red, soon passing to yellow; stannous chlorid, or colorless NH_4HS, changes the red color to violet. (2.) Chlorin-water, or Cl, colors brucin bright red, changed to yellowish-brown by NH_4HO.

Alkaloids of the Solanaceæ.—Solanin—$C_{43}H_{71}NO_{16}$—857—obtained from many species of *Solanum;* crystallizes in small, white, bitter, sparingly soluble prisms. Concentrated H_2SO_4 colors it orange-red, passing to violet and then to brown. It is colored yellow by concentrated HCl. It dissolves in concentrated HNO_3, the solution being at first colorless, but after a time becomes purple.

Hyoscyamin—$C_{17}H_{23}NO_3$—occurs, along with another base, **hyoscin**, both isomeric with atropin, in *Hyoscyamus niger*. It crystallizes, when pure, in odorless, white, silky needles whose taste is very sharp and disagreeable, and which are very sparingly soluble in water. As most commonly met with, it forms a yellowish, soft, hygroscopic mass which gives off a peculiar, tobacco-like odor. It neutralizes acids. Its sulfate—**Hyoscyaminæ sulfas, U. S.**—forms yellowish crystals, very soluble in water, hygroscopic, and neutral in reaction.

See Atropin (p. 427).

Alkaloids of the Aconites.—The different species of *Aconitum* contain, probably, a number of alkaloids, but our knowledge of them is as yet extremely imperfect. The substances described as *aconitin, lycoctanin, napellin* are impure. It appears, however, that the principal alkaloids of *aconitum napellus* and of *A. ferox*, although differing from each other, are both compounds formed by the union of **aconin, $C_{26}H_{39}NO_{11}$**, with the radical of benzoic acid in the former, and with that of veratric acid in the latter.

Aconitin—$C_{33}H_{43}N_{12}$ (?)—the principal alkaloid of *A. napellus*, is a crystalline solid, almost insoluble in water, and very bitter. It is decomposed by H_2O at 140° (284° F.) and by KHO into aconin and benzoic acid. It is very poisonous.

Pseudo-aconitin—$C_{36}H_{49}NO_{12}$—occurs in *A. ferox*. It is a crystalline solid, having a burning taste, and is extremely poisonous. On decomposition by H_2O at 140° (284° F.) it yields aconin and veratric acid.

Japaconitin—$C_{66}H_{88}N_2O_{21}$—has been obtained from the root of *A. japanicum*, and is a crystalline solid which is decomposed by alkalies into benzoic acid and **japaconin, $C_{26}H_{41}NO_{10}$**.

The color reactions described as characteristic of "aconitine" are not due to the alkaloid.

TOXICOLOGY.—Aconite and "aconitin" have been the agents used in quite a number of homicidal poisonings.

The symptoms usually manifest themselves within a few minutes; sometimes are delayed for an hour. There is numbness and tingling, first of the mouth and fauces, later becoming general. There is a sense of dryness and of constriction in the throat. Persistent vomiting usually occurs, but is absent in some cases. There is diminished sensibility, with numbness, great muscular feebleness, giddiness, loss of speech, irregularity and failure of the heart's action. Death may result from shock if a large dose of the alkaloid be taken, but more usually it is by syncope.

The treatment should be directed to the removal of unabsorbed poison by the stomach-pump, and washing out of the stomach with infusion of tea holding powdered charcoal in suspension. Stimulants should be freely administered.

Alkaloids from other Sources.—**Ergotin**—$C_{50}H_{52}N_2O_3$—and **Ecbolin** are two brown, amorphous, faintly bitter, and alkaline alkaloids obtained from ergot. They are readily soluble in water and form amorphous salts. The medicinal preparations known as ergotin are not the pure alkaloid.

Colchicin—$C_{17}H_{19}NO_5$—occurs in all portions of *Colchicum autumnale* and other members of the same genus. It is a yellowish-white, gummy, amorphous substance, having a faintly aromatic odor and a persistently bitter taste. It is slowly but completely soluble in water, forming faintly acid solutions. It forms salts which are, however, very unstable.

Concentrated HNO_3, or, preferably, a mixture of H_2SO_4, and $NaNO_3$ colors colchicin blue-violet. If the solution be then diluted with H_2O, it becomes yellow, and on addition of NaHO solution, brick-red.

Veratrin—**Veratrina, U. S.**—$C_{32}H_{52}N_2O_8$—occurs in *Veratrum officinalis = Asagræa officinalis*, accompanied by **Sabadillin**—$C_{41}H_{66}N_2O_{13}$—**Jervin**—$C_{30}H_{46}N_2O_3$—and other alkaloids. The substance to which the name **Veratrina, U. S.**, applies is not the pure alkaloid, but a mixture of those occurring in the plant.

Concentrated H_2SO_4 dissolves veratrin, forming a yellow solution turning orange in a few moments, and then, in about half an hour, bright carmine-red. Concentrated HCl forms a colorless solution with veratrin, which turns dark red when cautiously heated.

Berberin—*Xanthopicrite*—$C_{20}H_{17}NO_4$—occurs in *Berberis vulgaris*, *Cocculus palmatus*, and many other plants. It crystallizes in fine yellow needles or prisms; bitter in taste and neutral in reaction. It is difficultly soluble in cold water, readily soluble in alcohol and in boiling water. It forms well-defined, crystalline, yellow salts.

Physostigmin—Eserin—$C_{15}H_{21}N_3O_2$—is an alkaloid existing in the Calabar bean, *Physostigma venenosum*. It is a colorless, amorphous solid, odorless and tasteless, alkaline and difficultly soluble in water. It neutralizes acids completely, with formation of tasteless salts. Its salicylate—**Physostigminæ salicylas, U. S.**—forms short, colorless, prismatic crystals, sparingly soluble in water.

Concentrated H_2SO_4 forms a yellow solution with physostigmin or its salts, which soon turns olive-green. Concentrated HNO_3 forms with it a yellow solution. If a solution of the alkaloid in H_2SO_4 be neutralized with NH_4HO, and the mixture warmed, it is gradually colored red, reddish-yellow, green, and blue.

Curarin—$C_{18}H_{35}N$ (?)—is an alkaloid obtainable from the South American arrow-poison, *curare*, or *woorara*. It crystallizes in four-sided, colorless prisms, which are hygroscopic, faintly alkaline, and intensely bitter.

Curarin dissolves in H_2SO_4, forming a pale violet solution, which slowly changes to red. If a crystal of potassium dichromate be drawn through the H_2SO_4 solution, it is followed by a violet coloration, which differs from the similar color obtained with strychnin under similar circumstances, in being more permanent, and in the absence of the following pink and yellow tints.

Emetin—$C_{28}H_{40}N_2O_5$—an alkaloid existing in *ipecacuanha* which crystallizes in colorless needles or tabular crystals, slightly bitter and acrid; odorless, and sparingly soluble in water.

It dissolves in concentrated H_2SO_4, forming a green solution, which gradually changes to yellow. With Fröhde's reagent it gives a red color, which soon changes to yellowish-green and then to green.

Ptomains.—This name, derived from *πτῶμα*=that which is fallen—*i.e.*, a corpse—was first suggested by Selmi to apply to a class of substances, first distinctly recognized by him, which are produced from albuminoid substances under the influence of putrefactive decomposition, and which are distinctly alkaloidal in character.

The ptomains are possessed of all of the distinguishing characters of the vegetable alkaloids. They are alkaline in reaction, and combine with acids to form salts. Some are liquid, others are solid and crystalline. Some are actively poisonous, others are practically inert. They behave toward the general reagents for alkaloids in much the same way as do the vegetable alkaloids.

Although the names *ptomains* and *cadaveric alkaloids* are applied to alkaloids of animal origin, it is certain that such alkaloids may be and are produced during life in the animal economy.

It was feared that, as alkaloidal substances in many respects resembling those of vegetable origin are produced in the animal body, not only after death, but during life, grave doubts would be cast upon the results of analyses made to detect the presence of poisonous vegetable alkaloids in the cadaver in cases of suspected poisoning. Such fears were by no means groundless, as there is abundant evidence that ptomains have been mistaken for vegetable alkaloids in chemico-legal analyses. The ptomains, however, as well as the vegetable alkaloids, may be positively identified by a careful analysis, based upon the use, not of a single reaction, but of *all known reactions* for the alkaloid in question. Therefore, it is possible to positively predicate the existence or non-existence of a given vegetable alkaloid in a cadaver, but it can only be done after a thorough and conscientious examination by all physiological and chemical reactions.

The ptomains have of recent years assumed great importance to the physician by reason of their bearing upon the etiology of disease, and sufficient experimental evidence has already been obtained to warrant the belief that the method of action of many of the known pathogenic bacteria is by their production of alkaloidal poisons (see below).

One of the first of the putrid alkaloids to be formed in cadaveric matter is *cholin* (see pp. 276, 361), which undoubtedly has its origin in the decomposition of the lecithins.

Mydalein is a putrid alkaloid, of undetermined composition, forming a difficultly crystallizable, hygroscopic chlorid, which is actively poisonous. Five milligrammes administered hypodermically to a cat causes death after profuse diarrhœa and secretion of saliva, violent convulsions, and paralysis, beginning with the extremities and extending to the muscles of respiration.

Mydin—$C_6H_{11}NO$—is a base produced after continued putrefaction at comparatively low temperatures. It is a powerful base and a strong reducing agent, and has an ammoniacal odor. It is non-poisonous.

Mydatoxin—$C_6H_{13}NO_2$—is a strongly alkaline syrup, which produces, when administered to animals, violent clonic spasms, followed by paralysis and death.

An alkaloid, many of whose chemical reactions have been determined, although its composition is unknown, has been obtained from the internal organs, and dejecta of cholera victims, as well as from cultures of the comma bacillus. This alkaloid, when administered to animals, causes symptoms of poisoning and death.

From the cultures of the Koch-Eberth typhus bacillus an alkaloid has been isolated—**Typhotoxin**, $C_7H_{17}NO_2$—which, when administered to animals, causes paralysis, copious diarrhœa, and death.

Tetanin—$C_{13}H_{30}N_2O_4$—is an alkaloid obtained from cultures of a bacillus originating from a wound which had been the cause of death by tetanus. It forms a deliquescent chlorid, and a very soluble chloroplatinate. The free base or its chlorid, when injected into mice or guinea-pigs, causes clonic or tonic convulsions of the greatest intensity, which terminate in death.

Mytilitoxin—$C_6H_{15}NO_2$—is an alkaloid obtained from poisonous mussels, which, when administered to animals in small amount, causes the same symptoms as are produced by the mussels.

For other ptomains see Trimethylamin, p. 275; Cholin, p. 276; Muscarin and neurin, p. 277; Neuridin, pp. 277, 333; Diamins and triamins, pp. 333 *et seq.;* Pyridin derivatives, pp. 424 *et seq.* See also Toxalbumins, below.

ALBUMINOID SUBSTANCES.

PROTEIN BODIES.

The substances of this class are never absent in living vegetable or animal cells, to whose "life" they are indispensable. They are as yet the products exclusively of the organized world.

Physical Characters.—They are almost all uncrystallizable and incapable of dialysis. Some are soluble in water, others only in water containing traces of other substances, others are insoluble. Their solutions are all lævogyrous. Some are separated as solids from their solutions, in a permanently modified form, by heat and by certain reagents; a change called **coagulation.** When once coagulated they cannot be redissolved. The temperature at which coagulation by heat occurs varies with different albuminoids, and is of value in distinguishing them from one another.

Composition.—They consist of C, N, H, O, and usually a small quantity of S, and form highly complex molecules, whose exact composition is uncertain. Of their *constitution* nothing is definitely known, although there is probability that they are highly complex amids, related to the ureids, and formed by the combination of glycollamin, leucin, tyrosin, etc., with radicals of the acetic and benzoic series.

Decompositions.—The study of the products of decomposition of the albuminoids is of great importance, being the means by which a knowledge of their constitution and chemical relationships must be sought for.

Oxidizing agents attack the molecule of the albuminoids profoundly, yielding products far removed from the original substance: A mixture of H_2SO_4 and manganese dioxid, or potassium dichromate, produces aldehydes, and acids of the fatty and benzoic series, hydrocyanic acid, and cyanids from the albuminoids. When heated under pressure with Br and H_2O they yield CO_2, oxalic and aspartic acids, amido-acids, and bromin derivatives of the fatty and benzoic series. Potassium permanganate produces from them urea, CO_2, NH_3 and H_2O.

Dilute acids decompose them into two substances: one insoluble, amorphous, yellowish, called **hemiprotein**; the other soluble in water, insoluble in alcohol, faintly acid, called **hemialbumin.** A prolonged boiling with moderately concentrated H_2SO_4 decomposes them, forming well-defined substances—glycocol, leucin, tyrosin; aspartic and glutamic acids.

Alkalies dissolve them more or less readily; on boiling the solution, part of the sulfur is converted into sulfid and hyposulfite. Their alkaline solutions, when neutralized by acids, deposit Mulder's **protein.** Concentrated alkalies decompose them into amido-acids. By fusion with alkalies, alkaline cyanids are also produced.

The action of hydrating agents, comparable with those by which the fats are saponified, the compound ethers decomposed, and the starches converted into sugar, have yielded the most important results. The most manageable reagent for the purpose is barium hydroxid in the presence of H_2O at elevated temperatures under pressure. The product of the reaction gives off ammonia and has the odor of fecal matter. It contains, if the albuminoid decomposed was gelatin, ammonia, carbon dioxid, oxalic acid, acetic acid, and amido-derivatives. The last named belong to two classes: *leucins*, glycocol, alanin, amidobutyric acid, amidovaleric acid, caproic leucin—*leuceïns*, which are amido derivatives corresponding to pyrrol and related to the dimethyl and trimethyl pyrrols existing in oil of Dippel. When the albuminoid decomposed by BaH_2O_2 is albumin the products of the reaction are more complex. If the decomposition is effected at 100° (212° F.), there are produced, besides the substances obtained from gelatin, *glucoproteïns*, having the formula $C_nH_{2n}N_2O_4$, which are the first products of the hydration and some of which by further hydration are decomposed into leucins and leuceïns; and a substance crystallizing with difficulty, transparent, sweet in taste, called *diluceïn*, which on further hydration, at 180° (356° F.), yields a glucoproteïn and *proteic acid.*

As a result of the study of the products of hydration of gelatin and of albumen the empirical formula of the former has been determined to be $C_{32}H_{52}N_{10}O_{12}$, and that of the latter $C_{66}H_{100}N_{18}O_{22}$.

