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## ORGANIC CHEMISTRY

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# ORGANIC CHEMISTRY

(PART 1)

## INTRODUCTION

### DETERMINATION OF ATOMIC WEIGHTS

**1.** The first part of this Paper is given up to a review of facts and principles treated in the various Sections on *Physics* and in the different Sections on *Inorganic Chemistry*, to all of which the student will be frequently referred. Here, the laws and principles in the above mentioned Papers have been more fully treated, in order that further study may be facilitated and the study of Organic Chemistry better understood.

It is imperative that the student give careful attention to Organic Chemistry, for it is by no means an easy subject. He should not rest satisfied with merely reading this Paper, but should give it thorough study and frequent review, for, once mastered, the principles here taught will be of great assistance in future work.

**2. Determination of Atomic Weights.**—An accurate determination of the atomic weight of each of the elementary constituents of matter is of the greatest importance to the chemist, as no satisfactory classification of the facts of chemistry that relate to combination, analysis, etc. can be made until the atomic weights of the elements are established.

Further than this, the attention paid to this subject during recent years has led to the alteration of many of the numbers, and has brought with it the conclusion of the existence of an intimate relation between the atomic weights and the physical and chemical properties of the elements themselves.

**3. Atomic Weight of Elements in the Gaseous Condition.**—In the remarks that have been made in previous Instruction Papers, it was pointed out that an examination of the composition and volume relations of gaseous compounds, together with considerations based on Avogadro's law, suffice to indicate the atomic weight of the majority of the non-metallic elements.

When, however, it becomes necessary to deal with the metals, it will be found that in very few cases compounds exist in the gaseous state at ordinary conditions, and that the arguments which hold good in the case of gaseous bodies cease to be applicable. In certain cases, however, even the metallic elements or their compounds can be examined in the gaseous state by adopting special expedients.

**4. Determination of Vapor Densities.**—For the direct comparison of the densities of gases, the relation between the weight of a known volume of a gas as compared with either air, hydrogen, or any other suitable gas may be ascertained by *Regnault's method*, which simply consists in counterpoising two equal-sized glass globes—one filled with the gas in question, and the other with the gas that we wish to compare.

Substances that are, however, at ordinary conditions, either solids or liquids, have to be vaporized by heat, and the comparison is then most conveniently made with air; and since the density of air is approximately 14.43 times that of hydrogen, and the molecule of hydrogen consists of 2 atoms, we obtain the formula

$$\text{Molecular weight} = 28.86D,$$

where $D$ is the specific gravity, or density of the gas compared with air. The chief methods employed in the determination of the density at higher temperatures are those of

Dumas and Victor Meyer. The general proceedings according to both methods have already been treated in former Sections.

Victor Meyer's method, however, is the more important method of the two, and as it is applicable over a considerable range of temperature, easy to manipulate, and the determinations can be made with comparatively small quantities of the substance, it is deemed advisable to treat it somewhat more extensively. Fig. 1 represents a Victor Meyer apparatus of the latest style. (The student will notice that the improvement consists in the introduction of the stop-cock *f*.) It consists of a wide glass tube *a* narrowed in the upper part and then widened again, so as to form a cup near the top. The narrow part is closed by a stop-cock *f* and the cup *g* by a rubber stopper *h*; this arrangement has the advantage that the substance can be dropped into the tube without loss of heat. This is accomplished by closing the stop-cock, placing the substance in the receiver *g*, replacing

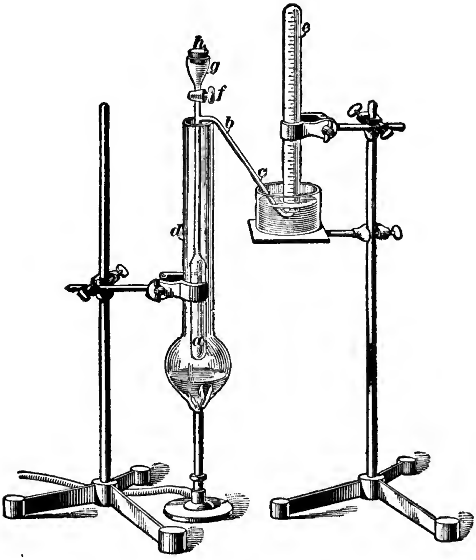

FIG. 1

the rubber stopper *h*, and then opening the stop-cock *f*, through the wide hole of which the body readily drops down. Near the top of the narrow portion there is a side tube *b c* of the form shown in the illustration. An outer jacket *d* of either glass, copper, or iron, about the same length as the tube *a*, is provided; in this is placed a quantity of material suitable for heating the glass bulb—according to the temperature required to volatilize the substance under examination—the bulb being so placed as to leave a clear space around it. A graduated tube *e* is filled with water and inverted over the end of the side tube *b c*. The stop-cock being closed and the cork inserted in its place, the jacket is heated, and the temperature of the glass tube raised in this way to that of the vapor of the bath. Owing to the expansion of the air, bubbles pass out.

When the temperature becomes constant the bubbles cease; the cork *h* is then withdrawn, a weighed amount, say from .1 gram to .2 gram, of the substance is dropped into the receiver *g*, the cork replaced, and the stop-cock opened so as to allow the substance to slide down to the bottom of *a*, after which the stop-cock is again closed. If the experiment is performed with proper care, the substance will be very rapidly vaporized, and an equal volume of air will be expelled by the side tube. This is carefully measured and the temperature *t* and pressure *p* of the room in which the experiment is performed are noted. Reduced to normal temperature and pressure, this will give the volume that the vapor would occupy. Thus,

$$V = \frac{v \times 273 \times (p - s)}{(273 + t) \times 760};$$

*s* being the tension of the aqueous vapor at the temperature *t*. This is the volume occupied by the weight *w* of the substance taken, when transformed into vapor; and it is readily seen that the density *D* compared with air will be *

$$D = \frac{w}{.001293\,V};$$

---

* 1 cubic centimeter of air under normal conditions weighs .001293 gram. See Gas Analysis.

and as compared with hydrogen, it will be

$$D = \frac{w}{.0000896\ V}$$

Provided that the temperature in the outer jacket $d$ is constant and high enough to insure rapid vaporization of the substance, the actual temperature employed need not be known. This will be readily understood, if the student bears in mind that the volume of the air actually displaced and collected at the graduated tube is at the temperature of the room; the vapor of the substance occupies precisely the volume that this air would have occupied at the temperature of volatilization. We have, therefore, the volume that the vapor would occupy if it could be collected at the temperature of the room.

**5. Determination of the Formula of a Compound.** An analysis of chloride of uranium gave the following composition:

| | |
|---|---|
| Uranium........ | 63%, |
| Chlorine ........ | 37%. |

The atomic weight of uranium has been at various times taken as 120, or some multiple or submultiple of this; that of chlorine we know positively to be 35.4. Taking 120 as the atomic weight of uranium, we have, as representing the relation of the number of atoms of uranium and chlorine in the compound,

$$\frac{63}{120} = 0.525$$

$$\frac{37}{35.4} = 1.045$$

The relation of these numbers is at once recognized as being practically 1 : 2, but may be expressed just as well by 2 : 4, or 3 : 6, or 4 : 8, etc. From the results of the analysis, together with the atomic weights assumed, we are in a position to accept either $UCl_2$ or $U_2Cl_4$, or to generalize the deduction $U_xCl_{2x}$, as the formula for the chloride.

A few years ago Dr. Zimmermann, a German chemist, determined the vapor density $D$ of the chloride by means of the Victor Meyer apparatus. The results of his investigation were the following:

| | |
|---|---|
| Weight of chloride taken.... | 0.082 g. |
| Air expelled ............... | 5.8 c. c. |
| Temperature............... | 28° C. |
| Pressure.................... | 714 mm. of mercury. |

Calculating from these numbers we find

$$D = 13.36,$$
$$\text{Molecular weight} = 28.86\,D = 385.57$$

Of the possible formulas previously given,

$$UCl_2 \text{ would give } 120 + (35.4 \times 2) = 190.8;$$
$$U_2Cl_4 \text{ would give } (120 \times 2) + (35.4 \times 4) = 381.6;$$
$$U_3Cl_6 \text{ would give } (120 \times 3) + (35.4 \times 6) = 572.4.$$

Clearly, $U_2Cl_4$ corresponds closely to the value as obtained from the determination of vapor density, and if 120 is to be accepted as the atomic weight of uranium, then the formula of the chloride is $U_2Cl_4$.

But up to this point there is no evidence that 120 is the true atomic weight of uranium—it may be 240 or 60. If we take it as 240 and repeat the calculations from the results of the analysis as before, we shall find as possible formulas $UCl_4$, $U_2Cl_8$, or, in general, $U_xCl_{4x}$; using the vapor-density determination, we shall find that of these only $UCl_4$ fulfils the required conditions.

Similarly, if we take 60 as the atomic weight of uranium, we shall find that, of the formulas derived from the analysis, $UCl$, $U_2Cl_2$, or, to generalize it, $U_xCl_x$, only $U_4Cl_4$ yields the value required by the vapor density. Summing up, therefore, we may state that, if the atomic weight of uranium is 60, the chloride has the formula $U_4Cl_4$; if 120, $U_2Cl_4$; and if 240, $UCl_4$.

We cannot go further than this at present, but later on evidence will be brought forward that will enable us to decide which of these values must be accepted as actually representing the atomic weight of uranium. When this is done, it will be possible to state the formula of the chloride on this basis, and those of other compounds of uranium in accordance therewith.

**6.** It has already been mentioned that some of the elements which exist at ordinary temperatures in the solid or liquid condition may be vaporized, and the density of the vapor determined by the various methods previously described. If we assume that the molecule of the vapor consists of two atoms, then the atomic weight may be arrived at immediately from the vapor density (this being the weight of a given volume of the vapor expressed in terms of the weight of an equal volume of hydrogen at the same temperature and pressure). But this assumption would not be correct in the case of such elements as arsenic, phosphorus, sulphur, and iodine.

**7. Nature of the Ultimate Particles of Matter.**—The acceptance of a theory concerning the existence of atoms carries with it, as an unavoidable consequence, the fact that the process of division of matter cannot be carried on to an infinite extent, but that there must be a limit to it, and that particles must ultimately be obtained, which, though extremely small, are still possessed of finite dimensions. These particles are the *atoms* or the *aggregate of atoms*, termed, as we have previously stated, *molecules*.

The size of molecules has been made the subject of various investigations, and their size is usually stated as being larger than $\frac{1}{1250000000}$ of an inch and smaller than $\frac{1}{5000000000}$ of an inch.

As we are, however, really ignorant of the actual form and character of a molecule, it appears premature to accept such measurements as anything else than an approximation, but the investigations serve, nevertheless, to support the view that the ultimate particles of matter, if extremely small, have yet a definite size.