Albuminoids are subject to a form of decomposition peculiar to themselves and known as putrefaction, which has been the subject of much careful study of recent years. **Putrefaction is a decomposition of dead albuminoid matter under the influence and**

as a result of the processes of nutrition of certain bacteria, and attended by the evolution of more or less fetid products.

That putrefaction may occur certain conditions are necessary: (1) The presence of living bacteria, or of their germs; (2) the presence of air; (3) the presence of moisture; (4) a temperature between 5° and 90° (41°–194° F.).

The bacteria which cause putrefaction are quite numerous, and it is probable that the products are somewhat different with different species. Their germs exist in the air, in the animal intestinal canal, and possibly in the pancreas. Although the bacteria causing putrefaction are anærobic, putrefaction does not progress in the absence of air, and in sealed vessels the process is either arrested or proceeds with extreme slowness. Albuminoids which have been deprived of moisture, either by drying or by the action of dehydrating agents, such as strong alcohol, do not enter into putrefaction unless water is supplied to them, when the process proceeds as usual. The temperature most favorable to putrefaction is about 40° (104° F.). High or low temperatures arrest putrefaction or prevent it, the former, if sufficiently high, permanently (if the material be protected from new bacteria) by destroying the vitality of the bacteria; the latter, even if extreme, only temporarily, and so long as the low temperature is maintained.

Putrefaction may, therefore, be prevented either (1) by the action of agents or substances which interfere with the development of bacteria (germicides and antiseptics); (2) by the exclusion of air; (3) by the exclusion of water; (4) by a temperature below 5° (41° F.) or above 90° (194° F.).

Germicides are substances or agents which destroy bacteria and their germs. Mercuric chlorid and heat are germicides.

Antiseptics are substances which prevent or restrain putrefaction. Antiseptics are either germicides, which prevent putrefaction by destroying the organisms which cause it, or are agents which interfere with the development of these organisms, without destroying their vitality. The salts of aluminium are antiseptic by reason of their chemical action on the albuminoids, although their germicidal powers are slight.

Deodorizers, or air purifiers, are substances which destroy the odorous products of putrefaction.

Disinfectants are substances which restrain infectious diseases by destroying or removing their specific poisons.

Putrefaction is attended by the breaking down and liquefaction of the material if it be solid; or its clouding and the formation of a scum upon the surface if it be liquid. The products of putrefaction vary with the conditions under which it occurs. The most prominent are: (1) Inorganic products such as N, H,

H_2S, NH_3, and simple organic compounds, such as CO_2 and hydrocarbons; (2) acids of the fatty series in great abundance, and acids of the oxalic and lactic series; (3) non-aromatic monamins and diamins, such as trimethylamin, putrescin and certain of the ptomaïns; (4) aromatic products, among which are: (*a*) phenols, such as tyrosin, oxyaromatic acids, phenol and cresol; (*b*) phenylic derivatives, such as phenyl acetic and phenyl propionic acids; (*c*) indol, scatol, scatol-carbonic acid, etc.; (*d*) ptomaïns of undetermined constitution, but belonging to the aromatic series; pyridin derivatives.

Under certain imperfectly defined conditions, buried animal matter is converted into a substance resembling tallow, and called **adipocere,** which consists chiefly of palmitate, stearate, and oleate of ammonium, phosphate and carbonate of calcium, and an undetermined nitrogenous substance.

There occurs a decomposition of vegetable tissues under the influence of warmth and moisture, which is known as **eremacausis**, differing from putrefaction in that the substances decomposed are the carbohydrate instead of the azotized constituents, and in the products of the decomposition, there being no fetid gases evolved (except there be simultaneous putrefaction), and the final product is a brownish material (humus or ulmin).

General Reactions.—The albuminoids all respond to a great number of general reactions, which may be classified in three groups: I. Color reactions; II. Precipitations in an insoluble combination; *alkaloidal reactions;* III. Precipitations in a form which permits of easy resolution in the primitive form.

I. (1.) A purple-red color when warmed to 70° (158° F.) with Millon's reagent. The reagent is made by dissolving, by the aid of heat, 1 pt. Hg in 2 pts. HNO_3 of sp. gr. 1.42, diluting with 2 vols. H_2O, and decanting after 24 hours. (2.) A yellow color with HNO_3; changing to orange with NH_4HO (xanthoproteic reaction). (3.) A purple color with Pettenkofer's test (*q.v.*). (4.) With a drop or two of cupric sulfate solution and liquor potassæ a violet color. (5.) A solution of an albuminoid in excess of glacial acetic acid is colored violet and rendered faintly fluorescent by concentrated H_2SO_4. (6.) With Fröhde's reagent (see Morphin) solid albuminoids give a fine blue color. (7.) If an alkaline solution of an albuminoid or a peptone be mixed with an alkaline solution of diazobenzosulfonic acid a red-brown or orange color is produced. If powdered Zn or sodium amalgam be added the color becomes a brilliant red. (8.) Add to the albuminous liquid two drops of an alcoholic solution of benzoic aldehyde, then some H_2SO_4 diluted with an equal bulk of H_2O, and finally a drop of ferric sulfate solution: a dark blue color is produced either immediately on warming, or slowly in the cold. (9.) Albumins dissolve in boiling concentrated HCl (sp. gr. 1.19) with a violet-blue color, and coagulated albumins are similarly colored by boiling HCl. The color is the more distinct the purer the albuminoid. The reaction may be applied to the albumin coagulated from urine after collection on a filter and washing with water, alcohol, and ether.

II. The albuminoids are precipitated in an insoluble form by: 1, the concentrated mineral acids, notably HNO_3; 2, by potassium ferrocyanid in presence of acetic acid; 3, by certain organic acids in the presence of concentrated solutions of NaCl or Na_2SO_4; 4, by tannin in acid solution; 5, by phosphomolybdic or phosphotungstic acid; 6, by double iodid of potassium and mercury, or double iodid of potassium and bismuth, in acid solution; 7, by solutions of the salts of Pb, Cu, Ag, Hg, U; 8, by chloral, picric acid, phenol or trichloracetic acid.

III. Some of the albuminoids are precipitated in a form capable of resolution by solutions of certain salts, notably by the sulfates and phosphates of the alkaline metals, ammonium and magnesium.

Classification.—Until the constitution of the albuminoids shall have been established, a rational classification of them will remain impossible. For the present a provisional arrangement of the albuminoids of animal origin, based upon their solubilities, is adopted. The vegetable albuminoids are conveniently classified by themselves. The division into albuminoids and gelatinoids formerly followed, and based upon the production of aromatic derivatives by decomposition of the former and the absence of such products in the case of the latter, has been abandoned for the reason that benzoic acid and other aromatic substances have been obtained by decomposition of gelatin.

The provisional classification is as follows:

1. ALBUMINS.—*Soluble in pure water; coagulated by heat.*—Egg albumin; serum albumin.

2. GLOBULINS.—*Insoluble in pure water, but soluble in solutions of neutral salts* (NaCl, KCl, $MgSO_4$, etc.); *coagulated by heat.*—Vitelin, myosin, paraglobulin, fibrinogen.

3. FIBRINS.—*Insoluble in pure water, swell in solutions of neutral salts, and in dilute acids; coagulated by boiling water.*—Blood fibrin.

4. COAGULATED ALBUMINOIDS.—*Insoluble in water and in saline solutions, only moderately swelled by the latter and by dilute acids, not colored by iodin.*—Produced from 1, 2, and 3 by heat.

5. AMYLOID MATTER.—*Insoluble in water, saline solutions or dilute acids or alkalies, colored red-brown or violet by iodin.*

6. ACID-ALBUMINS.—*Insoluble in water, in dilute saline solu-*

tions and in alcohol. When freshly precipitated readily soluble in dilute acids or alkalies; but insoluble when mixed with calcium carbonate suspended in water.

7. Alkali-Albumins.—*Very sparingly soluble in water and in saline solutions; slightly soluble in hot alcohol. Shaken with water and calcium carbonate they dissolve with displacement of carbon dioxid.*

8. Albumoses or Propeptones.—*Resemble the acid-albumins, but dissolve in dilute solutions of NaCl. Precipitated in the cold by HNO_3, but redissolve on heating.*

9. Peptones.—*Very soluble in water, not coagulated by heat. Are not precipitated by potassium ferrocyanid in the presence of acetic acid, by NaCl in excess in presence of an acid, by HNO_3, or by boiling with ferric acetate.*

10. Proteids.—*May be decomposed into an albuminoid and other substances.*—Hæmoglobins, casein, mucin, chondrin, and some nucleins.

11. Albuminoids.—*Insoluble, not dissolved by digestive secretions.*—Keratins, elastin, fibroïn.

12. Gelatinous Substances.—*Soluble in hot H_2O without modification.*—Gelatin.

13. Spongeous Substances.—*Dissolved by boiling water only after modification.*—Spongin, cornein.

The vegetable albuminoid substances have been much less perfectly studied than those of animal origin. A crude classification of them similar to that of the animal albuminoids is provisionally made into four groups:

1. Vegetable Albumins.—*Soluble in H_2O, coagulated by heat.*

2. Albuminoids of Gluten.—*Insoluble in H_2O and in absolute alcohol; soluble in aqueous alcohol; coagulated by heat.*—Gluten-fibrin, gliadin, mucedin.

3. Vegetable Caseins.—*Insoluble in water and in saline solutions; soluble in dilute acids or alkalies; coagulated by heat.*—Gluten-casein, legumin.

4. Vegetable Globulins.—*Similar to animal globulins, but dissolve appreciably in pure water. Precipitated from aqueous solution by NaCl, but redissolved by an excess of the salt, and again precipitated by a large excess.*

I. Albumins.—**Egg albumin** exists in solution, imprisoned in a network of delicate membranes, in the white of egg. It is obtained in an impure condition by cutting the whites of eggs with scissors, expressing through linen, diluting with an equal volume of water, filtering, and concentrating the filtrate at a temperature below 40° (104° F.); mineral salts, which adhere to it tenaciously, are separated by dialysis. It is a mixture of two kinds of proteids. (1.) Those coagulable by heat. Of these, two are globulins (*q. v.*) precipitable by $MgSO_4$. Their coagulation temperatures are: **oviglobulin** α, 57°.5 (135°.5 F.); **oviglobulin** β, 67° (152°.6 F.). Three are albumins which coagulate: α at 72° (161°.6 F.), β at 76° (168° F.), and γ at 82° (179°.6 F.). (2.) Peptones, which increase in amount with the staleness of the egg.

Solutions of egg albumin are not precipitated by a small quantity of HCl, but an excess of that acid produces a deposit which is difficultly soluble in HCl, H_2O, and salt solution. It is coagulated by agitation with ether. Solutions of salts of Cu, Ag, and Pb form precipitates with albumin, which contain definite proportions of the metals. Egg albumin may be distinguished from serum albumin by Maurel's reagent, which is a mixture of 25 cc. NaHO solution, 5 cc. of a 3% solution of $CuSO_4$ and 70 cc. glacial acetic acid. Ten cc. of this reagent added to 2 cc. of the liquid under examination precipitates egg albumin even from dilute solution, but does not precipitate serum albumin.

When oxidized with potassium permanganate, egg albumin yields a definite nitrogenized and sulfurated body, **oxyprotein-sulfuric acid**, which is also produced from serum albumin, fibrin, casein and conglutin, but not from peptones or propeptone; and by more energetic oxidation **peroxyproteic acid.** See Acid-albumins and Alkali-albumins, below.

Serum-albumin exists in blood-serum, chyle, lymph, pericardial fluid, the fluids of cysts and of transudations, in milk and, pathologically, in the urine. It is best obtained from blood-serum, after removal of paraglobulin (*q.v.*), by a tedious process, and only then in a state of doubtful purity. It is less abundant in the blood of some animals than paraglobulin, but more abundant in that of man.

Solutions of serum-albumin are lævogyrous $[\alpha]_D = -56°$; they are not precipitated by CO_2, by acetic or phosphoric acid, by ether or by magnesium sulfate. They are precipitated by mineral acids, tannic acid, metaphosphoric acid, and most metallic salts. When heated they become opalescent at 60° (140° F.), and coagulate in the flocculent form at 72°–75° (161°.6–167° F.).

Human serum-albumin consists of three distinct proteids α, β, and γ, coagulating at 73° (163°.4 F.), 77° (170°.6 F.), and 84° (183°.2 F.). The blood of some animals contains but two of these. They are all precipitated, after removal of serum-globulin by saturation with $MgSO_4$, by saturation with Na_2SO_4. Potassium acetate also precipitates them without coagulation.

Detection and Determination of Albumin in Urine.—If the urine be not perfectly clear it is filtered; if this do not render it *perfectly* transparent, it is treated with a few drops of magnesia mixture (p. 120, note), and again filtered. The filtrate, if alkaline, is rendered *just* acid by adding dilute acetic acid guttatim (nitric acid should not be used, and the acidulation of alkaline urine is imperative). The urine is now heated to near boiling, and if a cloudiness or precipitate be formed, HNO_3 is added slowly to the extent of about 10 drops. If heat produce a cloudiness, which clears up completely on addition of HNO_3, it is due to an excess of earthy phosphates. If a cloudiness produced by heat do not clear up (it may increase) on addition of HNO_3, it is due to albumin.

Small quantities of albumin may sometimes be better detected by **Heller's test:** A layer of HNO_3 is placed in a test-tube, which is then held at an angle, and the urine allowed to flow *slowly* upon the surface of the HNO_3 (Fig. 42) so as to form a distinct layer, with the minimum of mixing of the two liquids. The test-tube is then brought to the vertical slowly, and the point of junction of the two liquids examined against a dark background. If albumin be present a white, opaque band, whose upper and lower borders are *sharply defined*, will be seen at the line of junction of the two liquids. When urates are present in excess, a white band will be observed, but its position will be rather above the line of junction, and its upper border will not be sharply defined, but gradually diminished in density from below upward. In non-albuminous urines there is usually a darkening, but never an opacity at the line of junction.


FIG. 42.

QUANTITY.—The only method of determining the quantity of albumin in urine, with an approach to accuracy, is gravimetric: 20–50 c.c. (5.4–13.5 fl ℥) of the filtered urine (according as the qualitative testing shows albumin to be present in large or small quantity) are diluted with an equal volume of water, and slowly heated over the water-bath. As the boiling temperature is approached, 3-4 drops of dilute acetic acid are added. After the urine has boiled for a few moments, and the coagulated albumin has become flocculent, it is thrown upon a dried and weighed filter. The coagulum is washed with boiling H_2O, then with H_2O acidulated with HNO_3, then with alcohol, and finally with ether. By these washings impurities are removed, and the albumin is caused to contract firmly. The filter and the albumin are dried at 110° (230° F.) until they cease to lose weight, and again weighed. The difference between the two weighings is the weight of dry albumin in the volume of urine used.

II. GLOBULINS.—**Vitelin** exists in the yolk of egg and in the crystalline lens. It is soluble in dilute solution of sodium chlorid, from which it is precipitated by excess of H_2O; by heating to 75°–80° (167°–176° F.); and by alcohol. It is not precipitated by solid sodium chlorid. It dissolves in weak alkaline solutions without alteration, and in very dilute HCl (1–1000), by which it is quickly converted into syntonin.

Myosin—is one of the principal constituents of the muscular fibre in rigor mortis. It is a faintly yellow, opalescent, distinctly alkaline liquid, which, when dropped into distilled H_2O, deposits the myosin in globular masses, while the H_2O assumes an acid reaction. It is insoluble in H_2O, easily soluble in dilute salt solution, from which it is precipitated by the addition of solid sodium chlorid, or by a heat of 55°–60° (131°–140° F.). Very dilute HCl dissolves and converts it into syntonin.

Paraglobulin.—This substance has been described by various authors under the names: *plasmine* (Denis), *serum casein* (Panum), *serum globuline, fibrino-plastic matter* (Schmidt), *serin* (Denis). It exists in blood-serum, in pericardial fluid, hydrocele fluid, lymph and chyle, and, accompanying serum-albumin, in albuminous urine. It is obtained by diluting blood-serum, or hydrocele fluid, with 10–15 volumes of ice-cold H_2O, treatment of the solution with strong current of CO_2, and washing the collected deposit with H_2O as long as a portion of the filtrate precipitates with acetic acid and potassium ferrocyanid, or with silver nitrate. It is a granular substance, which gradually becomes more compact; insoluble in H_2O, sparingly soluble in H_2O containing CO_2; soluble in dilute alkalies, in lime-water, in solutions of neutral alkaline salts, in dilute acids. Its solution in very dilute alkaline fluids is perfectly neutral and is not coagulated by heat, except after *faint* acidulation with acetic or mineral acids; it is precipitated by a large volume of alcohol; its solutions are also precipitated incompletely by dissolving sodium chlorid in them to saturation, and completely by similar solution of magnesium sulfate; this last method of precipitation is used for the separation of paraglobulin from serum-albumin (see Fibrin).

Fibrinogen.—After the separation of paraglobulin from blood-plasma, as described above, if the liquid be still further diluted, and again treated with CO_2, a substance is obtained which, although closely resembling paraglobulin in many characters, is distinct from it, and, unlike paraglobulin, it cannot be obtained from the serum separated from coagulated blood.

Paraglobulin and fibrinogen are both soluble in a solution of sodium chlorid containing 5–8 per cent. of the salt; when the degree of concentration of the salt solution is raised to 12–16 per cent., the fibrinogen is precipitated, while the paraglobulin remains in solution and is only precipitated, and then incompletely, when the percentage of salt surpasses twenty (see Fibrin).

III.—Fibrins.—**Fibrin** is obtained when blood is allowed to coagulate or is whipped with a bundle of twigs. When pure it is at first a gelatinous mass, which contracts to a white, stringy, tenacious material, made up of numerous minute fibrils; when dried it is hard, brittle, and hygroscopic. It is insoluble in water, alcohol, ether; in dilute acid it swells up and dissolves slowly and incompletely. When heated with water to 72° (161°.6 F.), or by contact with alcohol, it is contracted, and is no longer soluble in dilute acids, but soluble in dilute alkalies. In solutions of many neutral salts of 6-10 per cent., it swells up and is partially dissolved; from this solution it separates on the addition of water, or upon the application of heat to 73° (163°.4 F.), or by acetic acid or alcohol. Moist fibrin has the property of decomposing hydrogen peroxid with copious evolution of oxygen.

Fibrin does not exist as such in the blood, and the method of its formation and of the clotting of blood has been the subject of much experiment and argument; nor can the question be said to be definitely set at rest. In the light of the researches of Denis, Schmidt, and especially of Hammarsten, it may be considered as almost proven that fibrin is formed from fibrinogen under favorable circumstances, and by a transformation which is not yet understood. Whether paraglobulin plays any part directly in the formation of fibrin or not, is still an open question.

IV.—Coagulated albumins—are obtained, as described above, from the soluble varieties by the action of acids, heat, alcohol, etc. They are insoluble in water, alcohol, solutions of neutral salts; difficultly soluble in dilute alkaline solutions. In acetic acid they swell up and dissolve slowly; from this solution they are precipitated by concentrated salt solution. Concentrated HCl dissolves them with formation of syntonin. By the action of gastric juice, natural or artificial, they are converted first into syntonin, then into peptone.

V.—Amyloid—is a pathological product, occurring in fine grains, resembling starch-granules in appearance, in the membranes of the brain and cord, in waxy and lardaceous liver, and in the walls of the blood-vessels. Its composition is that of the albuminoids, from which it differs in being colored red by iodin; violet or blue by iodin and H_2SO_4. Soluble in HCl with formation of syntonin; and in alkalies. It is not attacked by the gastric juice, and is not as prone to putrefaction as the other albuminoids.

VI.-VII.—Acid-albumins and Alkali-albumins—These substances resemble each other so closely that they have been considered by some writers as identical. They are, however, distinct substances, and while acid-albumin may be readily transformed into alkali-albumin by the action of alkalies, the reverse transformation is not possible. The change of the albumin in conversion into alkali-albumin is attended by the separation of sulfur as alkaline sulfid and causes a deeper modification of the molecule than that which occurs in the formation of acid-albumin.

Alkali-albumins.—If a concentrated solution of caustic potash be added to white of egg, a compact, translucent jelly is formed in a few moments, and similar jellies are produced by other alkalies or from other albuminoids. These jellies dissolve in H_2O, and from these solutions the alkali-albumin is precipitated by dilute acetic acid.

When freshly precipitated, alkali-albumin is in white flocks, distinctly acid to litmus, not absolutely insoluble in H_2O, but still not sufficiently soluble to communicate to it an acid reaction, and not more readily soluble in solution of NaCl. It is easily soluble in excess of caustic alkali solution or in solutions of disodic phosphate or sodium carbonate. Solutions of alkali-albumin in solutions containing a minimum of alkali are distinctly acid in reaction, and are coagulated by a temperature somewhat above 100° (212° F.), or by the addition of excess of NaCl. It is probable that each albumin yields a different alkali-albumin, and also that different products may be obtained from the same albumin, as it has been observed that on dissolving precipitated alkali-albumin in an alkali four or five times each successive solution is attended by the formation of an alkaline sulfid.

Acid-albumins—Syntonins.—The term *acid-albumin* was first applied to the product obtained by the simultaneous action of an acid and a large excess of a neutral salt on an albuminoid, and the term *syntonin* to the product similarly obtained from myosin. The two terms are now indifferently applied to a product obtained from an albuminoid by the action of an acid.

The acid-albumins are produced from the albuminoids by the action of dilute acids, either added in solution or by passing air charged with acid vapors through solutions of the albuminoids or by floating dialysors containing albuminous solutions on dilute acid solutions. They are precipitated from their solutions in the form of flocculent jellies by alkalies, or, with a minimum of free acid, by dilution with H_2O.

They are white, gelatinous, translucent, soluble in HCl 1:1,000, but less soluble after prolonged contact with H_2O, soluble in alkaline solutions, and are precipitated from their solutions by neutral salts, but not by heat. They are precipitated from alkaline solutions by a current of CO_2.

VIII. ALBUMOSES—PROPEPTONES—are transitory products produced during peptic and pancreatic digestion of albuminoids, intermediate between the acid-albumins and the peptones. They differ from the peptones in that they are precipitated by acetic acid and sodium chlorid, by nitric acid and by many metallic salts, and from the true albumins in the remarkable quality of their precipitates, which dissolve when heated and reappear on cooling. It is probable that each albuminoid produces its own albumose.

Hemialbumose—*Propeptone*—is the product of the peptic digestion of fibrin, and exists in abundance in the stomach during the digestion of meat, as well as in the blood during digestion. It has also been obtained from marrow, pancreas, spleen, liver, kidneys, lungs, milk, spermatic fluid, and pathologically in the urine in osteomalachia, scarlet fever, and nephritis.

By the peptic digestion of fibrin two products may be obtained; one: *acid hemialbumose*, which still contains 5% of acetic acid, which is a yellowish powder, soluble in H_2O and in hot dilute alcohol. It is precipitated from aqueous solution by excess of solid NaCl. This precipitate redissolves in a small quantity of hot H_2O and is not precipitated on cooling. Neither pure hemialbumose and salt water, nor acid hemialbumose and pure H_2O exhibit this solubility, which requires the concurrent action of hemialbumose, acid, and salt. By gradually adding NaCl to a clear solution of acid hemialbumose in salt water an increasing precipitation is produced, which disappears on addition of acid, until the proportion of NaCl reaches 4%, when the alternation of precipitation and solution ceases. Nitric acid forms a precipitate in solutions of acid hemialbumose, which dissolves with an intense yellow color on heating, and is deposited again on cooling. It is precipitated by pyrogallic acid, the deposit redissolving on heating. With KHO and $CuSO_4$ it gives a violet color. Its solutions precipitate with phospho-molybdic acid, tannin, and with acetic acid and ferrocyanid. With Millon's reagent it gives a deep red solution, except in presence of excess of NaCl.

If acid hemialbumose solution be exactly neutralized, concentrated, and dialysed, *pure hemialbumose* is obtained as a white powder insoluble in H_2O and in saline solutions.

Other albumoses are produced by the action of natural or artificial gastric juice upon egg albumin, upon globulins (*globuloses*), upon vitellin (*vitelloses*) and upon casein (*caseoses*).

IX.—PEPTONE—ALBUMINOSE—is the product of the action of the gastric and pancreatic juices upon albuminoids during the process of digestion. It is soluble in H_2O, insoluble in alcohol and in ether. Its watery solution is neutral, not precipitable by acids or alkalies, or by heat when faintly acid. Alcohol precipitates it in white, casein-like flocks, which, if slowly heated to 90° (194° F.), while still moist form a transparent, yellowish liquid, and, on cooling, an opaque, yellowish, glassy mass. It has a greater power than other albuminoids of combining with acids and bases.

The most important character of peptone, in which it differs from other albuminoids, is that it is readily dialyzable. Its presence in the blood has not been demonstrated, and it is probable that immediately upon its entrance into the circulation it is converted into albuminoids resembling, yet differing from, those from which it was derived.

Peptone is produced by the action of many chemical reagents upon albuminoids; and also as one of the first products of putrefaction. When produced by putrefaction, or by artificial digestion, it is accompanied by **peptotoxin**, a crystallizable and actively poisonous substance.

It has been claimed that the gastric digestion of different albuminoids produces, not a single substance, but a distinct peptone for each albuminoid. If such be the case, and the present state of our knowledge does not permit of a definite answer to the question, these bodies are very closely related.

Peptone responds to the general reactions for the albuminoids (see p. 475), from which it may be distinguished by the *biuret reaction*. If a mere trace of $CuSO_4$ solution be added to a solution of peptone and then KHO or NaHO solution, a purple or reddish-violet color is produced. A similar appearance is produced with acid albumins.

X.—PROTEIDS—**Hæmoglobin and its Derivatives**—*Hæmatocrystallin.*—The coloring matter of the blood is a highly complex substance, resembling the albuminoids in many of its properties, but differing from them in being crystallizable and in containing iron.

Hæmoglobin exists in the red-blood corpuscles in two conditions of oxidation; in the form in which it exists in arterial blood it is loosely combined with a certain quantity of oxygen, and is known as **oxyhæmoglobin**. The mean of many nearly concording analyses shows its composition to be $C_{600}H_{960}N_{154}FeS_3O_{179}$. When obtained from the blood of man and from that of many of the lower animals, it crystallizes in beautiful red prisms or rhombic plates; that from the blood of the squirrel in hexagonal plates; and that from the guinea-pig in tetrahedra. The crystals are always doubly refracting. It may be dried in vacuo at 0° (32° F.); if thoroughly dried below 0° (32° F.), it may be heated to 100° (212° F.) without decomposition, but the presence of a trace of moisture causes its decomposition at a much lower temperature. Its solubility in water varies with the species of animal from whose blood it was obtained; thus, that from the guinea-pig is but sparingly soluble, while that from the pig is very soluble. It is also dissolved unchanged by very weak alkaline solutions, but is decomposed by acids or salts having an acid reaction.

Hæmoglobin, or **reduced hæmoglobin,** is formed from oxyhæmoglobin in the economy during the passage of arterial into venous blood; and by the action of reducing agents, or by boiling its solution at 40° (104° F.) in the vacuum of the mercury pump.

Oxyhæmoglobin is of a much brighter color than the reduced, and has a different absorption spectrum. The spectrum of oxyhæmoglobin varies with the concentration. In concentrated solutions the light is entirely absorbed, in more dilute solutions the spectrum 10, Fig. 16, is observed, and in still further dilutions 11, Fig. 16; in which the band at D is narrower, darker, and more sharply defined than the other. In highly diluted solution the band at D is alone visible. The spectrum of hæmoglobin consists of a single band much broader and fainter than either of the oxyhæmoglobin bands (12, Fig. 16). (See p. 22.)

Hæmoglobin, in contact with O or air, is immediately converted into oxyhæmoglobin. With CO it forms a compound resembling oxyhæmoglobin in the color of its solution, but in which the CO cannot be replaced by O; for which reason hæmoglobin, once combined with CO, becomes permanently unfit to fulfil its function in respiration (see p. 317).