The examinations of the physical properties of matter show that the space occupied by it is not entirely taken up by the molecules themselves, but that in the liquid, and even in the solid, condition there are interspaces between the adjacent molecules, and that in the gaseous condition, these interspaces are (in comparison with the dimensions of the molecule) rather large, so that the mean distance between two molecules is about ten to fifteen times the diameter of the molecule itself. From this, the conclusion is drawn that while in the liquid and solid condition the movements a molecule can make are rather limited; these movements are not so limited in the case of gaseous bodies, whose molecules are able to move freely and with a rather high degree of velocity.

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## KINETIC THEORY

**8. The Kinetic Theory of Gases.**—We quote below an extract from "Maxwell's Theory of Heat" (a book that can be highly recommended to the student for private study), which gives a short and precise outline of the conception of gaseous matter regarded from the point of view of the *kinetic theory.*

"A gaseous body is supposed to consist of a great number of molecules moving with great velocity. During the greater part of their course the molecules are not acted on by any sensible force, and therefore move in straight lines with uniform velocity. When the molecules come within a certain distance of each other, a mutual action takes place between them, which may be compared to the collision of two billiard balls. Each molecule has its course changed, and starts on a new and different path. I have concluded from some experiments of my own that the collision between two hard spherical balls is not an accurate representation of what takes place during the encounter of two molecules.

"A better representation of such an encounter will be obtained by supposing the molecules to act on one another in a more gradual manner, so that the action between them goes on, for a finite time, during which the centers of the molecules first approach each other, and then separate.

"We shall refer to this mutual action as an encounter between two molecules, and we shall call this course of a molecule between one encounter and another the '*free path of the molecule.*'

"In ordinary gases the free motion of a molecule takes up much more time than that occupied by an encounter. As the density of the gases increases, the free path diminishes, and in liquids no part of the course of a molecule can be spoken of as its free path."

Such a conception of matter is of great interest to the chemist, as we shall see that it throws considerable light upon the phenomena of chemical reaction and on the manner in which these phenomena undergo modification according to the condition (solid, liquid, or gaseous) affected by the interacting bodies.

**9. The Pressure of a Gas According to the Kinetic Theory.**—Let us consider the case of a gas contained within a cubical vessel, as shown in Fig. 2. The molecules of the gas are in continual motion according to the manner just described. Let there be $N$ molecules each of mass $M$ moving with a velocity $V$. Let us further suppose at first that all the molecules are moving in one direction with uniform velocity; viz., perpendicular to the plane *a b c d.* The number that actually meet the plane in unit time will manifestly be proportional to the number of molecules present and the velocity with which they travel, i. e., to $N V$; also, the momentum communicated to the wall *a b c d* by one molecule of mass $M$ will be $M V$. For $N V$ molecules it will be proportional to $N V \times M V$, that is $M N V^2$.

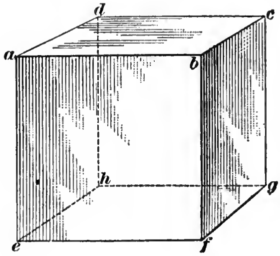

FIG. 2

This is, of course, quite simple, but let us consider now the molecules moving in all directions with a like velocity, and we shall refer their momentum not to one plane, but to the three planes at right angles to one another; viz., *a b c d*, *a b e f*, and *b c f g*. A molecule moving parallel to one of the planes, say *a b c d*, would not meet that plane and would produce no effect there; its whole momentum would be communicated along one or both of the other two planes. So long as we confine our attention to individual molecules traversing particular paths, it is not easy to see that the effect produced by collision with each of the surfaces *a b c d*, *a b e f*, and *b c f g*, would be the same. But if we consider the immense number of molecules and the high velocity with which they travel, we certainly shall be prepared to admit that the *average resultant effect* for each plane is really the same. The momentum $M N V^2$, therefore, is distributed equally over the three planes, and for each plane it is proportional to $\frac{1}{3} M N V^2$.

The momentum—that is, the pressure—on, say, the surface *a b c d* of the cubical vessel is proportional, therefore, to $\frac{1}{3} M N V^2$, and if we suppose the atmosphere to shut in the gas at this surface, then the pressure exerted on the atmosphere is $\frac{1}{3} M N V^2$. But since, according to Avogadro's hypothesis, the number of molecules in equal volumes of gases under like conditions is the same, $M N$ is equivalent to $\beta$ the density, that is, the pressure of a gas at the surface *a b c d* is equal to $\frac{1}{3} \beta V^2$.

**10. Boyle's Law According to the Kinetic Theory.** If by any means we introduce more molecules of gas into the vessel (say $n$ more), then the pressure increases from $\frac{1}{3} M N V^2$ to $\frac{1}{3} M (N+n) V^2$, or in the proportion $N : N+n$, while the space occupied by the same number of molecules of the gas has decreased in the proportion $N+n : N$. This gives an expression in accordance with the kinetic theory for *Boyle's law;* that *the volume occupied by a gas is inversely as the pressure to which it is subjected.*

**11. The Internal Energy of the Molecule.**—The remarks in the previous articles have been made under the assumption that the molecules of all gases are similar in their nature and that there is no complication arising from movements of atoms within the molecule. It has, however, been already stated in various places in the Sections on *Inorganic Chemistry* that the molecules of some elements are more complex than those of others. Taking this complexity into consideration, it now remains to examine whether the whole of the energy communicated to a gas goes to promote the agitation of the molecules as such, or whether some part of it is spent in promoting the activity of the atoms composing the molecule. That is to say, it is conceivable that the increment of energy may be distributed so that it goes partly to increase the activity of the molecule as a whole, and partly to increase the activity of the mobile atoms constituting the molecule.

**12. The Behavior of the Monatomic Molecule.** Let us start to investigate the conditions obtained when heat is communicated to a gas to which the simplest possible constitution can be assigned, that is the monatomic molecule. The effect of the heat will be found to be twofold, namely :

*First*, expressed in the terms of the kinetic theory of gases, it will increase the energy of agitation of the molecules of the gas ; that is to say, the progressive motion of the molecules, as molecules, will increase, or regarding it from the point of view of the indications given by the thermometer, it will raise the temperature of the gas. The increment of energy for a molecule, whose mass is $M$ and whose velocity is $V$, may be expressed by the general term $\frac{1}{2}MV^2$, and if $N$ is the number of molecules in unit volume, the increment of energy per unit volume must be $\frac{1}{2}MNV^2$. Since, according to Avogadro's law, equal volumes of gases under equal conditions of temperature and pressure contain the same number of molecules, we may substitute for $MN$, the density of the gas, and representing this, as before, by $\beta$, the expression then becomes $\frac{1}{2}\beta V^2$.

*Second*, unless placed in confined space, the gas expands. Under ordinary circumstances a gas expands according to the well-known Gay-Lussac's law, and during the expansion it is subjected to the pressure of the atmosphere. An expansion under such conditions necessarily implies that the expanding gas does a certain amount of work; namely, the work of lifting the atmosphere through the interval over which the expansion extends. The energy associated with this has already been deduced according to the kinetic theory, and will be found to be equivalent to $\frac{1}{3}\beta V^2$.

If, then, the gas be freed to expand under atmospheric pressure, the total energy expended upon it will be

$$\tfrac{1}{2}\beta V^2 + \tfrac{1}{3}\beta V^2, \text{ or } \tfrac{5}{6}\beta V^2.$$

If it be enclosed within a vessel so that while its temperature is being raised its volume remains constant, the work of overcoming the pressure of the atmosphere is no longer a factor in the operation, and the energy that must be communicated is only that which goes to intensify the agitation of the molecules. The value of this has been shown to be $\frac{1}{2}\beta V^2$.

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## SPECIFIC HEAT

**13. Specific Heat at Constant Pressure and Constant Volume.**—As has been previously explained, the specific heat, or the capacity for heat of a body, is the amount of heat required to raise the temperature of 1 gram of the substance in question 1° C. as compared with the amount required to raise the temperature of 1 gram of water 1° C. This definition is meant to apply to determinations made under standard atmospheric pressure and temperature.

A similar determination, however, made for gas in a closed space has been termed the *specific heat under constant volume*, and, for purposes of distinction, the specific heat under ordinary conditions is spoken of as the *specific heat under constant pressure*. We may conveniently express these by the symbols $C_v$ and $C_p$; then, as we have seen,

$$C_p = \tfrac{5}{6}\beta V^2;$$
$$C_v = \tfrac{1}{2}\beta V^2;$$

and

$$\frac{C_p}{C_v} = \tfrac{5}{3} = 1.666.$$

For the sake of brevity we will express the relation $\frac{C_p}{C_v}$ by the symbol $K$. The value for $C_p$ can be directly measured, and the energy necessary to overcome the pressure of the atmosphere (i. e., $C_p - C_v$) can be calculated and $C_v$ deduced; we give these in Table I for several gases.

TABLE I

| Name of Gas | $C_p$ | $C_v$ | $\frac{C_p}{C_v}$ |
|---|---|---|---|
| Hydrogen | 3.4090 | 2.4190 | 1.49 |
| Oxygen | 0.2175 | 0.1555 | 1.40 |
| Nitrogen | 0.2438 | 0.1724 | 1.41 |
| Carbon dioxide | 0.2169 | 0.1719 | 1.26 |
| Marsh gas | 0.5929 | 0.4962 | 1.26 |
| Ammonia | 0.5084 | 0.3919 | 1.30 |
| Ethyl ether | 0.4796 | 0.4528 | 1.06 |

The student will notice, by referring to the last column of Table I, that the value for the ratio of specific heat at constant pressure to that of constant volume (which we have termed above as $K$) is, as a rule, lower than that estimated on the assumptions already made, which have placed it at 1.666. Moreover, the variation from this value is seen to be greater for the compound than for the elementary gases, as an inspection of the table will show.

**14. Intramolecular Work in the Complex Molecule.**—This discrepancy suggests that there must be some other form in which energy is disposed in the molecule, which so far has not been taken into account. As a natural consequence, our attention must then be given to changes that may possibly occur *with the molecule itself;* that is, the internal work associated with the motion of the atoms making up the aggregate molecule—the former calculations having been made on the assumption that the molecule is monatomic—and that there is, consequently, no intramolecular work. Calling this $I$, then for complex molecules, $\frac{\frac{5}{6}\beta V^2 + I}{\frac{1}{2}\beta V^2 + I}$ must be less than 1.666, and the larger $I$ is, the smaller this value becomes, though it can manifestly never fall to unity.

**15. Monatomic Molecules.**—Although the ordinary gases or vapors have complex molecules, consisting usually of two atoms, though sometimes of more, there is reason to believe that in certain cases the molecule is monatomic; as is the case with the vapors of mercury, cadmium, zinc, and the lately discovered gases, helium and argon.