When a solution of oxyhæmoglobin is boiled, it becomes turbid, and a dirty, brownish-red coagulum is deposited; the hæmoglobin has been decomposed into an albuminoid (or mixture of albuminoids), called by Preyer **globin,** and **hæmatin.** The latter, at one time supposed to be the blood-coloring matter, is a blue-black substance, having a metallic lustre and incapable of crystallization. It is insoluble in water, alcohol, ether, and dilute acids; soluble in alkaline solutions. It has the composition $C_{68}H_{70}N_8Fe_2O_{10}$. Its alkaline solutions exhibit the spectrum 13, Fig. 16. Although itself uncrystallizable, hæmatin combines with HCl to form a compound which crystallizes in rhombic prisms, and which is identical with the earliest known crystalline blood-pigment, **hæmin,** or **Teichmann's crystals.**

When reduced hæmoglobin is decomposed as above, in the absence of oxygen, hæmatin is not produced, but a substance identical with that called **reduced hæmatin,** and called by Hoppe-Seyler **hæmocromogen;** whose spectrum is shown in 14, Fig. 16.

If a solution of hæmoglobin be exposed for some time to air it changes in color from red to brownish, and assumes an acid reaction; it then exhibits the spectrum 15, Fig. 16, due to the production of **methæmoglobin,** probably a stage in the conversion of hæmoglobin into hæmatin and globin.

Milk casein—the most abundant of the albuminoids of the milk of mammalia, closely resembles alkali albumins, from which it differs in being coagulated by rennet in the presence of sodium phosphates, and in containing about 0.8% of phosphorus, which it loses by prolonged boiling with H_2O.

Casein, precipitated from cow's milk by acetic acid, and purified by washing with H_2O, solution in very dilute NaHO, precipitation with acetic acid, washing with alcohol and ether and drying, is a snow-white powder, almost insoluble in pure H_2O, soluble in alkalies and alkaline phosphates and carbonates. It is distinctly acid in reaction and decomposes the carbonates of Ca, Mg and Ba, suspended in H_2O, with evolution of CO_2. It also dissolves in lime or baryta water, and the solutions so formed do not coagulate when boiled.

Dilute acids precipitate casein from its solutions, the precipitate being soluble in an excess. Casein is also coagulated from neutral, acid, or alkaline solution by rennet (the product of the fourth stomach of the calf) at 40° (104° F.) by a process which differs from the precipitation by acids. If casein be precipitated by rennet from boiled milk the coagulum, in place of being compact as it is with unboiled milk, is light and finely flocculent. The coagulating action of rennet requires the presence of the mineral salts existing in milk, and is not manifested with milk which has been subjected to dialysis nor with a solution of pure casein in soda or in an alkaline phosphate. But a strong solution of casein in lime water, after neutralization with phosphoric acid, is coagulated by rennet more readily than milk.

The coagulation of casein is probably a decomposition into two other albuminoids, one, more abundant, which constitutes the coagulum (cheese), which is the more insoluble the greater the proportion of calcium phosphate in the liquid from which it was precipitated; the other soluble.

The casein in human milk and of mare's milk is very imperfectly coagulated in very fine flocks by acids and by rennet, in a form very different from the dense coagulum obtained from cow's milk. This difference is not due to the casein itself, which seems to be identical in the different varieties of milk, but to the existence of a larger proportion of calcium salts in the milk of the cow.

Milk.—The secretion of the mammary gland is water holding in solution casein, albumin, lactose, and salts; and fat and casein in suspension. **Cream** consists of the greater part of the fat, with a small proportion of the other constituents of the milk. **Skim-milk** is milk from which the cream has been removed. **Butter-milk** is cream from which the greater part of the fat has been removed, and consequently is of about the same composition as skim-milk.

The composition of milk differs in animals of different species:

	Human.	Cow.	Goat.	Sheep.	Ass.	Mare.	Cream	Condensed Milk.
Water....	88.35	84.28	86.85	83.30	89.01	90.45	45.99	25.68
Solids....	11.65	15.72	13.52	16.60	10.99	9.55	54.01	74.32
Casein....	3.15	3.57	2.53	5.73	3.57	2.53	6.33	16.83
Albumin..		0.78	1.26					
Fat	3.87	6.47	4.34	6.05	1.85	1.31	43.97	10.27
Lactose...	4.37	4.34	3.78	3.96	5.05	5.43	3.28	44.33*
Salts	0.26	0.63	0.65	0.68		0.29	0.42	2.80

* Including 28.98 parts of cane-sugar.

The composition of cows' milk varies considerably, according to the age, condition, breed, and food of the cow; to the time and frequency of milking; and to whether the sample examined is from the first, middle, or last part of each milking.

Cows' milk is very frequently adulterated, both by the removal of the cream and the addition of water. For ordinary purposes, the purity of the milk may be determined by observing the sp. gr. and the percentage of cream by the lactometer and creamometer, *neither of which, used alone, affords indications which can be relied upon.* The sp. gr. should be observed at the temperature for which the instrument is made, as in a complex fluid such as milk no valid correction for temperature is practical; it ranges in pure milk from 1027 to 1034, it being generally the lower in milk which has been watered, and in such as is very rich in cream, and the higher the less cream is present. The average sp. gr. is 1030; the average percentage of cream 13.

The percentage of cream is determined by the creamometer; a glass tube about a foot long and half an inch in diameter, the upper fifth (excluding about an inch from the top) being graduated into hundredths of the whole, the 0 being at the top. To use it, it is simply filled to the 0 with the milk to be tested, set aside for twenty hours and the point of separation between milk and cream read off. It should be above eight per cent.

This method of determining the purity of milk, although sufficient for ordinary purposes, should not be considered as affording evidence upon which to base legal proceedings; in such cases nothing short of a chemical determination of the percentage of fats, and of solids not fat, should be accepted as evidence of the impurity of milk.

Serum-casein—is a substance obtained from blood-serum diluted with 10 volumes of H_2O, freed from paraglobulin by CO_2, and from albumin by acetic acid and heat. It is insoluble in salt solutions, slowly soluble in a one-per-cent. solution of sodium hydroxid. Such a solution is partially precipitated by CO_2, almost completely by acetic acid, and completely by treating with excess of powdered sodium chlorid; incompletely soluble in dilute HCl.

Gluten-casein—that portion of crude gluten (a soft, elastic, grayish material best obtained from flour) which is insoluble in alcohol, hot or cold; **Legumin**—a sparingly soluble albuminoid obtained from peas, beans, etc.; and **Conglutin**—a substance closely related to legumin and to **gliadin,** but differing from them in some characters, obtained from almonds, are three vegetable albuminoids resembling casein.

They are insoluble in pure water, readily soluble in dilute alkaline solutions, from which they are precipitated by acids and by rennet.

Mucin—is a substance containing no S and existing in the different varieties of mucus, in certain pathological fluids, in the bodies of mollusks, in the saliva, bile, connective tissues, etc. Its solutions, like the fluids in which it occurs, are viscid. It is precipitated by acetic acid and by HNO_3, but is dissolved by an excess of the latter; it dissolves readily in alkaline solutions, and swells up in H_2O, with which it forms a false solution. It is not coagulated by heat.

Chondrin is the name given to a substance obtained from cartilaginous tissue and supposed to be distinct from gelatin. It is probably a mixture of gelatin and mucin.

XI.—ALBUMINOIDS.—**Keratin**—is the organic basis of horny tissues, hair, nails, feathers, whalebone, epithelium, tortoise-shell, etc. It is probably not a distinct chemical compound, but a mixture of several closely related bodies.

Keratin, prepared by boiling quills in strong acetic acid for 24 hours, filtering and evaporating over the water-bath, is now used as a coating for pills intended to pass through the stomach without solution; the coating being insoluble in the acid gastric secretion, but soluble in the alkaline liquids of the intestine.

Elastin—is obtained from elastic tissues by successive treatment with boiling alcohol, ether, water, concentrated acetic acid, dilute potash solution, and water. It is fibrous, yellowish; swells up in water and becomes elastic; soluble with a brown color in concentrated potash solution. It contains no S, and on boiling with H_2SO_4 yields glycol.

Fibroin—**Sericin**—is obtained from silk by removal of fat, albumin, coloring matters, etc., by the proper solvents. It dissolves, like cellulose, in ammonio-sulfate of copper solution. It does not contain S, and resembles gelatin in its chemical composition.

XII.—GELATINOUS SUBSTANCES.—**Collagen.**—Bony tissue is made up mainly of tricalcic phosphate, combined with an organic material called *ossein*, which is a mixture of collagen, elastin, and an albuminoid existing in the bone-cells. Collagen also exists in all substances which, when treated with H_2O, under the influence of heat and pressure, yield gelatin. It is insoluble in cold H_2O, but by prolonged boiling is converted into gelatin, which dissolves. It is dissolved by alkalies.

Gelatin—obtained as above, from ossein, exists in the commercial product of that name, and in a less pure form in glue. When pure it is an amorphous, translucent, yellowish, tasteless substance, which swells up in cold H_2O, without dissolving, and forms, with boiling H_2O, a thick, sticky solution, which on cooling becomes, according to its concentration, a hard glassy mass or a soft jelly—the latter even when the solution is very dilute. It is insoluble in alcohol and ether, but soluble, on warming, in glycerin; the solution in the last-named liquid forms, on cooling, a jelly which has recently been applied to various contrivances for copying writing. A film of gelatin impregnated with potassium dichromate becomes hard and insoluble on exposure to sunlight.

TOXALBUMINS—are bodies belonging among the albuminoid substances and possessed of poisonous qualities. A few are the products of the vegetable world, such as **abrin,** the poisonous principle of jequirity, but most of those which have been studied are the products of bacterial action, putrefactive or pathogenic, upon animal albuminoids. Some are true albumins, others albumoses, others peptones. The chemistry of these substances, which are of great pathological interest, is still in its infancy. Among them may be noted: (1), **Mycoprotein**—a product of putrefactive bacteria; (2), a substance bearing some relation to serum albumin and supposed to be the poison of diphtheria; (3), an albuminoid obtained from the cultures of the pneumonia bacillus; (4), an albumose produced in the cultures of the anthrax bacillus; (5), **Toxopeptone**—a peptone found in cultures of the comma bacillus; (6), a toxalbumin found in cultures of the bacillus of tetanus.

ANIMAL CRYPTOLYTES.

SOLUBLE ANIMAL FERMENTS.

Under this head are classed substances somewhat resembling the albuminoids, of unknown composition, occurring in animal fluids, and having the power of effecting changes in other organic substances, the method of whose action is undetermined.

Ptyalin—is a substance occurring in saliva, and having the power of converting starch into dextrin and a sugar resembling glucose (ptyalose), in liquids having an alkaline, neutral, or faintly acid reaction.

Pepsin—is the cryptolyte of the gastric juice. Attempts to separate it without admixture of other substances have hitherto proved fruitless; nevertheless, mixtures containing it and exhibiting its characteristic properties more or less actively have been obtained by various methods. The most simple consists in macerating the finely divided mucous membrane of the stomach in alcohol for 48 hours, and afterward extracting it with glycerin; this forms a solution of pepsin, which is quite active, and resists putrefaction well, and from which a substance containing the pepsin is precipitated by a mixture of alcohol and ether.

If pepsin be required in the solid form, it is best obtained by Brücke's method. The mucous membrane of the stomach of the pig is cleaned and detached from the muscular coat by scraping; the pulp so obtained is digested with dilute phosphoric acid at 38° (100°.4 F.), until the greater part of it is dissolved; the filtered solution is neutralized with lime-water; the precipitate is collected, washed with H_2O, and dissolved in dilute HCl; to this solution a saturated solution of cholesterin, in a mixture of 4 pts. alcohol and 1 pt. ether, is gradually added; the deposit so formed is repeatedly shaken with the liquid, collected on a filter, washed with H_2O and then with dilute acetic acid, until all HCl is removed; it is then treated with ether and H_2O: the former dissolves cholesterin and is poured off, the latter the pepsin; after several shakings with ether the aqueous liquor is evaporated at 38° (100°.4 F.), when it leaves the pepsin as an amorphous, grayish-white substance; almost insoluble in pure H_2O, readily soluble in acidulated H_2O; probably forming a compound with the acid, which possesses the property of converting albuminoids into peptone.

The so-called *Pepsina porci* is either the calcium precipitate obtained as described in the first part of the above method, or, more commonly, the mucous membrane of the stomach of the pig, scraped off, dried, and mixed with rice-starch or milk-sugar.

Pancreatin.—Under this name, substances obtained from the pancreatic secretion, and from extracts of the organ itself, have been described, and to some extent used therapeutically. They do not, however, contain all the cryptolytes of the pancreatic juice, and in many instances are inert albuminoids. The actions of the pancreatic juice are: (1) it rapidly converts starch, raw or hydrated, into sugar; (2) in alkaline solution—its natural reaction—it converts albuminoids into peptone; (3) it emulsifies neutral fats; (4) it decomposes fats, with absorption of H_2O and liberation of glycerin and fatty acids.

The pancreatic secretion probably contains a number of cryptolytes—certainly two. The one of these to which it owes its peptone-forming power has been obtained in a condition of comparative purity by Kühne, and called by him **trypsin**; in aqueous solution it digests fibrin almost immediately, but it exerts no action upon starch.

The diastatic (sugar-forming) cryptolyte of the pancreatic juice has not been separated, although a glycerin extract of the finely divided pancreatic tissue contains it, along with trypsin.

ANIMAL COLORING MATTERS.

Biliary pigments.—There are certainly four, and probably more, pigmentary bodies obtainable from the bile and from biliary calculi, some of which consist in great part of them.

Bilirubin—$C_{32}H_{36}N_4O_6$—is, when amorphous, an orange-yellow powder, and when crystalline, in red rhombic prisms. It is sparingly soluble in H_2O, alcohol, and ether; readily soluble in hot chloroform, carbon disulfid, benzene, and in alkaline solutions. When treated with HNO_3 containing nitrous acid, or with a mixture of concentrated HNO_3 and H_2SO_4, it turns first green, then blue, then violet, then red, and finally yellow. This reaction, known as Gmelin's, is very delicate, and is used for the detection of bile-pigments in icteric urine and in other fluids.

Biliverdin—$C_{32}H_{36}N_4O_8$—is a green powder, insoluble in H_2O, ether, and chloroform, soluble in alcohol and in alkaline solutions. It exists in green biles, but its presence in yellow biles or biliary calculi is doubtful. It responds to Gmelin's test. In alkaline solution it is changed after a time into biliprasin.

Bilifuscin—$C_{16}H_{20}N_2O_4$—obtained in small quantity from human gall-stones, is an almost black substance, sparingly soluble in H_2O, ether, and chloroform; readily soluble in alcohol and in dilute alkaline solutions. Its existence in the bile is doubtful.

Biliprasin—$C_{16}H_{22}N_2O_6$ (?)—exists in human gall-stones, in ox-gall, and in icteric urine. It is a black, shining substance, insoluble in H_2O, ether, and chloroform; soluble in alcohol and in alkaline solutions.

Urobilin—Hydrobilirubin—$C_{32}H_{40}N_4O_7$.—Under the name urobilin, Jaffé described a substance which he obtained from dark, febrile urine, and which he regarded as the normal coloring matter of that fluid; subsequently he obtained it from dog's bile and from human bile, from gall-stones and from fæces. **Stercobilin,** from the fæces, is identical with urobilin.

Urinary pigments.—Our knowledge of the nature of the substances to which the normal urinary secretion owes its color is exceedingly unsatisfactory. Jaffé in his discovery of urobilin shed but a transient light upon the question, as that substance exists in but a small percentage of normal urines, although they certainly contain a substance readily convertible into it. Besides the substance convertible into urobilin, and sometimes urobilin itself, human and mammalian urines contain at least one other pigmentary body, **uroxanthin,** or **indigogen.** This substance was formerly considered as identical with **indican,** a glucosid existing in plants of the genus *Isatis,* which, when decomposed, yields, among other substances, indigo-blue. Uroxanthin, however, differs from indican in that the former is not decomposed by boiling with alkalies, and does not yield any glucose-like substance on decomposition; the latter is almost immediately decomposed by boiling alkaline solutions, and, under the influence of acids and of certain ferments, yields, besides indigo-blue, **indiglucin,** a sweet, non-fermentable substance, which reduces Fehling's solution.

Uroxanthin is a normal constituent of human urine, but is much increased in the first stage of cholera, in cases of cancer of the liver, Addison's disease, and intestinal obstruction. It has also been detected in the perspiration.

In examining the color of urine it should be rendered strongly acid with HNO_3 or HCl, and allowed to stand six hours to liberate combined pigment, and then examined by transmitted light in a beaker three inches in diameter.

Melanin is the black pigment of the choroid, melanotic tumors, and skin of the negro; and occurs pathologically in the urine and deposited in the air-passages.

PART III.

LABORATORY TECHNICS.

CHEMISTRY is essentially a science of experiment; and not only is a knowledge of its truths much more rapidly and easily acquired by the student through the actual performance of experiment, than by any amount of reading or attendance upon illustrated lectures; but it is even doubtful whether a thorough knowledge of the facts and theories of the science can be obtained in any other way than by personal observation.

A description of the various manipulations of the general chemical laboratory would fill volumes. A short account of the more prominent of those required in a study of rudimentary chemistry, and in those processes of analysis which are likely to be of service to the physician will, we believe, not be out of place in a work of this nature.

GENERAL RULES.

"Cleanliness," said John Wesley, "is next to godliness." The chemist, whatever his supply of godliness, must be thoroughly imbued with the spirit of cleanliness; not so much as regards himself, for he who fears to soil his fingers is not of the material whereof chemists are made, but as regards the vessels and reagents which are his tools. Any substance foreign to the matter under examination and the reagents used, whatever be its nature, is *dirt* to the chemist.

Glass vessels should always be cleaned as soon as possible after using, as foreign substances are much more readily removed then than after they have dried upon the glass. Usually rinsing with clear water, and friction with a probang or bottle brush is sufficient; greasy and resinous substances may be removed with KHO solution; and other adherent deposits usually with HCl or HNO_3; the alkali or acid being removed by clear water. After washing, the vessels are drained upon a clean surface, and are not to be put away unless *perfectly bright.*

Order and system are imperative, especially if several operations are conducted at the same time. If there be "a place for everything, and everything in its place," much time will be spared. If a process be of such a nature that it requires a number of vessels, each vessel should be numbered with a small gum label, or by scratching on the glass with a writing diamond, and the notes of the operation should indicate the stage of the process in each vessel.

The habit of taking full and systematic notes of experiments and analyses in a book kept especially for the purpose, is one which the student cannot contract too early. He will be surprised, in looking over and comparing his notes, at the amount of information he will have collected in a short time; much of which, had the memory been trusted to, would have been lost.

REAGENTS.

The stock of reagents required varies, of course, with the nature of the work to be done; from the small number required in urinary analysis, to the array on the shelves of a fully-appointed analytical laboratory.

The liquid reagents and solutions should always be kept in glass-stoppered bottles (the 4½ ℥ bottles, with labels blown in the glass, serve very well). The solid reagents may be kept in cork-stoppered or, preferably, glass-stoppered bottles. The ordinary glass stoppers should never be laid upon the table, lest they take up particles of foreign matter and contaminate the contents of the bottle; but should be held between the third and little fingers of the right hand.

The reagents required for ordinary urinary analysis are:

Nitric acid,
Sulfuric acid,
Acetic acid,
Potassium hydroxid,
Ammonium hydroxid,
Cupric sulfate,
Fehling's solution,
Test papers.

Those required for ordinary qualitative analysis are:

Hydrochloric acid,
Nitric acid,
Sulfuric acid,
Acetic acid,
Hydrogen sulfid,
Ammonium sulfid,
Ammonium hydroxid,
Potassium hydroxid,
Ammonium chlorid,
Ammonium carbonate,
Ammonium oxalate,
Sodium carbonate,
Hydro-disodic phosphate,
Potassium ferrocyanid,
Potassium ferricyanid,
Potassium sulfocyanate,
Potassium carbonate,
Potassium chromate,
Barium chlorid,
Calcium sulfate,
Magnesium sulfate,
Cupric sulfate,
Argentic nitrate,
Mercuric chlorid,
Plumbic acetate,
Ferric chlorid,
Platinic chlorid.

The chemicals must be C. P. (= chemically pure); and the solutions must be made with distilled H_2O. It is well to put corresponding numbers on each bottle and stopper to prevent their becoming mixed in cleaning.

GLASS TUBING.

The tubing used in making all usual connections and apparatus is the soft German or American tubing. When the tube is to be strongly heated, Bohemian tubing must be used. The fashioning of tubing of the diameter generally used for gas connections is a simple matter.

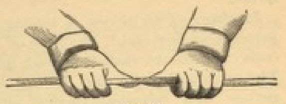


FIG. 43.

Cutting into desired lengths is accomplished by making a scratch with a triangular file at the desired point; holding the tube as shown in Fig. 43; and partly drawing, and partly bending it.

Larger glass surfaces may be cut in any required direction, by first making a deep scratch with the file; starting the break by bringing in contact with scratched spot a piece of red-hot glass tubing; and leading the break in the desired direction by applying a heated piece of ¼-inch iron wire, whose end is filed off square, moved in the desired direction in advance of the crack. Cut ends of tubing should always be rendered smooth by heating them to incipient fusion, or by trimming with a file.

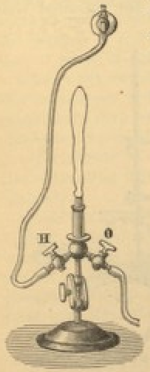


FIG. 44.

Glass surfaces may be filed without danger of breaking, if the file be moistened with a saturated solution of camphor in oil of turpentine. Holes may also be bored through glass with the sharp edges of a broken rat-tail file, kept moistened with the camphor-turpentine mixture, the hole being started from both surfaces and meeting in the middle.

Bending is done by heating the tube at the desired point in an ordinary gas flame (not a blow-pipe flame), without rotating it, until softened; removing from the flame and bending *toward* that surface which was nearest the orifice of the gas-jet.

Closing.—For this and other operations with glass tubing, the glass-blower's flame, obtained with a burner (Fig. 44) which permits of the injection of air into the gas flame, is required. To make a test-tube a piece of tubing of the length of two test-tubes is drawn out at the middle (see below). The small end of each piece is then heated and the superfluous glass removed by a warm glass rod, which is brought into contact for an instant and then drawn away. The closed end is then heated, during rotation, until soft, and rendered hemispherical by gently blowing into the open end. The open end is then heated, and, while hot, formed into a lip by a circular motion with a hot iron wire.

Drawing out consists in heating the tube at the point desired, during rotation, and drawing it apart after removal from the flame.

Joining.—Two pieces of tubing of different diameters may be joined end for end if they be of the same kind of glass. The ends of each are closed, heated, and blown out into thin bulbs. The bulb is then broken off, the ends heated, pressed firmly together, and reheated during alternate pressure and drawing apart, and gentle blowing into one end while the other is closed, until an even joint is obtained.

Stirring-rods are made by cutting glass rods to the required length and rounding the ends by fusion.

COLLECTION OF GASES.

Gases are collected over the *pneumatic trough*, by *displacement* of air; or over the *mercurial trough.*

In the pneumatic trough (Fig. 45) gases are collected over water in bell jars filled with that liquid. This method of collection can only be used for insoluble or sparingly soluble gases.

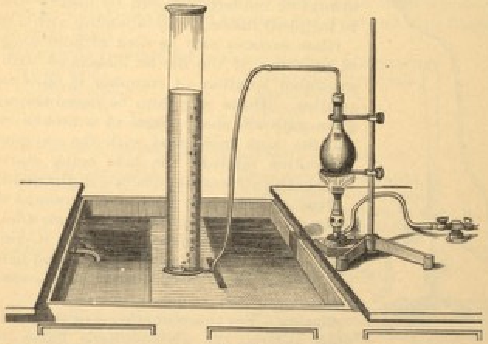


Fig. 45.

If heat have been used in the generation of the gas, the disengagement tube must be removed from the water *before* the heat is discontinued, to avoid an explosion.

Soluble gases are collected over mercury or by upward or downward displacement of air, according as they are without action on Hg, or heavier or lighter than air.

SOLUTION.

As the particles of liquids can be brought into closer contact than those of solids, reactions are usually facilitated by bringing the reagents into solution or into fusion.

At a given temperature solution of a solid is more rapid the greater the surface exposed to the solvent, *i.e.*, the greater the degree of subdivision.

Ordinary salts are ground to powder in Wedgwood or glass mortars. Very hard substances are first coarsely powdered in steel mortars, and then finely ground in agate mortars. Soft substances are best subdivided either by hashing, as in the case of muscular tissue, or by forcing through the meshes of a fine sieve, as in the case of white of egg, brain-tissue, etc.

When only certain constituents of the substance are to be dissolved, **percolation** may be resorted to. The substance to be extracted is packed in a percolator in such a manner that the extracting liquid filters through it slowly.

FIG. 46.

When the solvent is a volatile liquid—ether, chloroform, carbon disulfid—extraction is best accomplished in an apparatus such as that shown in Fig. 46, in which the liquid is boiled in A; the vapor passing through *a*, *b*, is liquefied in the condenser and flows back over the substance in B. The extract collects in A.

PRECIPITATION—DECANTATION—FILTRATION—WASHING.

When the conversion of an ingredient of a solution into an insoluble compound, and its separation from the liquid are desired, both the liquid and the reagent should be in clear solution, and the latter should be added to the former, which has been warmed. The vessel is then set in a warm place until the precipitate has subsided, a few drops of the precipitant are added to the clear liquid, and if no cloudiness be produced the precipitation is complete. Precipitation should be effected in Erlenmeyer flasks (Fig. 47) or in precipitating jars (Fig. 48), that the precipitate may not collect on the sides, and may be readily detached by the wash-bottle.

Precipitates are separated from the liquid in which they have been formed by *decantation* or *filtration*.

Decantation consists in allowing the precipitate to subside, and pouring off the supernatant liquid. It should always be employed as a preliminary to filtration, and is sometimes used exclusively, when the precipitate is washed by repeatedly pouring on clear water, and decanting it until it no longer contains any solid matter.


FIG. 47.

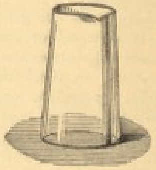


FIG. 48.

In pouring liquid from one vessel to another it should be guided by a glass rod, as shown in Fig. 49; the outer surface of the lip of the pouring vessel having been slightly greased.

Filtration is resorted to more frequently than decantation. Filters are made from muslin, paper, asbestos, or glass wool.

Muslin filters are only used for coarse filtration.

Paper filters are the most frequently used. For coarse work the ordinary gray or German white paper is used; but for analytic work a paper which leaves but a small amount of ash is required; the best now in the market is Schleicher & Schüll's Nos. 597 and 589. The filter should be taken of such size that when folded it will be smaller than the funnel in which it is to rest. It is folded across one diameter, and again over the radius at right angles to the first diameter; one of the four layers of paper, then seen at the circular portion of the filter, is separated from the other three, in such a way as to form a cone. The filter so formed is brought into the funnel, and, while held in position by a finger-nail over one of the folds, is wetted with water from the wash-bottle. After the paper has been brought in contact with the funnel by a glass rod, the liquid to be filtered is introduced, care being had not to overflow the filter, and to allow any supernatant liquid in the precipitating jar to pass through, before bringing the precipitate itself upon the filter. Funnels used for filtering should have an angle of 60°, and a long stem, the point of which is ground off at an acute angle.

Asbestos and glass wool plugs loosely introduced into the stem of a funnel, are used in filtering such liquids as would destroy paper.

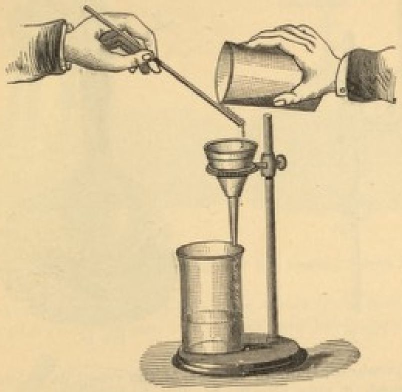


FIG. 49.

For filtrations which take place slowly the *filter-pump* is now extensively used. It is simply an appliance for exhausting the air in the stem of the funnel, and thus taking advantage of atmospheric pressure. A simple and effective form of pump is that shown in Fig. 50, in which the water (under 10 feet or more of pressure) enters at *a* and aspirates the air from *b* through *c*. When the pump is used a small cone of platinum foil must be placed at the apex of the funnel to support the point of the filter, which would otherwise be ruptured.