The proof that in such cases there is practically no internal energy associated with the molecule, is furnished by determining the velocity of transmission of **sound waves** in such mediums.

**16. Relations of Specific Heats Deduced from Sound Vibrations.**—It may be established on physical data that for two gases, the relation $K$ for the one to $K_1$ for the other, is proportional to the respective masses; i. e., molecular weights multiplied by the square of the lengths of the sound waves ($L$ and $L_1$) which they transmit under similar conditions, or

$$\frac{K}{K_1} = \frac{ML^2}{M_1 L_1^2}$$

If the comparison be made with air, then $K_1$ is known to be 1.405 and $M_1$ is 28.86; so that we have

$$\frac{K}{1.405} = \frac{ML^2}{28.86\, L_1^2}$$

The relation $L$ to $L_1$ can be determined by the following experiment:

A glass tube *a b*, as shown in Fig. 3, having its inner surface dusted with lycopodium powder, is furnished with side tubes *c* and *d*, by which it can be filled with the gas; by means of the two movable pistons *e* and *f* the tube is closed, and either by rubbing with the fingers moistened, or by

FIG. 3

other means, a musical note is produced and the gas thrown into vibrations, which are recorded by the lycopodium powder, and the length of the wave may be measured by taking the distance between two adjacent nodes. When this has been done for air, and for the vapor in question, the ratio $L : L_1$ is, of course, established.

In this way the value of $K$ for mercury vapor has been found to be 1.666, and for helium, 1.632.

Hence, for these two bodies there is practically no intramolecular work performed, and the conclusion has been drawn that in such cases the molecule is not complex, but consists of a single atom.

**17.** In the previous articles the bearing of atomic weight in the case of bodies that are capable of being volatilized without decomposition have only been considered; in the following articles the evidence on which the atomic weights are based, as derived from the behavior of substances that cannot be volatilized, will be taken into consideration.

The generalizations that are to be drawn from the following articles apply, therefore, to matter in either the solid or liquid state.

**18. Relation of the Specific Heat of Elements to Their Atomic Weight.**—It has been shown in various previous places that the atoms of all elementary bodies have approximately the same capacity for heat; a fact discovered by Dulong and Petit in 1819.

The adoption of this law led to the alteration of a number of the values then accepted for atomic weights. This of course was followed by a number of changes in the formulas of the compounds derived from these elements. In all instances, however, where revision has taken place, the effect has been to bring out in a clearer light the relations that the elements and their compounds bear to one another, and to throw them into natural groups, in which striking resemblances are shown between the members of the same group. It is on this ground that the generalization of Dulong and Petit has appealed so strongly to chemists. In Table II the atomic weights and specific heats of a number of elements are given, as well as the product of atomic weight multiplied by the specific heat (the so called atomic heat), which is in most cases, as we have already seen, a constant, its value being approximately 6.4.

**TABLE II**

| Elements | Atomic Weight $A$ | Specific Heat $C$ | $AC$ |
|---|---|---|---|
| Sodium | 23.0 | .293 | 6.7 |
| Magnesium | 24.0 | .250 | 6.0 |
| Aluminum | 27.0 | .214 | 5.8 |
| Phosphorus | 31.0 | .174 | 5.4 |
| Sulphur | 32.0 | .178 | 5.7 |
| Potassium | 39.0 | .166 | 6.5 |
| Calcium | 39.9 | .170 | 6.8 |
| Chromium | 52.4 | .121 | 6.3 |
| Manganese | 54.8 | .122 | 6.7 |
| Iron | 55.9 | .114 | 6.4 |
| Copper | 63.2 | .095 | 6.0 |
| Zinc | 65.1 | .094 | 6.1 |
| Arsenic | 74.9 | .081 | 6.1 |
| Bromine | 79.8 | .084 | 6.7 |
| Silver | 107.7 | .057 | 6.1 |
| Tin | 118.8 | .055 | 6.5 |
| Antimony | 119.6 | .051 | 6.1 |
| Iodine | 126.5 | .054 | 6.8 |
| Platinum | 194.3 | .032 | 6.3 |
| Gold | 196.7 | .032 | 6.4 |
| Mercury | 199.8 | .032 | 6.4 |
| Lead | 206.4 | .031 | 6.4 |
| Bismuth | 207.3 | .030 | 6.4 |
| Uranium | 239.0 | .028 | 6.7 |

The student will notice, by consulting Table II, that a number of elements have not been mentioned and for which we should account. Among these are the following notable exceptions:

Carbon, $AC = 1.8$
Hydrogen, $AC = 2.3$
Boron, $AC = 2.7$
Beryllium, $AC = 3.7$
Silicon, $AC = 3.8$
Oxygen, $AC = 4.0$

Quite a number of years ago observations were made on the behavior of carbon, boron, and silicon, which disclosed the fact that the specific heat of these elements increased in proportion to the increase of temperature, but that at a certain limit it remained constant through a considerable range of temperature; thus, for instance, from 800° to 980°, $AC$ for carbon was 5.5; from 130° to 230°, $AC$ for silicon was 5.7; at 600°, $AC$ for boron was 5.5; and from 400° to 500°, $AC$ for beryllium was 5.6.

We must, as a matter of fact, remember that the application of the discovery of Dulong and Petit should not be for the correction of atomic weight as determined from the results of the analysis of definite compounds, for the simple reason that by analysis much more accurate results are obtained, but that it helps to decide between certain alternative values, all of which satisfy the relations deduced from analysis.

**19.** As an example of where the application of Dulong and Petit's law will prove itself valuable, we will refer to Art. **5**, where an examination of the composition and vapor density of chloride of uranium led to the acceptance of the formulas $U_4Cl_4$, $U_2Cl_4$, and $UCl_4$, if the atomic weight of uranium were taken as 60, 120, and 240, respectively. By applying Dulong and Petit's discovery to practical use, we will find ourselves in the position to determine which of these figures really is the true atomic weight.

The specific heat of uranium has been found to be, as given in Table II, .028, and if 60 is accepted as the atomic weight, the product $AC$ is 1.68 ; if 120, $AC$ is 3.36 ; and if 240, $AC$ is 6.72.

From this evidence there can hardly be any doubt that the atomic weight must be 240, and that $UCl_4$ expresses the true composition of chloride of uranium. This fact being once established, the formulas of other salts of uranium are of course easily deduced.

**20. Specific Heat of Compounds.**—Further investigations based on Dulong and Petit's discovery rapidly disclosed the fact that the specific heat of a compound multiplied by its molecular weight is practically the same for compounds of a like character. For instance, for

$PbCl_2$, $C = .0664$; $AC = .0664 \times 277.5 = 18.4$
$PbBr_2$, $C = .0533$; $AC = .0533 \times 366.5 = 19.6$
$PbI_2$, $C = .0427$; $AC = .0427 \times 459.5 = 19.6$
Aragonite, $CaCO_3$, $C = .206$; $AC = .206 \times 100 = 20.6$
Strontianite, $SrCO_3$, $C = .145$; $AC = .145 \times 147 = 21.3$
Witherite, $BaCO_3$, $C = .109$; $AC = .109 \times 197 = 21.4$
Cerussite, $PbCO_3$, $C = .080$; $AC = .080 \times 266.5 = 21.3$

The next logical conclusion drawn from above data naturally was that the specific heat remained materially the same whether the element exists in a free or combined state. The product $AC$ for lead being determined directly and found to be 6.4, that for the haloid elements combining with lead could be readily calculated in the following manner :

$$\text{Chlorine, } \frac{18.4 - 6.4}{2} = 6.0$$

$$\text{Bromine, } \frac{19.6 - 6.4}{2} = 6.6$$

$$\text{Iodine, } \frac{19.6 - 6.4}{2} = 6.6$$

In exactly the same way it may be found that the atomic heat of $CaCO_3$, $SrCO_3$, $BaCO_3$, and $PbCO_3$ being almost identical, that of $Ca$, $Sr$, $Ba$, and $Pb$ must also be nearly identical. By using this method, it is possible to ascertain the "atomic heat" of such elements as hydrogen, oxygen, and nitrogen, which would represent extreme difficulties in the way of direct determination in either the solid or liquid state.

**21. Isomorphism and Atomic Weight.**—Although Le Blanc in 1784 noticed that crystals which separate out of a solution containing both cupric sulphate $CuSO_4$ and ferrous sulphate $FeSO_4$ contain both these salts, and that their form remains the same, even though the proportions of the salts they contain may vary, it was not until 1819 that Mitscherlich established a distinct connection between crystalline form and chemical composition. He found that the acid arsenates and phosphates of potassium and ammonium all crystallized in the tetragonal system and in identical forms. Other bodies were consequently examined by him with a similar result, and as the outcome of his researches he established the fact that bodies having a similar chemical composition must also have the same crystalline form, and such bodies he termed isomorphous. The exact crystalline form was not usually identical, but the crystal system was the same, and also, in general, the form and habit of the crystal; the variations that occurred were of a minor character, and were affected only by the angles between the faces of the crystal and the relative length of the axes. Further investigations have very much extended our knowledge of isomorphous crystals.

As examples of such isomorphous bodies, we may mention:

1. $NH_4H_2PO_4$ and $KH_2PO_4$, both of which crystallize in the tetragonal system in the form indicated in Fig. 4, consisting of the tetragonal prism in combination with the pyramid.

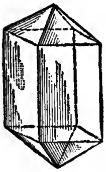


FIG. 4

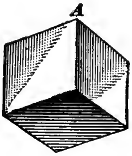


FIG. 5

2. The isomorphous carbonates, calcite $CaCO_3$, magnesite $MgCO_3$, siderite $FeCO_3$, rhodochrosite $MnCO_3$, smithsonite $ZnCO_3$, all of which crystallize typically in

rhombohedrons, as shown in Fig. 5. These rhombohedrons are identical, with the exception that the angle at *A* varies slightly with the nature of the mineral; e. g., with

| | |
|---|---|
| Calcite | it is 105° 5′ |
| Rhodochrosite | it is 106° 51′ |
| Siderite | it is 107° 0′ |
| Magnesite | it is 107° 29′ |
| Smithsonite | it is 107° 40′ |

3. Another interesting series of isomorphous bodies, which are also carbonates, may here be cited; it consists of the compounds

| | |
|---|---|
| Aragonite | $CaCO_3$ |
| Strontianite | $SrCO_3$ |
| Witherite | $BaCO_3$ |
| Cerussite | $PbCO_3$ |

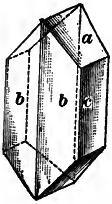


FIG. 6

All these compounds crystallize in the rhombic system, after the form shown in Fig. 6, in which *b*, *b* are the prism faces, *a* is a brachydome face, and *c* is a brachypinacoid face. The only variation is in the interfacial angles, those between the prism faces and the brachydome faces being for

| | Prism | Brachydome |
|---|---|---|
| Aragonite | 116° 10′ | 108° 26′ |
| Cerussite | 117° 14′ | 108° 16′ |
| Strontianite | 117° 19′ | 108° 12′ |
| Witherite | 117° 48′ | 107° 48′ |

4. Another series of isomorphous bodies is of considerable interest; it consists of the compounds:

| | |
|---|---|
| Chlorapatite | $3Ca_3(PO_4)_2, CaCl_2$ |
| Fluorapatite | $3Ca_3(PO_4)_2, CaF_2$ |
| Pyromorphite | $3Pb(PO_4)_2, PbCl_2$ |
| Mimetisite | $3Pb_3(AsO_4)_2, PbCl_2$ |
| Vanadinite | $3Pb_3(VO_4)_2, PbCl_2$ |

All these compounds crystallize in the hexagonal system in the form shown in Fig. 7. The faces developed here are: *a*, *a*, *a*, prism faces; *b*, *b*, *b*, pyramid faces; *c*, the basal plane terminating the prism.