When the precipitate has been collected upon the filter, it must be *washed* until free from extraneous matter. This is effected by blowing into the tube *a* of the wash-bottle (Fig. 51), while the end of the tube *b* is held so as to deliver a *gentle* stream into the filter; care being had that the precipitate is not lost by spurting, overflowing, or *creeping* up the sides of the funnel. The completeness of the washing is *not to be guessed at*, but is to be judged by adding reagents, suitable to the case, to portions of the filtrate until they fail to cause a cloudiness.

FIG. 50.

FIG. 51.

If the precipitate adhere to walls of the vessel in which it has been formed, it may usually be detached by rubbing with a brush, formed by slipping a short section of rubber tube over the end of a stirring-rod, or, if this fail, the precipitate must be redissolved and reprecipitated by an appropriate solvent and precipitant.

EVAPORATION—DRYING—IGNITION.

Evaporations are usually conducted on the sand- or water-bath. The sand-bath is simply a flat, iron vessel, filled with sand and heated. By its use the heat is more evenly distributed than with the naked flame.

The water-bath, usually of the form shown at *a* Fig. 52, is used where the temperature is to be kept below 100° (212° F.). It should *always* be used in evaporating liquids containing organic matter, and care should be had that it does not become dry.

In cases where it is desired to boil an aqueous liquid in a glass or porcelain vessel; this is supported on a piece of wire gauze and a Bunsen burner or spirit lamp brought under it (Fig. 53). A piece of sheet-iron may be substituted for the wire gauze, with

FIG. 52.

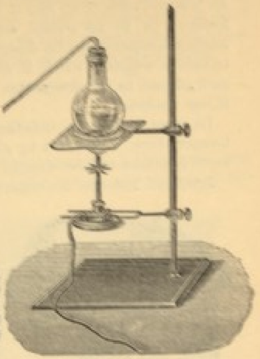


FIG. 53.

flat-bottomed vessels. The outside of the heated vessel must be *dry.*

In heating liquids in test-tubes, *the mouth of the tube must be held away from the person.* It is best held by a piece of thick

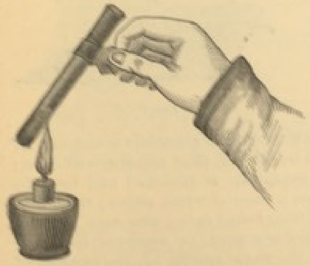


FIG. 54.

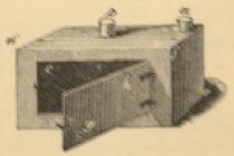


FIG. 55.

paper bent around the upper end of the tube (Fig. 54). The tube should be heated near, not at its bottom.

In no case should flame, or the sand of the sand-bath, come in contact with a glass vessel above the level of the liquid within.

Drying is always necessary as a preliminary to weighing, whether the substance is hygroscopic or not. It is usually effected in water-ovens (Fig. 55), if a temperature of 100° (212° F.) be sufficient; or in air-ovens, somewhat similarly constructed, if a higher temperature be desired. As a substance can never be accurately weighed while it is warm, it is removed from the oven and placed in the **desiccator** (Fig. 56), over H_2SO_4 or $CaCl_2$, until it has cooled.

In cases where the substance would be injured by elevation of temperature, it is dried by allowing it to remain in the desiccator until it ceases to lose weight.

Ignition has for its object the removal of organic matter by burning, and is conducted in platinum or porcelain crucibles. If a filter and precipitate are to be ignited, they are first well dried; as much as possible of the precipitate is detached and brought into the crucible, placed upon a sheet of white paper; the filter, with adherent precipitate, is then rolled into a thin cone, around which a piece of platinum wire is wound; by means of the platinum wire the filter is held in the flame and burnt; the remains of the filter are then added to the contents of the crucible, which is supported in the position shown in Fig. 57, in which it is heated, at first moderately, and the heat gradually increased to bright redness, at which it is maintained until no carbon remains. Before weighing, the crucible is to be cooled in the desiccator.

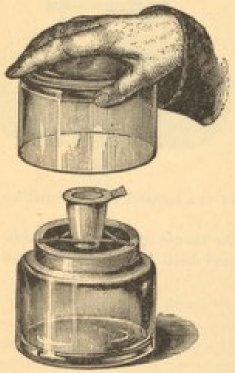


FIG. 56.

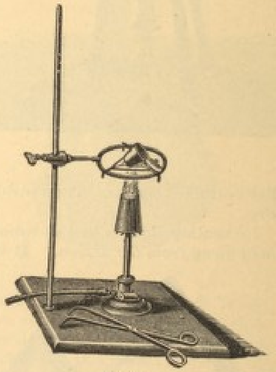


FIG. 57.

In igniting it must not be forgotten that mineral substances may be modified or lost. Carbon at high temperature deoxidizes easily reducible substances; alkaline chlorids are partly volatilized; mineral bases combined with organic acids are converted into carbonates. In every instance only that amount of heat which is required is to be applied. In some cases it is well to accelerate the oxidation by the addition of ammonium nitrate.

WEIGHING.

The balance (Fig. 58) should always be kept in a glass case, containing a vessel with $CaCl_2$, and in a situation protected from the fumes of the laboratory. The weights should be kept in a box by or in the balance case, which is to be closed when not in use.

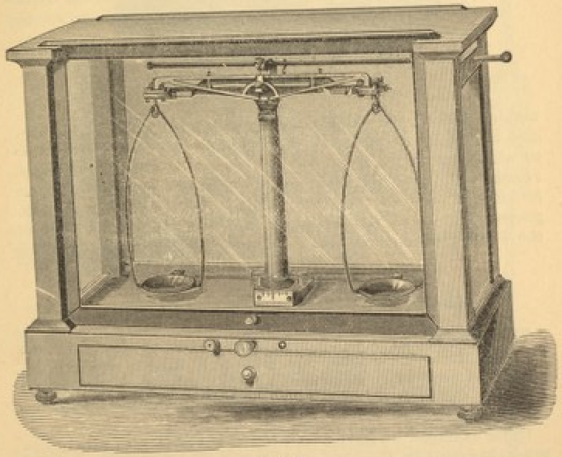


FIG. 58.

In weighing observe the following rules:

(1.) See that the balance is in adjustment before using, especially if more than one person use it. (2.) Always put the substance to be weighed in the same pan, usually the left-hand one, and the weights in the other. (3.) Never bring any chemical in contact with the pans, but have a pair of large watch-glasses of equal weight, one in either pan. Pieces of paper will *not* serve the purpose. (4.) Always put the balance out of action before adding anything to, or taking anything from, either pan. (5.) Never weigh anything warm. (6.) In weighing a substance which has been dried, do not consider the weight correct until two successive weighings, with an intervening drying of a half-hour, give identical results. (7.) In adding the weights, do so in regular order from above downward. (8.) In counting the weights, reckon the amount first by the empty holes in the box, and then tally in replacing the weights. (9.) Substances liable to absorb moisture from the air are to be weighed in closed vessels. Thus, when a filter and its adherent precipitate are to be weighed together, they must be placed between the two watch-glasses (Fig. 59) as soon as taken from the drying-oven; one of the watch-glasses being used to support the filter in the oven.

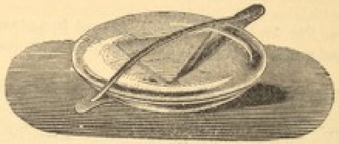


FIG. 59.

MEASURING—VOLUMETRIC ANALYSIS.

The principle upon which volumetric analysis is based is that by determining the volume of a solution of known strength, required to accurately neutralize another solution of unknown strength, the amount of active substance in the latter may be calculated.

If, for example, we have a solution of silver nitrate which contains 170 grams to the litre, and we find that 12 c.c. of this solution precipitate all the chlorin from 10 c.c. of a solution of NaCl, it follows that the NaCl solution contains 70.20 grams of that substance per litre, because:

$$\underset{170}{AgNO_3} + \underset{58.5}{NaCl} = \underset{85}{NaNO_3} + \underset{143.5}{AgCl}$$

and therefore each c.c. of the $AgNO_3$ solution will accurately precipitate 0.0585 grm. NaCl; but as it has required 12 c.c. of the $AgNO_3$ solution to neutralize 10 c.c. of the NaCl solution, the latter contains 0.0585×12=0.702 grm. NaCl, or 1,000 contain 0.702×100=70.20 grms. NaCl.

It is obvious, therefore, that the value of volumetric methods depends, among other things, greatly upon the accuracy of the **standard solutions,** as the solutions of known strength are called, and upon the accuracy of the measurements of volume.

A standard solution containing in a litre of liquid a number of grams of the active substance, equal to its molecular weight, is a **normal solution**; one containing $\frac{1}{10}$ that amount is a **decinormal solution.**

An **indicator** is a substance which, by some characteristic reaction (*end reaction*), which will occur only when the substance to be determined has been completely removed, indicates the point when a proper volume of the standard solution has been added.


FIG. 60.


FIG. 61.

The apparatus required for volumetric analysis consists of:

(1.) A **litre-flask** (Fig. 60); a flask of such size that, when filled to the mark on the neck, at the temperature for which it has been graduated, it contains exactly 1,000 c.c. of water.

(2.) A **burette,** which is a glass tube graduated into cubic centimetres, and having a stopcock or pinch-cock at its lower extremity.

(3.) A series of **pipettes** (Fig. 61), which are glass tubes, having bulbs blown upon them of such size that when they are filled to a mark on the tube above the bulb, they contain a given number of cubic centimetres.

(4.) Small beakers; stirring-rods; bottles for standard solutions.

In making a standard solution the object to be attained is to have a solution, one litre of which shall contain a known quantity of the active material. If then in the formula for the normal solution of silver nitrate:

Silver nitrate....................	170 grams.
Distilled water................	1,000 c.c.

we weigh out the $AgNO_3$ on the one hand, and measure the H_2O on the other, and mix the two, we will have, not what is desired, a solution containing 170 grms. $AgNO_3$ in 1,000 c.c., but a solution of 170 grms. $AgNO_3$ in 1,000+x c.c. of liquid, in which x=the volume occupied by the $AgNO_3$. Therefore, in making standard solutions, weigh out the active substances; introduce them into the litre-flask; and then fill that to the mark with H_2O. Too much caution cannot be used in having pure chemicals and making accurate weighings in preparing volumetric solutions; indeed, the great disadvantage of the use of these methods by physicians is that the solutions which they use are carelessly prepared and, consequently, the time which they spend in obtaining inaccurate, but seemingly accurate, results is worse than thrown away.

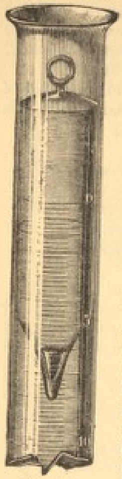


FIG. 62.

To use a volumetric solution it is poured into the burette, whose stopcock has been closed, until above the 0 mark; the stopcock is then slightly opened so as to expel *all* air from the delivery tube. The float (Fig. 62) is now introduced from above, and touched with a glass rod to free it from adhering air-bubbles; and the solution allowed to flow out from below until the mark on the float is opposite the 0 of the burette. All is now ready for use; a given quantity of the solution to be analyzed is measured into a pipette and placed in a beaker, a few drops of the indicator solution are added, and the standard solution allowed to flow in until the end reaction is reached. The reading of the burette is then taken and the calculation made.

SCHEME FOR DETERMINING THE COMPOSITION OF URINARY CALCULI.

1. Heat a portion on platinum foil :
a. It is entirely volatile 2
b. A residue remains.. 5

2. Moisten a portion with HNO_3 ; evaporate to dryness at low heat ; add NH_4HO :
a. A red color is produced...................................... 3
b. No red color is produced.................................... 4

3. Treat a portion with KHO, without heating :
a. An ammoniacal odor is observed..*Ammonium urate.*
b. No ammoniacal odor. ....*Uric acid.*

4. *a.* The HNO_3 solution becomes yellow when evaporated ; the yellow residue becomes reddish-yellow on addition of KHO, and, on heating with KHO, violet-red ....*Xanthin.*
b. The HNO_3 solution becomes dark brown on evaporation. ....*Cystin.*

5. Moisten a portion with HNO_3 ; evaporate to dryness at low heat ; add NH_4HO :
a. A red color is produced...................................... 6
b. No red color is produced.,.................................. 9

6. Heat before the blow-pipe on platinum foil :
a. Fuses 7
b. Does not fuse.. 8

7. Bring into blue flame on platinum wire :
a. Colors flame yellow..................*Sodium urate.*
b. Colors flame violet................*Potassium urate.*

8. The residue from 6 :
a. Dissolves in dil. HCl with effervescence ; the solution forms a white ppt. with ammonium oxalate..............................*Calcium urate.*
b. Dissolves with slight effervescence in dil. H_2SO_4 ; the solution, neutralized with NH_4HO, gives a white ppt. with HNa_2PO_4... .*Magnesium urate.*

9. Heat before the blow-pipe on platinum foil :
a. It fuses...........*Ammonio-magnesian phosphate.*
b. It does not fuse.. 10

10. The residue from 9, when moistened with H_2O, is :
a. Alkaline.. 11
b. Not alkaline........ ....*Tricalcic phosphate.*

11. The original substance dissolves in HCl :
a. With effervescence..............*Calcium carbonate.*
b. Without effervescence.............*Calcium oxalate.*

Note.—A fresh portion of the powdered calculus is to be taken for each operation except where otherwise stated.

APPENDIX.

APPENDIX A.

ORTHOGRAPHY AND PRONUNCIATION OF CHEMICAL TERMS.

In 1887 a committee was appointed by the American Association for the Advancement of Science, to consider the question of securing uniformity in the spelling and pronunciation of chemical terms. The work of this committee extended through the four following years. As a result of widespread correspondence and detailed discussion at the annual meetings of the Chemical Section of the American Association the following rules have been formulated and adopted by the Association.

A circular embodying the substance of these rules has been issued by the Bureau of Education at Washington, and distributed among chemists and teachers of chemistry, with a recommendation of their general adoption.

GENERAL PRINCIPLES OF PRONUNCIATION.

1. The pronunciation is as much in accord with the analogy of the English language as possible.
2. Derivatives retain as far as possible the accent and pronunciation of the root word.
3. Distinctly chemical compound words retain the accent and pronunciation of each portion.
4. Similarly sounding endings for dissimilar compounds are avoided, hence -ĭn, -ĭd, -īte, -āte.

ACCENT.

In polysyllabic chemical words the accent is generally on the antepenult; in words where the vowel of the penult is followed by two consonants, and in all words ending in -ic, the accent is on the penult.

PREFIXES.

All prefixes in strictly chemical words are regarded as parts of compound words, and retain their own pronunciation unchanged (as ă′ceto-, ă′mĭdo-, ă′zo-, hȳ′dro-, ĭ′so-, nī′tro-, nītrō′so-).

ELEMENTS.

In words ending in **-ium**, the vowel of the antepenult is short if **i** (as īrĭ′dium), or **y** (as dĭdy̆′mium), or if before two consonants (as că′lcium), but long otherwise (as tītā′nium, sēlē′nium, chrō′mium).

alū′minum
a′ntimony
a′rsĕnic
bā′rium
bi′smuth (biz)
bō′ron
brō′mīn
că′dmium
că′lcium
ca′rbon
cē′rium
cē′sium
chlō′rīn
chrō′mium
cō′balt
colū′mbium
co′pper
dĭdy̆′mium
e′rbium
flū′orīn
gă′llium
germā′nium
glū′cinum
gold
hȳ′drogen
ĭ′ndium
ī′odīn
īrĭ′dium
iron
lă′nthanum
lead
lĭ′thium
magnē′sium (zhium)
ma′nganese (eze)
me′rcury
mōly̆′bdenum
nĭ′ckel
nī′trogen
ŏ′smium
ŏ′xygen
pallā′dium
phŏs′phorus
plă′tinum
potă′ssium
rhō′dium
rubĭ′dium
ruthē′nium
samā′rium
scă′ndium
sēlē′nium
sĭ′licon
silver
sō′dium
strŏ′ntium (shium)
sŭ′lfur
tă′ntalum
tellū′rium
te′rbium
thă′llium
thō′rium
tin
tītā′nium
tŭ′ngsten
ūrā′nium
vănā′dium
ytte′rbium
ȳ′ttrium
zinc
zircō′nium

Also: ămmō′nium, phosphō′nium, hă′logen, cy̆ă′nogen, ămĭ′dogen.

Note in the above list the spelling of the halogens, cesium and sulfur; **f** is used in the place of **ph** in all derivatives of sulfur (as sulfuric, sulfite, sulfo-, etc.).

TERMINATIONS IN -ic.

The vowel of the penult in polysyllables is short (as cy̆ă′nic, fūmă′ric, arsĕ′nic, silĭ′cic, īŏ′dic, būty̆′ric), except (1) **u** when not used before two consonants (as mercū′ric, prŭ′ssic), and (2) when the penult ends in a vowel (as benzō′ic, olē′ic); in dissyllables it is long except before two consonants (as bō′ric, cĭ′tric). Exception: acē′tic or acĕ′tic.

The termination **-ic**, is used for metals only where necessary to contrast with **-ous** (thus avoid aluminic, ammonic, etc.).

Fāte, făt, fär, mēte, mĕt, pīne, pĭn, marïne, nōte, nŏt, möve, tūbe, tŭb, rüle, mȳ, ȳ = I.

′ Primary accent; ″ secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

TERMINATIONS IN -ous.

The accent follows the general rule (as plă´tinous, sŭ´lfurous, phŏ´sphorous, coba´ltous). Exception: acē´tous.

TERMINATIONS IN -ate AND -ite.

The accent follows the general rule (as ă´cetāte, vă´nadāte): in the following words the accent is thrown back: ă´bietāte, ă´lcoholāte, ă´cetonāte, ă´ntimonīte.

TERMINATIONS IN -id (FORMERLY -ide).

The final **e** is dropped in every case and the syllable pronounced **id** (as chlō´rĭd, ī´odĭd, hȳ´drĭd, ŏ´xĭd, hȳdrŏ´xĭd, sŭ´lfĭd, ă´mĭd, ă´nilĭd, mūrĕ´xĭd).

TERMINATIONS IN -ane, -ene, -ine, AND -one.

The vowel of these syllables is invariably long (as mĕ´thāne, ĕ´thāne, na´phthalēne, a´nthracēne, prō´pīne, quī´nōne, ă´cetōne, kē´tōne).

A few dissyllables have no distinct accent (as benzēne, xȳlēne, cētēne).

The termination **-ine** is used only in the case of doubly unsaturated hydrocarbons, according to Hofmann's grouping (as propīne).

TERMINATIONS IN -in.

In names of chemical elements and compounds of this class, which includes all those formerly ending in **-ine** (except doubly unsaturated hydrocarbons), the final **e** is dropped, and the syllable pronounced **-in** (as chlō´rĭn, brō´mĭn, etc., ă´mĭn, ă´nilĭn, mo´rphĭn, quī´nĭn (kwī´nĭn), vanī´llĭn, alloxă´ntĭn, absi´nthĭn, emŭ´lsĭn, că´ffeĭn, cō´caĭn).

TERMINATIONS IN -ol.

This termination, in the case of specific chemical compounds, is used *exclusively* for alcohols, and when so used is never followed by a final **e**. The last syllable is pronounced **-ol** (as gly´cōl, phē´nōl, crē´sōl, thȳ´mōl (ti), glȳ´cerol, quī´nōl. Exceptions: ălcohōl, a´rgōl.

Fāte, făt, fär, mēte, mĕt, pīne, pĭn, marïne, nōte, nŏt, mŏve, tūbe, tŭb, rūle, mȳ, ȳ = ī.

´ Primary accent; ´´ secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

TERMINATIONS IN **-ole.**

This termination is always pronounced **-ole,** and its use is limited to compounds which are not alcohols (as Ĭ′ndōle).

TERMINATIONS IN **-yl.**

No final **e** is used; the syllable is pronounced **yl** (as ă′cetȳl, ă′mȳl, cē′rotȳl, cē′tȳl, ĕ′thȳl).

TERMINATIONS IN **-yde.**

The **y** is long (as ă′ldehȳde).

TERMINATIONS IN **-meter.**

The accent follows the general rule (as hydrŏ′meter, barŏ′meter, lactŏ′meter). Exception: words of this class used in the metric system are regarded as compound words, and each portion retains its own accent (as cĕ′ntime″ter, mi′llime″ter, kĭ′lome″ter).

MISCELLANEOUS WORDS

which do not fall under the preceding rules.

Note the spelling: albumen, albuminous, albuminiferous, asbestos, gramme, radical.

Note the pronunciation: a′lkalīne, a′lloy (n. and v.), a′llotropy, a′llotropism, ī′somerism, pŏ′lymerism, apparā′tus (sing. and plu.), āqua regia, barȳ′ta, cĕntigrade, co′ncentrated, crystallĭn or crystallīne, electrŏ′lysis, līter, mŏ′lecule, mōlĕ′cular, nō′menclā″ture, olē′fiant, vā′lence, ū′nivā″lent, bī′vā″lent, trī′vā″lent, qua′drivā″lent, tī′trate.

A LIST OF WORDS WHOSE USE SHOULD BE AVOIDED IN FAVOR OF THE ACCOMPANYING SYNONYMS.

For—	*Use—*
sodic, calcic, zincic, nickelic, etc., chlorid, etc.	sodium, calcium, zinc, nickel, etc., chlorid, etc. (vid. terminations in -ic supra).
arsenetted hydrogen	arsin
antimonetted hydrogen	stibin
phosphoretted hydrogen	phosphin
sulfuretted hydrogen, etc	hydrogen sulfid, etc.

Fāte, făt, fär, mēte, mĕt, pīne, pĭn, marïne, nōte, nŏt, möve, tūbe, tŭb, rüle, mȳ, ȳ = ī.

′ Primary accent; ″ secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

For—	*Use—*
beryllium	glucinum
niobium	columbium
glycerin	glycerol
hydroquinone (& hydrochinon)	quinol
pyrocatechin	catechol
resorcin, etc.	resorcinol, etc.
mannite	mannitol
dulcite, etc.	dulcitol, etc.
benzol	benzene
toluol, etc	toluene, etc.
thein	caffein

For—	*Use—*
furfurol	furfuraldehyde
fucusol	fucusaldehyde
anisol	methyl phenate
phenetol	ethyl phenate
anethol	methyl allylphenol
alkylogens	alkyl haloids
titer (n.)	strength or standard
titer (v.)	titrate
monovalent	univalent
divalent, etc.	bivalent, etc.
quantivalence	valence

Fāte, făt, fär, mēte, mĕt, pīne, pĭn, marine, nōte, nŏt, möve, tūbe, tŭb, rüle, mȳ, y̆ = ĭ.

′ Primary accent ; ″ secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

APPENDIX B.—TABLES.

TABLE I.—SOLUBILITIES.

FRESENIUS.

W or w = soluble in H_2O. A or a = insoluble in H_2O; soluble in HCl, HNO_3, or aqua regia. I or i = insoluble in H_2O and acids. W–A = sparingly soluble in H_2O, but soluble in acids. W–I = sparingly soluble in H_2O and acids. A–I = insoluble in H_2O, sparingly soluble in acids. Capitals indicate common substances.

	Aluminium.	Ammonium.	Antimony.	Barium.	Bismuth.	Cadmium.	Calcium.	Chromium.	Cobalt.	Copper.	Ferrous.	Ferric.
Acetate	W	W	..	W	w	w	a	w	w	W	w	W
Arsenate	a	w	a	a	a	a	a	a	a	a	a	a
Arsenite	..	w	a	a	..	..	a	..	a	A	a	a
Benzoate	w	w	..	w	..	w	w	..	..	a	w	a
Borate	a	w	..	a	a	w–a	a	a	a	a	a	a
Bromid	w	W	w–a	w	w–a	w	w	w–i	w	w	w	w
Carbonate	a	W	..	A	A	a	A	a	A	A	A	a
Chlorate	w	w	..	W	w	w	w	w	w	w	w	w
Chlorid	w	W[2]	W–A[6]	W	W–A[10]	W	W	W–I	W	W	W	W
Chromate	..	w	a	a	a	a	w–a	a	a	w	..	w
Citrate	w	w	..	a	..	a	w–a	w	w	w	w	W
Cyanid	..	w	..	w–a	..	a	w	a	a–i	a	a–i	..
Ferricyanid	..	w	..	..	..	..	w	..	i	..	I	W
Ferrocyanid	..	w	..	w–a	..	..	w	..	i	i	i	I
Fluorid	w	W	w	a–i	w	w–a	A	w	w–a	a	w–a	w
Formate	w	w	..	w	w	w	w	w	w	w	w	w
Hydrate	A	W	A	W	a	a	W–A	A	A	a	a	A
Iodid	w	W	w–a	w	a	W	w	w	w	w	W	W
Malate	w	w	..	w–a	..	..	w–a	..	..	..	..	w
Nitrate	w	W	..	W	W[11]	w	w	W	W	W	W	W
Oxalate	a	W	a	a	a	a	A	w–a	A	a	a	a
Oxid	A–I	..	a[7]	W	a	a	W–A	A–I	A	A	a	A
Phosphate	a	W[3]	w–a	w–a	a	a	W–A	a	a	a	a	a
Silicate	A–I	..	..	a	..	a	a	a	a	a	a	a
Succinate	w–a	w	..	w–a	..	w	w–a	..	w–a	w–a	w	..
Sulfate	W[1]	W[4]	a	A	w	W	W–I	W–A[12]	W[13]	W	W	W
Sulfid	a	W	A[8]	W	a	A	W–A	a–i	a	A	A	A
Tartrate	w	w[5]	a[9]	a	a	w–a	a	w	w	w	w–a	W[14]

[1] $(Al_2)(NH_4)_2(SO_4)_4 = W$; $(Al_2)K_2(SO_4)_4 = W$. [2] $As(NH_4)Cl_4 = W$; $Pt(NH_4)Cl_6 = W–I$. [3] $HNa(NH_4)PO_4 = W$; $Mg(NH_4)PO_4 = A$. [4] $Fe(NH_4)_2(SO_4)_2 = W$; $Cu(NH_4)_2(SO_4)_2 = W$. [5] $C_4H_4O_6K(NH_4) = W$. [6] $SbOCl = A$. [7] Sb_2O_3 = soluble in HCl, not in HNO_3. [8] Sb_2S_3 = sol. in hot HCl, slightly in HNO_3. [9] $C_4H_4O_6K(SbO) = W$. [10] $BiOCl = A$. [11] $(BiO)NO_3 = A$. [12] $(Cr_2)K_2(SO_4)_4 = W$. [13] CoS = easily sol. in HNO_3, very slowly in HCl. [14] $(C_4H_4O_6)_4(Fe_2)K_2 = W$.

TABLE I.—SOLUBILITIES.—Continued.

FRESENIUS.

W or w = soluble in H_2O. A or a = insoluble in H_2O; soluble in HCl, HNO_3, or aqua regia. I or i = insoluble in H_2O and acids. W–A = sparingly soluble in H_2O, but soluble in acids. W–I = sparingly soluble in H_2O and acids. A–I = insoluble in H_2O, sparingly soluble in acids. Capitals indicate common substances.