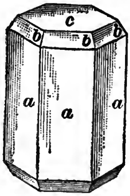


FIG. 7

Again, in this case also, the typical forms exhibited by the various compounds mentioned are identical, a slight variation in the angles being the only essential difference.

**22. Isodimorphous and Isotrimorphous Series.** There are, however, some cases in which the same substance crystallizes in two different forms, which forms we may call $A$ and $B$; while other bodies allied to it chemically, not only yield two forms $A_1$ and $B_1$, but these different forms agree crystallographically $A$ with $A_1$, and $B$ with $B_1$. Thus, for instance, antimony trioxide crystallizes in the regular system as senarmontite, and in the rhombic system as valentinite; so arsenic trioxide crystallizes in the regular system as arsenolite, and in the rhombic system as claudetite. Potassium and sodium nitrate crystallize in both the hexagonal and in the rhombic system in similar forms. Such substances are said to be *isodimorphous.* Instances are also known of bodies adopting even as many as three similar forms, being thus known as *isotrimorphous* bodies.

*These examples of isomorphism will suffice to show that there is an intimate relation between the chemical composition of bodies and the crystalline form which they assume.*

Continuous researches, however, did not only produce a large number of examples of bodies associating a similarity of composition and form, but they also disclosed and proved the fact that there are numerous bodies, which though similar in crystalline forms, widely diverge in chemical composition and character. This is especially the case in regard to substances that crystallize in the regular system. We are not, therefore, justified in assuming that all bodies which show a certain uniformity of their crystalline forms, are also allied to each other in their chemical composition.

**23.** In the mineral kingdom it is common to find crystals composed of mixtures of compounds, and they may also be in many cases so obtained in the laboratory. *Aragonite* $CaCO_3$ and *witherite* $BaCO_3$ are isomorphous, *alstonite* is a mixture of $CaCO_3$ and $BaCO_3$, crystallizing in the same form as these; similarly, *heavy spar* $BaSO_4$ and *celestine* $SrSO_4$ are isomorphous, while *barytocelestine*, a mixture of $BaSO_4$ and $SrSO_4$, crystallizes in the same form as these. Experiments with solutions of mixed salts have led to the same results. It had been already recognized by Mitscherlich, in 1819, that when substances adopt the same crystalline form, and are also chemically related to one another, they crystallize intimately together. It was afterwards found that if a crystal of the one isomorphous substance was placed in a solution of the other, a *coating* or *overgrowth* of the second substance would form.

Here we have a means of separating isomorphous bodies into two classes, for with substances chemically unlike, but crystallizing in similar forms, overgrowths do not occur. This has led to a modification of the statement of the law of isomorphism in the direction of further limitation, and at the present day it is usually held that bodies are only truly isomorphous when they fulfil all the following conditions:

1. *They must crystallize in the same form.*

2. *They must be capable of crystallizing intimately together and in all proportions.* (This, of course, is limited by the solubility of the salts.)

3. *They must be capable of forming overgrowths.*

Bodies that fulfil all these conditions ought to show an analogous chemical composition.

**24.** A few examples will suffice to show the bearing of the law of isomorphism as a control for chemical composition, and consequently for atomic weight.

In the early part of this century, the atomic weight of copper was generally supposed to be 63.4 and that of silver 216.6; on this basis the formula of the mineral sulphides of copper and silver were $Cu_2S$ and $AgS$. The minerals, however, not only crystallized in the same form, but replaced one another in varying proportions in minerals of a more complex nature; these minerals, therefore, should have an analogous character. Accepting, for instance, $Cu_2S$ as the formula for one, the other naturally should be $Ag_2S$, but this would imply that the atomic weight of silver should not be 216.6, but 108.3. This number therefore (or, in view of the later more accurate determinations, 107.66) should, under the control of the law of isomorphism, be accepted as the atomic weight of silver. Or, as another example may serve the fact, the formulas generally accepted by earlier chemists for permanganate and perchlorate of potassium were $KO, Mn_2O_7$ and $KO, ClO_7$, the atomic weight of chlorine being double that adopted at the present time. It was observed, however, that these salts were isomorphous, and this led to the reducing of the atomic weight of chlorine to its present weight, the formulas then becoming $KO$, $Mn_2O_7$ and $KO, Cl_2O_7$, showing a true analogy of chemical composition. Owing to researches, based on Dulong and Petit's investigations, the atomic weight of potassium was also reduced to its present value and the formulas ultimately adopted were $K_2O, Mn_2O_7$ and $K_2O, Cl_2O_7$, or $KMnO_4$ and $KClO_4$.

**25. Isomorphous Elements.**—If we were to collect the elements that can replace one another without substantial alteration of their crystalline form, we would have the elements arranged in series, the members of each series being in this sense termed isomorphous elements. Thus, in the examples given in Art. **21,** from example 1, $K$ and $NH_4$ replace each other without alteration of crystalline form. In example 2, $Ca$, $Mg$, $Fe$, $Mn$, and $Zn$ replace one another in like manner, and are isomorphous elements. In example 3, $Ca$, $Sr$, $Ba$, and $Pb$ are isomorphous elements. Finally, in example 4, the isomorphism of chlorapatite and fluorapatite points to $Cl$ and $F$ as isomorphous elements; that of pyromorphite, mimetisite, and vanadinite points to $P$, $As$, and $V$ as isomorphous elements, and that of apatite and pyromorphite indicates that *Ca* and *Pb* are isomorphous elements. An examination of the whole of the groups of isomorphous compounds would enable us in this way to draw up in groups a fairly complete list of the elements on this basis. The principal of the groups are given in Table III.

TABLE III

| Group | List of Isomorphous Elements |
|---|---|
| I | *F*, *Cl*, *Br*, *I* (*CN*); also, *Mn* in permanganates. |
| II | *S*, *Se*, *Te* in binary compounds, and in sulphates, selenates, and tellurates. |
| III | *As*, *Sb*, *Bi*; also, *As*, *P*, and *V* in salts. |
| IV | *H* (?), the alkalies and $NH_4$ in most of their compounds; *Ag*; also, *Tl* and *Cu* in thallious and cuprous compounds. |
| V | Alkaline earths, *Pb*. |
| VI | *Al*, *Fe*, *Cr*, *Mn* in sesquioxides and the salts of these. |
| VII | *Fe*, *Ni*, *Co*, *Mn*, *Zn*, *Mg* in the salts of monoxides. |
| VIII | The platinum metals, and in some compounds *Au*, *Sn*, *Fe*, *Ni*. |
| IX | *C*, *Si*, *Ti*, *Ge*, *Zr*, *Sn*, *Th*. |
| X | *Ta*, *Nb*. |
| XI | *Cr*, *Mo*, *W*, especially in trioxides and derivatives of these. |

This table is not without significance, even if we regard it as a classification of the elements according to their chemical relationships, and in itself serves to show how intimate is the connection between chemical composition and crystalline form.

The special point of view here, however, is that with the aid of the law of isomorphism, it is in most cases possible to establish the formula by which a compound should be represented in analogy with other compounds, and by this means to decide as to whether a certain value should be accepted as an atomic weight, or whether some multiple or submultiple of this value is to be taken.

**26.** If we place a piece of zinc and platinum in dilute sulphuric acid and connect these two metals outside the liquid by means of a metallic wire, such as platinum wire for instance, a current of electricity will be transmitted along the wire, but no change of composition is effected by it. If we connect the ends of the wire with a strip or bar of any other metal, the current will pass through it also without effecting any permanent change.

If, however, we place a drop of sodium-sulphate solution on a piece of litmus paper and bring the wire ends into the drop of the solution, without allowing the wire ends to touch each other, or in other words, if we make the sodium-sulphate solution the medium of connecting the wires, we will find that the sodium-sulphate solution is decomposed, which is shown by the fact that the litmus paper near the end of the wire connected with the piece of platinum becomes red, owing to the presence of an acid, while the paper near the end of the wire connected with the piece of zinc remains unchanged, owing to the presence of an alkali.

This leads us to see the necessity of classifying such bodies as conduct a current of electricity into (1) *conductors*, or bodies that conduct electricity without undergoing any change of composition, and (2) *electrolytes*, or bodies that conduct electricity but undergo decomposition.

To the first class belong most of the elements, while the second consists of compounds either in fused condition or in solution.

The solution of sodium sulphate is an electrolyte, and is decomposed during the passage of the electric current; the products formed in the presence of water being caustic soda and sulphuric acid.

This electrical-decomposition process is known to the chemist as *electrolysis*, while the wires that come in contact with the electrolyte are known as *electrodes*, being distinguished as the positive electrode, or *anode*, attached to the platinum, and the negative electrode, or *cathode*, attached to the zinc.

The phenomena that take place during the process of electrolysis are usually of a complex character. For instance, there are good reasons to believe that sodium sulphate decomposes primarily into sodium and $SO_4$; these, however, cannot exist in the presence of water, on which they react as expressed in the two following equations:

$$Na_2 + 2H_2O = 2NaOH + H_2$$
$$SO_4 + H_2O = H_2SO_4 + O$$

The sodium hydroxide and the sulphuric acid remain necessarily in the liquid, while at the cathode hydrogen is set free, and at the anode oxygen is liberated. If a solution of copper sulphate is electrolyzed, the copper does not react on the water, but deposits on the cathode, while oxygen, as before, is set free at the anode.

Faraday, who investigated electrolysis, discovered that if a current is passed through a solution, the amount of the element either liberated or deposited at the electrode at a given time was directly proportional to the strength of the current; that is, if the same current was passed through solutions of different salts, the amounts of the elements liberated at the electrode always showed a definite relation to one another.

If, for instance, the same current was passed successively through acidulated water, a solution of silver nitrate, and a solution of cupric sulphate, and the amount of hydrogen liberated from the acidulated water was .01083 gram, then the amount of silver deposited from the silver nitrate was always 1.118 grams and the amount of copper from the cupric sulphate was always .3281 gram.