	Lead.	Magnesium.	Manganese.	Mercurous.	Mercuric.	Nickel.	Potassium.	Silver.	Sodium.	Strontium.	Stannous.	Stannic.	Zinc.
Acetate	W	w	w	w–a	w	w	W	w	W	w	w	w	W
Arsenate	a	a	a	a	a	a	W	a	W	a	a	a	..
Arsenite	a	a	a	a	a	a	w	a	w	a	a	..	..
Benzoate	a	w	w	a	w–a	..	w	w–a	w	..	..	..	..
Borate	a	w–a	a	..	..	a	W	a	W	a	a	..	a
Bromid	w–i	w	w	a–i	w	w	W	a	W	w	..	..	w
Carbonate	A	A	A	a	a	A	W	a	W	A	..	..	A
Chlorate	w	w	w	w	w	w	W	w	w	w	w	..	w
Chlorid	W–I	W	W	A–I	W^{16}	W	W^{20}	I	W	W	W	W	W
Chromate	A–I	w	w	a	w–a	a	W	a	w	w–a	a	..	w
Citrate	a	w	a	a	w–a	w	w	a	W	a	..	..	w–a
Cyanid	a	w	a	..	W	a–i	W	i	w	w	..	..	a
Ferricyanid	w–a	w	i	..	..	i	W	i	w	..	..	..	a
Ferrocyanid	a	w	a	..	..	i	W	i	w	w	..	..	a–i
Fluorid	a	a–i	a	..	w–a	w–a	w	w	w	a–i	w	w	w–a
Formate	w–a	w	w	w	w	w	w	w	w	w	w	..	w
Hydrate	a	A	a	..	..	a	W	..	W	w	a	a	a
Iodid	W–A	w	w	A	A	w	W	i	w	w	w	w	w
Malate	w–a	w	w	a	w–a	..	w	w–a	w	w	w	w	w
Nitrate	W	w	w	W	W	W	W	W	W	W	..	..	w
Oxalate	a	a	w–a	a	a	a	W	a	W	a	a	w	a
Oxid	A	A	A^{15}	A	A	A	W	a	W	W	a	A–I	A
Phosphate	a	a^{3}	a	a	a	a	w	a	W	a	a	a	a
Silicate	a	a	a	..	..	a	W	..	W	a	..	..	a
Succinate	a	w	w	a	w–a	w	w	a	w	w–a	..	a	w–a
Sulfate	A–I	W	W	w–a	W^{17}	W	W^{12}	W–A	W	I	w	..	W
Sulfid	A	a	a	a	A^{18}	A^{19}	W	a^{21}	W	w	a^{22}	A^{22}	A^{23}
Tartrate	a	w–a	w–a	w–a	a	a	W	a	w	a	a	..	a

[15] MnO_2 = sol. in HCl; insol. in HNO_3. [16] Mercurammonium chlorid = A. [17] Basic sulfate = A. [18] HgS = insol. in HCl and in HNO_3, sol. in aq. regia. [19] See 13. [20] $PtKCl_6$ = W–A. [21] Only soluble in HNO_3. [22] Sn sulfides = sol. in hot HCl; oxidized, not dissolved, by HNO_3. Sublimed $SnCl_4$ only sol. in aq. regia. [23] Easily sol. in HNO_3, difficultly in HCl.

Au_2S = insol. in HCl and in HNO_3, sol. in aq. regia. $AuBr_3$, $AuCl_3$, and $Au(CN)_3$ = w; AuI_3 = a. PtS_2 = insol. in HCl, slightly sol. in hot HNO_3; sol. in aq. regia. $PtBr_4$, $PtCl_4$, $Pt(CN)_4$, $Pt(NO_3)_4$, $(C_2O_4)_2Pt$, $Pt(SO_4)_2$ = w; PtO_2 = a; PtI_4 = i.

TABLE II.—WEIGHTS AND MEASURES.

MEASURES OF LENGTH.

1 millimetre = 0.001 metre = 0.0394 inch.
1 centimetre = 0.01 " = 0.3937 "
1 decimetre = 0.1 " = 3.9371 inches.
1 METRE = 39.3708 "
1 decametre = 10 metres = 32.8089 feet.
1 hectometre = 100 " = 328.089 "
1 kilometre = 1000 " = 0.6214 mile.

Inch.		Millimetres.	Inches.		Centimetres.	Inches.		Centimetres.
$\frac{1}{64}$	=	0.3819	2	=	5.08	9	=	22.86
$\frac{1}{32}$	=	0.7638	3	=	7.62	10	=	25.40
$\frac{1}{16}$	=	1.5875	4	=	10.16	11	=	27.94
$\frac{1}{8}$	=	3.175	5	=	12.70	12	=	30.48
$\frac{1}{4}$	=	6.35	6	=	15.24	18	=	45.72
$\frac{1}{2}$	=	12.7	7	=	17.78	24	=	60.96
1	=	25.4	8	=	20.32	36	=	91.44

MEASURES OF CAPACITY.

1 millilitre = 1 c.c. = 0.001 litre = 0.0021 U. S. pint.
1 centilitre = 10 " = 0.01 " = 0.0211 " "
1 decilitre = 100 " = 0.1 " = 0.2113 " "
1 LITRE = 1000 " = 1.0567 " quart.
1 decalitre = 10 litres = 2.6418 " galls.
1 hectolitre = 100 " = 26.418 " "
1 kilolitre = 1000 " = 264.18 " "

♏.	c.c.	♏.	c.c.	♏.	c.c.	Fl ℥.	c.c.
1 =	0.06	26 =	1.60	51 =	3.14	5 =	147.81
2 =	0.12	27 =	1.66	52 =	3.20	6 =	177.39
3 =	0.19	28 =	1.73	53 =	3.26	7 =	206.96
4 =	0.25	29 =	1.79	54 =	3.32	8 =	236.53
5 =	0.31	30 =	1.85	55 =	3.39	9 =	266.10
6 =	0.37	31 =	1.91	56 =	3.46	10 =	295.68
7 =	0.43	32 =	1.98	57 =	3.52	11 =	325.25
8 =	0.49	33 =	2.04	58 =	3.58	12 =	354.82
9 =	0.55	34 =	2.10	59 =	3.64	13 =	384.40
10 =	0.62	35 =	2.16	60 =	3.70	14 =	413.97
11 =	0.68	36 =	2.22	Fl ʒ.		15 =	443.54
12 =	0.74	37 =	2.28	1 =	3.70	16 =	473.11
13 =	0.80	38 =	2.34	2 =	7.39	O.	Litres.
14 =	0 86	39 =	2.40	3 =	11.09	1 =	0.47
15 =	0.92	40 =	2.46	4 =	14.79	2 =	0.95
16 =	0.99	41 =	2.52	5 =	18.48	3 =	1.42
17 =	1.05	42 =	2.58	6 =	22.18	4 =	1.89
18 =	1.11	43 =	2.66	7 =	25.88	5 =	2.36
19 =	1.17	44 =	2.72	8 =	29.57	6 =	2.84
20 =	1.23	45 =	2.77	Fl ℥.		7 =	3.31
21 =	1.29	46 =	2.84	1 =	29.57	8 =	3.79
22 =	1.36	47 =	2.90	2 =	59.14	9 =	4.26
23 =	1.42	48 =	2.96	3 =	88.67	10 =	4.73
24 =	1.48	49 =	3.02	4 =	118.24	11 =	5.20
25 =	1.54	50 =	3.08			12 =	5.67

WEIGHTS.

1 milligram = 0.001 gram = 0.015 grain Troy.
1 centigram = 0.01 " = 0.154 " "
1 decigram = 0.1 " = 1.543 " "
1 GRAM = 15.432 grains "
1 decagram = 10 grams = 154.324 " "
1 hectogram = 100 " = 0.268 lb. "
1 kilogram = 1000 " = 2.679 lbs. "

Grains.		Grams.
$\frac{1}{64}$	=	0.001
$\frac{1}{32}$	=	0.002
$\frac{1}{16}$	=	0.004
$\frac{1}{8}$	=	0.008
$\frac{1}{4}$	=	0.016
$\frac{1}{2}$	=	0.032
1	=	0.065
2	=	0.130
3	=	0.194
4	=	0.259
5	=	0.324
6	=	0.389
7	=	0.454
8	=	0.518
9	=	0.583
10	=	0.648
11	=	0.713
12	=	0.778
13	=	0.842
14	=	0.907
15	=	0.972
16	=	1.037
17	=	1.102
18	=	1.166
19	=	1 231
20	=	1 296

Grains.		Grams.
21	=	1.361
22	=	1.426
23	=	1.458
24	=	1.555
25	=	1.620
26	=	1.685
27	=	1.749
28	=	1.814
29	=	1.869
30	=	1.944
31	=	2.009
32	=	2.074
33	=	2.139
34	=	2.204
35	=	2.268
36	=	2.332
37	=	2.397
38	=	2.462
39	=	2.527
40	=	2.592
41	=	2.657
42	=	2.722
43	=	2.787
44	=	2.852
45	=	2.916
46	=	2.980

Grains.		Grams.
47	=	3.046
48	=	3.110
49	=	3.175
50	=	3.240
51	=	3.305
52	=	3.370
53	=	3.434
54	=	3.499
55	=	3.564
56	=	3.629
57	=	3.694
58	=	3.758
59	=	3.823
60	=	3.888

ʒ		
1	=	3.888
2	=	7.776
3	=	11.664
4	=	15.552
5	=	19.440
6	=	23.328
7	=	27.216
8	=	31.103

℥		Grams.
1	=	31.103
2	=	62.207
3	=	93.310
4	=	124.414
5	=	155.517
6	=	186.621
7	=	217.724
8	=	248.823
9	=	279.931
10	=	311.035
11	=	342.138
12	=	373.250

Lbs.		Kilos.
1	=	0.373
2	=	0.747
3	=	1.120
4	=	1.493
5	=	1.866
6	=	2.240
7	=	2.613
8	=	2.986
9	=	3.359
10	=	3.733

TABLE III.

WEIGHT OF ONE CUBIC CENTIMETRE OF NITROGEN.

Temperature in Centigrade.	720	722	724	726	728	730	732	734	736	738	740	742	744
10°	1.1338	1.1370	1.1402	1.1434	1.1466	1.1498	1.1529	1.1561	1.1593	1.1625	1.1657	1.1689	1.1721
11°	1.1288	1.1320	1.1352	1.1384	1.1415	1.1447	1.1479	1.1511	1.1542	1.1574	1.1606	1.1638	1.1670
12°	1.1237	1.1269	1.1301	1.1333	1.1364	1.1396	1.1428	1.1459	1.1491	1.1523	1.1554	1.1586	1.1618
13°	1.1187	1.1219	1.1251	1.1282	1.1314	1.1345	1.1377	1.1409	1.1440	1.1472	1.1503	1.1535	1.1566
14°	1.1136	1.1168	1.1200	1.1231	1.1263	1.1294	1.1326	1.1357	1.1389	1.1420	1.1452	1.1483	1.1515
15°	1.1085	1.1117	1.1149	1.1180	1.1211	1.1243	1.1274	1.1305	1.1337	1.1368	1.1399	1.1431	1.1462
16°	1.1034	1.1066	1.1097	1.1128	1.1160	1.1191	1.1222	1.1253	1.1285	1.1316	1.1347	1.1378	1.1409
17°	1.0983	1.1014	1.1045	1.1076	1.1107	1.1138	1.1170	1.1201	1.1232	1.1263	1.1294	1.1325	1.1356
18°	1.0930	1.0961	1.0992	1.1023	1.1054	1.1085	1.1117	1.1148	1.1179	1.1209	1.1241	1 1272	1.1303
19°	1.0877	1.0908	1.0939	1.0970	1.1001	1.1032	1.1063	1.1094	1.1125	1.1156	1.1187	1.1218	1.1248
20°	1.0825	1.0855	1.0886	1.0917	1.0948	1.0979	1.1009	1.1040	1.1071	1.1102	1.1133	1.1164	1.1194
21°	1.0771	1.0802	1.0832	1.0863	1.0894	1.0924	1.0955	1.0986	1.1017	1.1047	1.1078	1.1109	1.1139
22°	1.0717	1.0747	1.0778	1.0808	1.0839	1.0870	1.0900	1.0931	1.0961	1.0992	1.1023	1.1053	1.1084
23°	1.0662	1.0692	1.0723	1.0753	1.0784	1.0814	1.0845	1.0875	1.0906	1.0936	1.0967	1.0997	1.1028
24°	1.0606	1.0636	1.0667	1.0697	1.0728	1.0758	1.0789	1.0819	1.0849	1.0880	1.0910	1.0940	1.0971
25°	1.0550	1.0580	1.0610	1.0641	1.0671	1.0701	1.0732	1.0762	1.0792	1.0823	1.0853	1.0883	1.0913
	720	722	724	726	728	730	732	734	736	738	740	742	744

Barometric pressure in millimetres.

TABLE III.—Continued.

WEIGHT OF ONE CUBIC CENTIMETRE OF NITROGEN.

Temperature in Centigrade.	746	748	750	752	754	756	758	760	762	764	766	768	770
10°	1.1753	1.1785	1.1817	1.1848	1.1880	1.1912	1.1944	1.1976	1.2008	1.2040	1.2072	1.2104	1.2136
11°	1.1701	1.1733	1.1765	1.1717	1.1829	1 1860	1.1892	1.1924	1.1956	1.1988	1.2019	1.2051	1.2083
12°	1.1649	1.1681	1.1713	1.1744	1.1776	1.1808	1.1839	1.1871	1.1903	1.1934	1.1966	1.1998	1.2029
13°	1.1598	1.1630	1.1661	1.1693	1.1724	1.1756	1.1787	1.1819	1.1851	1.1882	1.1914	1.1945	1.1977
14°	1.1546	1.1577	1.1609	1.1640	1.1672	1.1703	1.1735	1.1766	1.1798	1.1829	1.1861	1.1892	1.1923
15°	1.1493	1.1525	1.1556	1.1587	1.1619	1.1650	1.1681	1.1713	1.1744	1.1775	1.1807	1.1838	1.1869
16°	1.1441	1.1472	1.1503	1.1534	1.1566	1.1597	1.1628	1.1659	1.1691	1.1722	1.1753	1.1784	1.1816
17°	1.1397	1.1419	1.1450	1.1481	1.1512	1.1543	1.1574	1·1605	1.1636	1.1667	1.1699	1.1730	1.1761
18°	1.1334	1.1365	1.1396	1.1427	1.1458	1 1489	1.1520	1.1551	1.1582	1.1613	1.1644	1.1675	1.1706
19°	1.1279	1.1310	1.1341	1.1372	1.1403	1.1434	1.1465	1.1496	1.1527	1.1558	1.1589	1.1620	1.1650
20°	1.1229	1.1256	1.1287	1.1318	1.1348	1.1379	1.1410	1.1441	1.1472	1.1502	1.1533	1.1564	1.1595
21°	1.1170	1.1201	1.1231	1.1262	1.1293	1.1324	1.1354	1.1385	1.1416	1.1446	1.1477	1.1508	1.1539
22°	1.1115	1.1145	1.1176	1.1206	1.1237	1.1268	1.1298	1.1329	1.1359	1.1390	1.1421	1.1451	1.1482
23°	1.1058	1.1089	1.1119	1.1150	1.1180	1.1211	1.1241	1.1272	1.1302	1.1333	1.1363	1.1394	1.1424
24°	1.1001	1.1032	1.1062	1.1092	1.1123	1.1153	1.1184	1.1214	1.1244	1.1275	1.1305	1.1336	1.1366
25°	1.0944	1.0974	1.1004	1.1035	1.1065	1.1095	1.1126	1.1156	1.1186	1.1216	1.1247	1.1277	1.1307
	746	748	750	752	754	756	758	760	762	764	766	768	770

Barometric pressure in millimetres.

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