If we now divide the weights of the deposited silver and copper by that of the liberated hydrogen, we obtain the following results:

$$\frac{1.118}{.01083} = 107.7 \text{ for silver}$$
$$\frac{.3281}{.01083} = 31.6 \text{ for copper}$$

Numbers obtained in this way are generally known as the *electrochemical equivalents.* A list of the electrochemical equivalents and the atomic weights of a number of elements are given in Table IV.

**TABLE IV**

| Name of Element | Electrochemical Equivalent | Atomic Weight |
|---|---|---|
| Potassium | 39.0 | 39 |
| Sodium | 23.0 | 23 |
| Gold | 65.4 | 196.2 |
| Silver | 107.7 | 107.7 |
| Copper | 31.6 | 63.2 |
| Mercury | 99.9 and 199.8 | 199.8 |
| Tin | 29.5 and 59 | 118 |
| Iron | 28 and 56 | 56 |
| Zinc | 32.5 | 65 |
| Lead | 103.2 | 206.4 |
| Oxygen | 8.0 | 16 |
| Chlorine | 35.4 | 35.4 |
| Bromine | 79.8 | 79.8 |
| Iodine | 126.5 | 126.5 |
| Nitrogen | 4.7 | 14 |

In examining this table the student will at once notice (1) that the atomic weight of an element is either identical with the electrochemical equivalent or some multiple of it; and (2) that some elements seem to have more than one electrochemical equivalent.

With regard to the first point, it must be remembered that the value obtained is the equivalent of hydrogen. We have already seen in discussing the subject of valence that elements are classified according to their combining power as monovalent, divalent, etc.

The equivalent of an element, as determined from its combining power, is therefore equal to

$$\frac{\text{Atomic Weight}}{\text{Valence}}$$

and would be, for instance, in the case of

$$\text{Silver, } \frac{107.7}{1} = 107.7$$

$$\text{Copper, } \frac{63.2}{2} = 31.6$$

$$\text{Gold, } \frac{196.2}{3} = 65.4$$

These numbers are precisely the same as those determined for the electrochemical equivalents.

The second point can easily be explained, if the student bears in mind that a number of metals form two independent series of salts; as, for instance, mercurous chloride $HgCl$ and mercuric chloride $HgCl_2$, stannous chloride $SnCl_2$ and stannic chloride $SnCl_4$, etc., and that those metals possess more than one valence. For example, we have for mercury $\frac{199.8}{1}$ and $\frac{199.8}{2}$, and for tin $\frac{118}{2}$ and $\frac{118}{4}$; and, as in the previous case, the values so obtained agree with the electrochemical equivalent. From all that is said in this article we can readily deduct the following law:

*The atomic weight of an element is equal to the electrochemical equivalent, as determined during the electrolysis of a compound, multiplied by the valence of the element in the compound.*

## CONSTITUTION OF COMPOUNDS IN THE GASEOUS CONDITION

**27.** Investigations of the nature and the constitution of the molecule of any gaseous compound may be made upon several independent lines; namely, by ascertaining any of the following:

1. The vapor density, and deduce from this the molecular weight.

2. The products that are formed when the compound is decomposed by heat or other means.
3. The way the compound is synthetically built up from either its elements or simpler compounds, as the case may be.
4. The behavior of the compound in the presence of certain reagents.

**28. The Effect of Heat.**—If a compound exists at ordinary temperature in the gaseous form, or if a solid or liquid compound can readily be brought into this form, little difficulty exists in ascertaining whether it behaves as a typical gas or not. For, if it does so, it expands regularly and equally with every increase of temperature (the volume varies *directly* with the *absolute* temperature). The volume of the gas at 0° C. being $v$, its volume at the temperature $t$ will be $\frac{v(273+t)}{273}$, the pressure remaining constant. Its density then will be

$$D = \frac{W}{w}$$

where $W$ is the weight of a given volume of the gas, and $w$ is the weight of the same volume of hydrogen under the same pressure and at the same temperature (hydrogen being taken as the unit). Or if, as it is very often the case, air is used in place of hydrogen as the medium for comparison, and the density thus found called $d$, the density for hydrogen may be expressed thus:

$$D = 14.43\,d$$

and the molecular weight, since the molecular weight of hydrogen is 2, would then be

$$2\,D, \text{ or } 28.86\,d$$

**29. Dissociation.**—There exist, however, numerous cases where the volume of gaseous compounds, after a certain temperature has been reached, is greater than it should be according to the law of Gay-Lussac referred to in the previous article. Let us consider the case of stannous chloride as an illustration. This compound, if its formula is $Sn_2Cl_4$, should have the vapor density 188.8, while as $SnCl_2$ its vapor density would be only 94.4. It boils at 606°, and at 619° its vapor density is 185.5, corresponding closely to $Sn_2Cl_4$, but a still further increase of heat causes the vapor density to diminish, until at 800° its vapor density is only 104, then approaching closely the value for $SnCl_2$, though still too high for it.

This vapor density undoubtedly indicates that stannous chloride, at the boiling point, has a molecular composition corresponding to $Sn_2Cl_4$; but that at higher temperatures these heavier molecules gradually dissociate into $SnCl_2$, though at 800° (and even at 1,100°) the complete dissociation has not been entirely effected.

Similarly, nitrogen tetroxide, if its formula is $N_2O_4$, should have a vapor density of 45.95. The vapor density of this compound has been made the subject of very thorough and interesting researches, and the values obtained at its boiling point are given here:

At 26.7°, $D = 38.30$
At 35.4°, $D = 36.56$
At 39.8°, $D = 35.25$
At 49.6°, $D = 32.80$
At 60.2°, $D = 30.16$
At 70.0°, $D = 27.84$
At 80.6°, $D = 26.01$
At 90.0°, $D = 24.85$
At 100.1°, $D = 24.27$
At 111.3°, $D = 23.70$
At 121.5°, $D = 23.41$
At 135.0°, $D = 23.12$
At about 140.0°, $D = 22.98$

The value given last, 22.98, would be the vapor density corresponding to the formula $NO_2$, from which it follows that at 140° nitrogen tetroxide is dissociated thus:

$$\underset{\text{1 molecule}}{N_2O_4} = \underset{\text{2 molecules}}{2NO_2} \text{ at } 140^\circ$$

But even at its boiling point, the density is considerably lower than 45.95, which is required for the formula $N_2O_4$, from which fact the conclusion has been drawn that $N_2O_4$ passes into the state of partial dissociation as soon as its boiling point is reached.

**30. Extent of Dissociation.**—From the observations (assuming that $N_2O_4$ and $NO_2$ are the only products) the number of molecules of each of these compounds may be readily calculated. Assuming that there are 100 molecules of $N_2O_4$ at the beginning, and of these, at a certain temperature, say 49.6°, $x$ are dissociated, forming $2x$ molecules of $NO_2$, and leaving $100-x$ molecules of $N_2O_4$; or, in other words, at 49.6°, 100 molecules of $N_2O_4$ become $(100-x)N_2O_4 + 2xNO_2$; there are now $(100+x)$ molecules in the place of the original 100, and the density will have diminished in the inverse proportion, so at 49.6°,

$$\frac{100}{100+x} = \frac{32.8}{45.95}$$

from which we readily calculate $x = 40$.

At 49.6°, therefore, the gas consists of 60 molecules of $N_2O_4$ and 80 molecules of $NO_2$.

The pressure that a gas exerts on the walls of a confined space is directly proportional to the volume of the gas (as measured under standard conditions) which is introduced into that space (according to Mariotte's law); hence, instead of determining the volume occupied by the gas at different temperatures, the increase of pressure may be measured, and the volume calculated from this—a method of procedure frequently adopted where high temperatures have to be employed.

**31. Dissociation Accompanied by Chemical Change.**—In the few cases so far considered, the changes that occur with the increase of the temperature are reversed when the temperature again falls; the $NO_2$ molecules gradually reunite to form $N_2O_4$ molecules, so that, for instance, starting with 200 molecules $NO_2$ at 140°, there will be found 60 molecules $N_2O_4$ and 80 molecules $NO_2$ when the temperature has fallen to 49.6°. The process may be represented as follows:

$N_2O_4 = NO_2 + NO_2$ for rising temperature
$NO_2 + NO_2 = N_2O_4$ for falling temperature

Such a reversible change is most conveniently expressed by a general equation; thus,

$$N_2O_4 \rightleftarrows NO_2 + NO_2$$

Many compound substances, when heated, undergo a change of composition, as for instance

$$\begin{aligned} 2Ag_2O &= 4Ag + O_2 \\ PCl_5 &= PCl_3 + Cl_2 \\ CaCO_3 &= CaO + CO_2 \end{aligned}$$

Conditions may be such that, with a fall in temperature, recombination occurs; while this is not always possible, it is known to be the case in the last two examples,

$$\begin{aligned} PCl_3 + Cl_2 &= PCl_5 \\ CaO + CO_2 &= CaCO_3 \end{aligned}$$

and it will be of interest to consider these two cases more in detail.

**32. Dissociation of Phosphorus Pentachloride.** The phenomena observed with nitrogen tetroxide, in regard to the reunion of molecules of similar chemical composition, take place in this case between molecules of different chemical composition, and are likewise classed as dissociation phenomena. Thus, if phosphorus pentachloride is heated in a closed glass tube, the colorless vapor of the pentachloride soon shows a greenish tint, which is due to free chlorine. On cooling, a recombination appears to gradually take place, for the greenish tinge slowly disappears. The well known French chemist Würtz made the interesting observation that, if $PCl_5$ was heated in an atmosphere of one of the products of dissociation—that is, in either $PCl_3$ or $Cl_2$—it became possible to vaporize the $PCl_5$ without decomposition. The effect of heating phosphorus pentachloride alone is therefore expressed by

$$\underset{\text{1 molecule}}{PCl_5} = \underset{\text{1 molecule}}{PCl_3} + \underset{\text{1 molecule}}{Cl_2}$$

Hence, the vapor density was indeed found to be 52.6, instead of 104 as required by the formula $PCl_5$.

Heated in presence of $PCl_3$ or of $Cl_2$, in order to prevent dissociation, the vapor density was 104, corresponding thus to the formula $PCl_5$.

**33. Dissociation of $CaCO_3$.**—In connection with $CaCO_3$, a typical case of dissociation of a solid substance (calcium carbonate) into the solid calcium oxide $CaO$ and the gaseous carbon dioxide $CO_2$ is encountered. The *dissociation tension* of $CaO$ by itself is so small that it may be neglected here, and the extent of the dissociation may be measured by the pressure exerted when calcium carbonate is heated in a closed space. The French chemist Le Chatelier has determined this pressure at various temperatures and found it to be:

| Temperature. Degrees C. | Pressure of Mercury. Millimeters |
|---|---|
| 547 | 27 |
| 610 | 46 |
| 625 | 56 |
| 740 | 255 |
| 745 | 289 |
| 810 | 678 |
| 812 | 763 |
| 865 | 1,333 |

The pressure exerted by the gas at each temperature is termed the *dissociation tension* for that temperature; thus, at 740° the dissociation tension is 255 mm. of mercury and at 812° it is 763 mm., approximately standard atmospheric pressure. On cooling, recombination of the $CaO$ and $CO_2$ occurs just as in the previous cases. So if the temperature is allowed to fall from 810° to 610°, this recombination takes place until the dissociation tension, 46 mm., corresponding to 610°, is reached, and if the temperature is then kept constant at this point, the dissociation tension will remain constant at 46 mm. If, then, calcium carbonate is heated under such conditions that the products formed remain in contact, the phenomena observed are true dissociation phenomena.

**34. Decomposition of Oxides by Heat.**—In considering the decomposition by heat, we shall first investigate the behavior of the oxides. Many of these readily give up either a part or the whole of their oxygen; thus,

$$\begin{aligned} 2HgO &= 2Hg + O_2 \\ 2Au_2O_3 &= 4Au + 3O_2 \\ 3MnO_2 &= Mn_3O_4 + O_2 \\ 4CrO_3 &= 2Cr_2O_3 + 3O_2 \end{aligned}$$

Other oxides, as, for instance, silica, alumina, magnesia, zinc oxide, etc., are able to resist a very large amount of heat, without giving any visible indication of decomposition.

Researches pertaining to the behavior of oxides disclose the fact that there exists a certain relation between the position of electropositive elements in the periodic system and the stability of their oxides.

The electropositive elements that, after forming oxides, readily part again, at even moderate temperatures, with all of their oxygen, belong either in Group VIII or in the uneven series of other groups (see a periodic table of the elements) of the periodic system. They are *Cl*, *Br*, *I*, *Ag*, *Au*, *Hg*, *Pd*, and *Pt*. It has been found, in fact, that the higher the atomic weight of an oxide-forming metal is in general, the more readily is the oxide decomposed; and if we extend our investigation and inquire into the effect of heat in presence of simple reducing agents, such as hydrogen or carbon, we will further discover that under these conditions many more oxides undergo decomposition. The oxides of the following elements must then be added to those previously given: *Cu*, *Zn*, *Cd*, *Ga*, *In*, *Tl*, *Ge*, *Sn*, *Pb*, *P*, *As*, *Sb*, *Bi*, *S*, *Se*, *Te*, *Fe*, *Co*, *Ni*, and the rest of the platinum metals. A glance at a periodic table of the elements will show that these elements belong either to Group VIII or to the uneven series of other groups.

The stability of the oxides is therefore a function of the atomic weight, for the elements whose oxides most readily give up the whole of their oxygen belong either to Group VIII or to the uneven series of the other groups.

**35. Decomposition of Other Compounds by Heat.** Other binary compounds, such as sulphides and chlorides, show a similar relationship. With more complex salts, such as the carbonates, nitrates, and sulphates, the primary products of decomposition are usually oxides that are liable to undergo further change or decomposition according to the conditions under which the experiment is performed. Nitrate of lead, for instance, forms, as ultimate products, $PbO$, $NO_2$, and $O_2$:

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

the temperature required to start and continue the decomposition being such that $N_2O_4$ cannot exist. But with nitrate of bismuth in the presence of moisture or water of crystallization, a lower temperature suffices to effect a decomposition, and the products obtained are the oxide of bismuth and nitric acid:

$$2Bi(NO_3)_3, 3H_2O = Bi_2O_3 + 6HNO_3$$

So with the carbonates, lead or calcium carbonate, for instance, give as products of decomposition the oxide of the metal and carbon dioxide; while, with silver carbonate, the oxide of silver also undergoes decomposition, and the ultimate products are silver, oxygen, and carbon dioxide:

$$2Ag_2CO_3 = 4Ag + 2CO_2 + O_2$$

**36. Formation of Compounds by Synthesis.**—Just as in numerous cases two elements unite to form a binary compound, such as an oxide, or chloride, etc., so the synthesis of more complex compounds may be effected by the combination of two binary compounds. Thus,

$PbO + SO_3$ readily form $PbSO_4$
$PbO_2 + SO_2$ readily form $PbSO_4$
$CaO + CO_2$ readily form $CaCO_3$
$KCN + AgCN$ readily form $KAg(CN)_2$
$H_2O + N_2O_5$ readily form $2HNO_3$
$2NH_3 + H_2S$ readily form $(NH_4)_2S$

This method of regarding salts as composed of two binary compounds was adopted by Berzelius and other chemists of his time, as a general explanation of the formation of the more complex bodies, and is known as the *dualistic theory*.

If our attention is principally given to inorganic compounds, many points in favor of this theory may be raised and sustained, but when we come to consider the complex compounds of organic chemistry, such an explanation of constitution is entirely insufficient, and at present it has given way to the *unitary theory*, a conception that regards the compound as made up of individual atoms, each of which exerts its influence on the nature and stability of the body.

## CONSTITUTION OF COMPOUNDS IN THE LIQUID STATE

**37. Molecular or Specific Volume.**—It has been shown in connection with the law of Mendeteef that a certain periodic relationship exists between the atomic volumes of the elements. Although a very few of the elements can be obtained in the liquid condition under such circumstances as to admit an accurate determination of their atomic volume, there are, however, many compounds, especially carbon compounds, that exist at ordinary temperatures and pressure in the liquid state, and Kopp, in 1842, showed that the specific gravity of such bodies stood in intimate relation to their composition. It was first discovered that some isomeric liquids (i. e., bodies having the same chemical composition but differing in chemical character) had the same specific volume (the specific volume, sometimes called the molecular volume of a compound, is the quotient of its molecular weight by its specific gravity), and furthermore, that in a series of compounds, which differed from one another only by $n\ CH_2$ groups, the specific volumes showed a regular difference corresponding to the number of these groups. Examples of this are given as follows:

| Substance | Formula | Molecular Weight | Specific Volume | Difference |
|---|---|---|---|---|
| Acetic acid | $CH_3CO_2H$ | 60 | 63.7 | |
| Methyl formate | $HCO_2CH_3$ | 60 | 63.4 | |
| Butyric acid | $C_3H_7CO_2H$ | 88 | 107.1 | |
| Ethyl acetate | $CH_3CO_2C_2H_5$ | 88 | 107.6 | |
| Methyl alcohol | $CH_3OH$ | 32 | 42.7 | 19.5 |
| Ethyl alcohol | $C_2H_5OH$ | 46 | 62.2 | 19.1 |
| Propyl alcohol | $C_3H_7OH$ | 60 | 81.3 | 20.3 |
| Butyl alcohol | $C_4H_9OH$ | 74 | 101.6 | 21.1 |
| Amyl alcohol | $C_5H_{11}OH$ | 88 | 122.7 | |

It is certainly evident from these figures that some relation must exist between the specific volume and the chemical composition of liquid compounds. We must, however, define what is understood by the specific gravity of a liquid and the condition under which it is determined, for its value will vary considerably according to the conditions under which it is measured.

In order that the results may be compared, it has been found necessary to take the specific gravity at the boiling point of the liquid, since then, apparently, liquids most nearly approach the same physical conditions.

**38. Determination of the Specific Gravity of a Liquid.**—The determination of the specific gravity of liquids has been already outlined in *Physics*, and will be briefly repeated here. The determination is generally accomplished by means of a *pycnometer* (Dr. Sprengel's pycnometer is a very convenient form). This little instrument is first weighed alone (let us call it weight $w$), and is then filled with water, adjusted to proper temperature, and weighed again (the weight thus obtained we will call $w_1$); finally it is filled with the liquid whose specific gravity is to be determined, and the weight (which we might call $w_2$) again taken.

It is evident, however, that the weight $w$ is not the absolute weight of the pycnometer, but practically that of this instrument plus the air it contains. The weight of the air may be considered to be calculated with sufficient accuracy by taking it as $\frac{1}{800}$ of that of the increase of weight when filled with water, that is, $\frac{1}{800}(w_1 - w)$. After deducting this, the weight of the vacuous pycnometer is obtained (this we will call $W$).

Then the specific gravity of the liquid $S$, compared with water as unity, is

$$S = \frac{w_2 - W}{w_1 - W}$$

By suspending the apparatus in a bath of liquid at any temperature, the specific gravity at that particular temperature may also be ascertained.

**39.** A more appropriate device for the purpose of making a succession of observations at different temperatures is the instrument shown in Fig. 8. It is known as a *dilatometer*, and consists of a glass tube $a$ which terminates in a bulb $b$. The bulb and the stem must be calibrated, and the stem is graduated so that the volume is known to any point of the graduation. The bulb is filled with the liquid in question and the increase in weight noted. If the bulb and its contents are now heated at successive temperatures, the liquid will expand and the volume it occupies at different temperatures may be measured by noting the graduated point to which it rises on the stem.

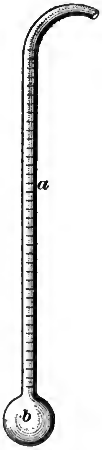


FIG. 8

It is very often possible to raise a liquid to its boiling point without ebullition actually taking place, and hence the actual volume at the boiling point may be determined. By these methods, the specific gravities of a large number of liquids have been determined, and we shall now see how the specific volumes of compounds and of the elements of which the former are composed may be deduced.

We have seen from the examples given in Art. **37** that the difference of specific volume by the introduction of the group $CH_2$ is approximately 22.

If we now compare two liquids similar in composition, except that the first contains $x$ carbon atoms more than the second, and the second $2x$ atoms of hydrogen more than the first, we shall find that they have equal specific volumes. Thus,

$$\text{Specific gravity of heptane } C_7H_{16} = .6138$$

$$\text{Specific volume of heptane } = \frac{100}{.6138} = 162.9$$

$$\text{Specific gravity of mesitylene } C_9H_{12} = .7370$$

$$\text{Specific volume of mesitylene } = \frac{120}{.7370} = 162.8$$

The increase of specific volume due to the introduction of the group $CH_2$ is 22, and the effect of one atom of carbon is equivalent to that of two atoms of hydrogen. The specific volume due to one atom of carbon is 11, and that due to one atom of hydrogen is 5.5.

Again, the specific gravity of water at its boiling point is .9579, and its specific volume therefore is $\frac{18}{.9579} = 18.8$.

If from this we deduct 11 as the value of $H_2$, there remains 7.8 as the specific volume of the atom of oxygen.

The specific volume of a considerable number of compounds, especially organic compounds, can now be calculated, and the values thus obtained compared with those originating from actual experiments. The following general formula may be used:

$$\text{Specific volume } = 11\,m + 5.5\,n + 7.8\,p,$$

where $m$, $n$, $p$, are the number of atoms of carbon, hydrogen, and oxygen, respectively.

For example, alcohol has the formula $C_2H_6O$; using the above given formula, we obtain

$$(11 \times 2) + (5.5 \times 6) + (7.8 \times 1) = 62.8$$

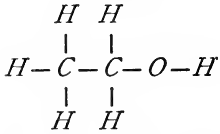
The actual value for the specific volume of alcohol as obtained by experiment is 62.2.

**40.** The formula above given, however, will not hold good in all cases, as we shall presently see. Many organic compounds containing oxygen display a considerable discrepancy between the calculated value and that obtained by actual experiment. For instance, acetone has a calculated specific volume of 73.8, its specific volume obtained experimentally is 78; acetic acid has a calculated specific volume of 59.6, its specific volume obtained experimentally is 63.7.

Investigations developed the fact that such discrepancies always occur whenever oxygen is directly combined to carbon *only*, while if it is combined to hydrogen the previous formula holds good.

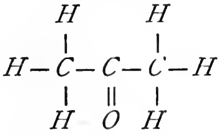
From the behavior of these compounds, and from the manner in which they are acted upon by reagents, there are good reasons for assuming that they may be structurally represented by the following graphic formulas:

ALCOHOL



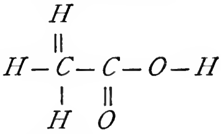
$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

ACETONE



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & \| & & | & & \\ & & H & & O & & H & & \end{array}$$

ACETIC ACID



$$\begin{array}{ccccccccc} & & H & & & & & & \\ & & \| & & & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & \| & & & & \\ & & H & & O & & & & \end{array}$$

Where the oxygen is combined directly with carbon only, we shall call it *carbonyl oxygen*, and where it is combined with hydrogen, we shall call it *hydroxyl oxygen*. From the graphic formulas given the student will readily perceive that alcohol contains hydroxyl oxygen, acetone contains carbonyl oxygen, and acetic acid contains one atom of each type.

Wherever carbonyl oxygen occurs, the specific volume of oxygen has a higher value, namely 12.2, and having allowed for this higher value, the modified expression is for

$$\text{Acetone } (11 \times 3) + (5.5 \times 6) + (12.2 \times 1) = 78.2;$$

$$\text{Acetic acid } (11 \times 2) + (5.5 \times 4) + (7.8 \times 1) + (12.2 \times 1) = 64.$$

A more searching comparison of the values calculated with those based on experimental determinations, has revealed the fact that in general, even with compounds containing only carbon and hydrogen, the specific volume is dependent in some degree on the constitution of the body. Moreover, sulphur and nitrogen, like oxygen, show different values, depending apparently on variations in their valence or manner of combination. Determinations of specific volume thus become of still greater importance, for they can not only be used to fix the molecular weight where the specific gravity is known, and vice versa, but they also afford a means of indicating peculiarities of constitution and valence. So far as inorganic compounds exist in the liquid state; e. g., $SiCl_4$, $SnCl_4$, $TiCl_4$, $POCl_3$, $VOCl_3$, etc., these liquids may be employed for the purpose of ascertaining the specific volume of the elements *Cl*, *Br*, *I*, *Si*, *Sn*, *Ti*, *P*, *V*, etc. The numbers representing the specific volumes for those elements, whose compounds have been examined, are given below in Table V.

**TABLE V**

| Element | Specific Volume |
|---|---|
| Hydrogen | 5.5 |
| Oxygen, *OH* | 7.8 |
| Oxygen, *CH* | 12.2 |
| Carbon | 11.0 |
| Chlorine | 22.8 |
| Bromine | 27.8 |
| Iodine | 37.5 |
| Nitrogen | 2.3 |
| Sulphur, hexavalent | 12.0 |
| Sulphur, tetravalent | 22.6 |
| Sulphur, divalent | 28.3 |
| Phosphorus | 25.4 |
| Silicon | 32.0 |
| Titanium | 35.0 |

In the case of chlorine and bromine, these values have been compared with those deduced from the uncombined elements in the liquid condition and found to agree closely:

| | Specific Gravity | Specific Volume |
|---|---|---|
| Liquid chlorine............. | 1.56 | 22.7 |
| Liquid bromine............. | 2.96 | 26.9 |

On the whole evidence it may therefore be concluded that *the volume occupied by the molecule of an element in the free state is usually the same as that which it occupies in combination in its liquid compounds, but that it undergoes modification according to the method of attachment of the individual atoms, or where the molecule of the compound is of a complex nature.*

Should we attempt to extend the operation of such a generalization to solid bodies, great irregularities appear; it may, however, be taken as generally true that where the compounds are chemically similar and isomorphous there is a fairly close agreement in specific volume, thus:

| | Specific Gravity | Specific Volume |
|---|---|---|
| $MgSO_4,7H_2O$ | 1.685 | 146.0 |
| $ZnSO_4,7H_2O$ | 1.853 | 146.9 |
| $NiSO_4,7H_2O$ | 1.931 | 145.6 |
| $CoSO_4,7H_2O$ | 1.924 | 146.0 |
| $FeSO_4,7H_2O$ | 1.884 | 147.5 |

### SOLUTION

**41.** If we mix oil and water and shake the mixture for some time, we will notice that both liquids are apparently broken up into minute globules which freely intermingle, but we will also notice that on allowing this mixture to become quiet, these intermingled globules separate, and a layer of oil gathers upon the water. If, on the other hand, alcohol and water are shaken together, the alcohol will become intimately associated with the water and evenly distributed throughout the mass without any separation afterwards occurring. In the first case the water and oil for the time being were intermingled, forming an emulsion, while in the latter case the alcohol is said to have dissolved in the water. In the case of alcohol and water, the two liquids may be brought together in any proportion desired without separation occurring afterwards, since alcohol (and a number of other liquids as well) may be associated with water in all proportions.

As a rule, however, the amount of a substance that can be disseminated through water is limited, and when this limit has been reached a *saturated solution* has been formed. Under certain conditions, water may however take up still more of the substance, and the solution is then said to be *supersaturated*.

Although we have been speaking so far only of water, this fact applies to all liquids. Alcohol, as we have frequently seen in previous Instruction Papers, is a good solvent for many salts, and bisulphide of carbon $CS_2$, though it is, as a rule, not a solvent of salts, takes up iodine, phosphorus, sulphur, and many sulphur compounds freely.

**42. Solubility of Salts.**—If we make a solution of common salt $NaCl$, at ordinary temperatures and a solution of it in boiling water, we can estimate the amount of salt dissolved by evaporating the solutions, and we will find in the first case that 35 grams of salt dissolved in 100 grams of water, and that in the second case 40 grams of salt were dissolved by the same weight of boiling water.

If we now repeat these experiments, but use sodium nitrate instead of salt, we will find that 80 grams at ordinary temperatures and 180 grams at the boiling point will dissolve in 100 grams of water.

From these simple experiments we can draw the conclusions that, (1) sodium nitrate is much more freely soluble in water than sodium chloride; (2) both salts are more freely soluble in hot, than in cold, water, and that the difference is much more distinct in the case of sodium nitrate than it is in the case of sodium chloride.

It may in general be laid down as a rule that solid substances are more soluble in hot, than in cold, water; but that there appears to be no simple relation between the amounts dissolved and the temperature. The solubility of a substance for all temperatures may be conveniently represented by a curve, and in Fig. 9 a diagram is given with some examples of these curves, the temperature being indicated along the horizontal line, and the number of grams dissolved in 100 grams of water along the vertical line.

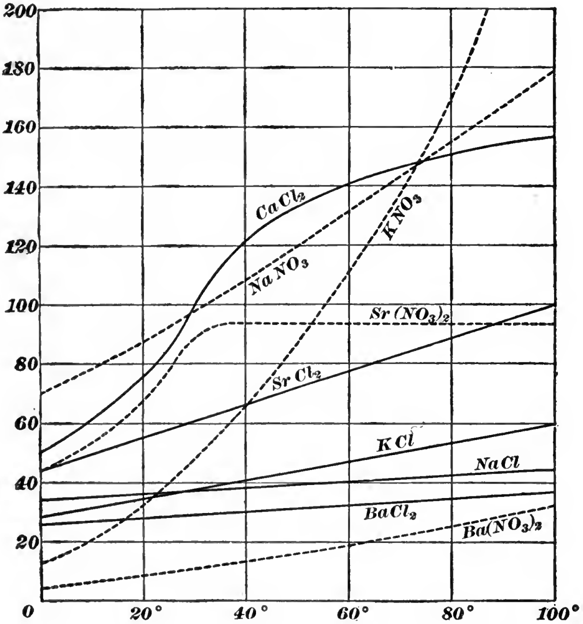


FIG. 9

The student will notice that in some cases the graphic representation is practically a straight line, that is, the amount dissolved increases directly as the temperature; and that in other cases, the amount dissolved increases in a more rapid ratio the higher the temperature.

In a few instances the curve of solubility is irregular, at first rising in the ordinary way and then falling rapidly. An interesting example of this is afforded by sodium sulphate. If crystals of this salt having the composition $Na_2SO_4 \cdot 10H_2O$ are dissolved in water, and the amounts entering into solution at different temperatures are measured, the curve that represents the result will take the form shown in Fig. 10, being in fact two curves. The explanation is that we are not here dealing with one solubility curve, but with two solubility curves. The curve below 33° ($AB$) is the solubility curve for $Na_2SO_4 \cdot 10H_2O$. The curve above 33° ($BC$) is the solubility curve of the anhydrous salt $Na_2SO_4$. When the hydrated salt $Na_2SO_4 \cdot 10H_2O$ is heated to 33°, it splits up into water and the anhydrous salt $Na_2SO_4$. The hydrated salt has no stable existence above 33°, and the only solid that the solution can be in contact with above that temperature is the anhydrous salt. To prove that we are dealing with two curves, we may bring the anhydrous salt in contact with water below 33°. It

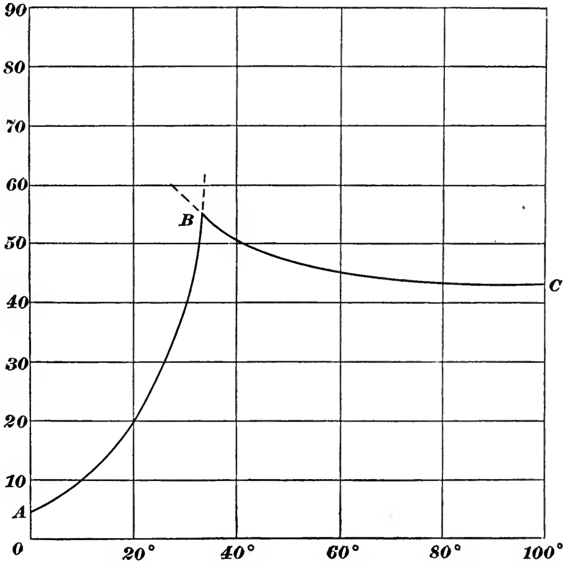


FIG. 10

does not at once unite with water to form the hydrated salt. We can have a solution that is not saturated with $Na_2SO_4$ and is supersaturated with $Na_2SO_4 \cdot 10H_2O$. This on contact with $Na_2SO_4$ will dissolve more of the solid, and on contact with $Na_2SO_4 \cdot 10H_2O$ will deposit crystals of $Na_2SO_4 \cdot 10H_2O$. It is necessary, therefore, to specify exactly the solid with respect to which a solution is saturated. This example is of very great interest, as it brings clearly before the student's mind the fact that in the process of solution we may look for changes taking place in the nature of the molecule; changes that usually imply a breaking up of the molecule. There is, indeed, much evidence—to some of which we shall have the opportunity to refer—that when a substance enters into solution, dissociation may take place, and that salts, even of the most stable character, in many cases, undergo a partial dissociation into the constituents when they are dissolved.

**43. Crystallization of Salts.**—If a solution that has been saturated at 100° is allowed to cool, more or less of the salt will separate according as it is much more or only slightly more soluble at higher temperatures than at the ordinary temperature. If the cooling takes place slowly, and the liquid is undisturbed, the conditions are favorable to the production of large and perfect crystals, while by cooling rapidly and with agitation, small crystals are obtained.

Substances that differ from one another in solubility may frequently be separated by the process of fractional crystallization. If, for instance, a solution containing 50 grams of calcium chloride and 20 grams of potassium chlorate to the liter, is concentrated until its volume is reduced to 100 c. c. and then allowed to cool, approximately 15 grams of potassium chlorate will separate from it. These crystals will contain very little of the extremely soluble calcium chloride, and if they are redissolved at 100° in just sufficient water and again cooled, potassium chlorate practically free from calcium chloride will be obtained.

Such a process is often of service for separating salts on a large scale, as, for instance, in the following case. Potassium chloride is less soluble at ordinary temperatures than sodium chloride, but while its solubility increases somewhat rapidly as the temperature rises, that of sodium chloride alters very little. A boiling saturated solution of the two chlorides will therefore contain considerable more potassium chloride than sodium chloride, and if such a solution is cooled down to about 40°, the salt that separates out will be chiefly potassium chloride.

**44. Solubility of Mixed Salts.**—We cannot, however, assume that in solutions of mixed salts the actual or even the relative solubility of the salts is the same which they possess when separately dissolved. Thus the chlorides of potassium and sodium at about 20° have practically the same degree of solubility (36 parts), but a saturated solution of the mixed salts will be found to contain about twice as much sodium chloride as potassium chloride (30 and 16 parts, respectively). To cite another case, ammonium chloride and barium chloride at the same temperature dissolve to the extent of 37 and 36 parts, respectively, but a solution saturated with a mixture of the two chlorides contains 34 parts of ammonium chloride and 12 parts of barium chloride.

If we attempt to classify substances qualitatively, according to their solubility, it becomes apparent that the salts of the alkalies are, as a rule, more readily dissolved than those of other elements, and while, for instance, the nitrates and chlorides are nearly all readily soluble, the phosphates, carbonates, silicates, and oxides are mostly insoluble in water.

Why some substances should be more soluble than others is still an unsolved problem, but it has been pointed out that the substances that dissolve most freely are also those that generally melt at the lowest temperatures. Such substances that are liquid at ordinary temperatures, as, for example, alcohol, sulphuric acid, nitric acid, etc., mix in any proportion with water, and there is reason for the assumption that in many cases, if not in all, a solution may be regarded as consisting in the association of the solvent with the salt as it passes into the fluid condition. Such a consideration will help to show why more salt should be dissolved at higher temperatures than at lower ones.

**45. Heat Phenomena of Solution.**—When a substance dissolves in water, the particles of the salt, or of any water of crystallization it may contain, are disseminated through the liquid, and a change takes place corresponding to the passage from the solid to the liquid state. We have previously seen that a change from the solid to the liquid state is usually accompanied by an absorption of heat and consequent lowering of temperature. Observations made upon salts in water show that in some cases in the act of solution, as should be expected, there is a fall in temperature. Examples of this are given in Table VI,

TABLE VI

| Compounds | Calories |
|---|---|
| $NaCl$ | — 1.18 |
| $KCl$ | — 4.44 |
| $NH_4Cl$ | — 3.84 |
| $NaNO_3$ | — 5.03 |
| $KNO_3$ | — 8.52 |
| $NH_4NO_3$ | — 6.32 |
| $Na_2SO_4$, $10H_2O$ | —18.76 |
| $CaCl_2$, $6H_2O$ | — 4.34 |
| $BaCl_2$, $2H_2O$ | — 4.93 |
| $MgSO_4$, $7H_2O$ | — 3.80 |
| $ZnSO_4$, $7H_2O$ | — 4.26 |
| $CuSO_4$, $5H_2O$ | — 2.75 |

where the numbers express the calories of heat absorbed during the solution of such quantities in grams as are expressed by the molecular weights (molecular gram weight) of the respective salts.

But there exist also a large number of cases, where just the reverse action occurs, that is, where a rise of temperature ensues when solution takes place. The heat in these cases originates in chemical action between the salt and the solvent, and is similar to the action that occurs when lime and water are brought in contact.

During solution, the following actions are recognized as occurring simultaneously:

1. The particles of the salt disseminate, involving the absorption of heat.
2. The salt combines with water, evolving heat.

Where the affinity of the body for water is considerable combination is prevalent, and thus overbalances the absorption of heat due to dissemination, the resultant effect being a manifestation of heat; where the salt in question possesses only a comparatively small affinity for water, the resultant effect is usually an absorption of heat and consequent lowering of temperature.

In Table VI are given (*a*) salts that crystalize at ordinary temperature without attaching to themselves water of crystallization, and that may be considered to possess only a small affinity for water; (*b*) salts that before solution have combined with water as water of crystallization. Both varieties belong to the latter category of bodies in which the predominant change is one in the direction of absorption of heat.

In Table VII is given the heat evolved when the molecule-

**TABLE VII**

| Salt | Calories |
|---|---|
| $Na_2SO_4$ | + 0.46 |
| $CaCl_2$ | +17.41 |
| $BaCl_2$ | + 2.07 |
| $MgSO_4$ | +20.28 |
| $ZnSO_4$ | +18.44 |
| $CuSO_4$ | +15.80 |

gram weights of the anhydrous salts, which have considerable affinity for water (as shown by their existence in the solid state in attachment to water of crystallization), are dissolved. It is evident from the table that the predominant effect is that due to the energy of attachment of water during solution, the heat evolved being, in many cases, quite considerable.

**46. Diffusion of Liquids.**—The law (according to Graham) governing the diffusion of gases has been already given. In gases, the ultimate particles possess great freedom of motion and the rate of diffusion is consequently large, depending entirely on the density of the gases ; in liquids, on the other hand, the freedom of motion is greatly restricted, and the diffusion is consequently much slower. So slowly does diffusion proceed that, since slight disturbing influences appear unavoidable, it is a matter of extreme difficulty to determine positively the laws governing it.

Graham, who laid down the law concerning the diffusion of gases, also investigated the diffusion of liquids by placing a vial filled with a solution of a salt in a jar with water, as shown in Fig. 11, taking due precautions to prevent any premature admixture of the two liquids while arranging the experiment. The process of diffusion was an exceedingly slow one, as may be inferred from the fact that with the most suitable substances, but 20 to 30 per cent. of the liquid passed from the vial into the surrounding water in the course of one week ; and years may elapse without the salt becoming equally diffused throughout the whole of the liquid.

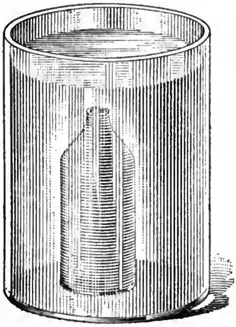


FIG. 11

The following statements, based on experiments of Graham and others may be considered as generally true:

1. The rate of diffusion increases with the temperature, and is approximately proportionate to the concentration.

2. There appears to exist no simple relation between the rate of diffusion of salts and their chemical composition.

It will, however, be interesting to add some observations on salts of the alkalies, especially in consideration of facts that have lately been accumulated relating to dissociation as recurring in solutions.

Solutions of lithium chloride, sodium chloride, and potassium chloride were prepared so as to contain their own molecular weight in grams per liter, and these solutions were allowed to diffuse under precisely the same conditions. The relative amounts that diffused in the same space of time were:

$$LiCl : NaCl : KCl :: 18 : 20 : 27$$

Molecular weight: 42.38 58.36 74.41

so that potassium chloride, which has the highest molecular weight, diffused the quickest, and lithium chloride, whose molecular weight is the lowest, diffused the slowest. There is reason to believe—and further evidence will be given—that the potassium-chloride molecules in solution undergo dissociation to such an extent that its molecular weight in that condition may in reality be even smaller than that of lithium chloride. Such a state of things would afford a reasonable explanation of the results of these diffusion experiments.

**47. Dialysis.**—Dialysis has been defined as the separation of different substances in solution by means of their unequal diffusion through membranes. If a solution of common salt and the white of an egg is poured upon the septa of the dialyzer and the whole left to itself for a day, it will be found that most of the salt has passed through the septa into the water below, while nearly the whole of the albumin (i. e., the white of the egg) has remained behind. Graham found that a number of substances readily pass through the septa, while to other substances it was practically impermeable; the former he called *crystalloids*, and the latter, owing to their glue character, *colloids*. The times of diffusion of equal amounts of some typical substances are as follows:

| | | |
|---|---|---|
| Hydrochloric acid | 1 | Crystalloids |
| Sodium chloride | 23 | |
| Sugar | 7 | |
| Magnesium sulphate | 7 | |
| Albumin | 49 | Colloids |
| Caramel | 98 | |

**48.** Having obtained some insight into the nature of the solution and the conditions that hold between the dissolved substance and the solvent containing it, we shall now proceed to examine other phenomena pertaining to solution, which are related to the molecular weight of the dissolved substance. In many cases, however, changes of a chemical nature ensue on solution, and the difficulty arises of distinguishing how far any effects that may be observed, result from the chemical changes of the body, and how far they are attributable to the physical molecules of which it is made up. We have seen, for instance, that when sodium sulphate is dissolved in water, there are evidences of dissociation which have to be taken in account.

Under certain conditions, however, the effect produced by chemical changes may be either kept constant or practically eliminated, and then it will be possible to study the variations that originate in the molecule, on the mass of which they are purely dependent. For this purpose the solutions used must be (1) in a very dilute condition and under like physical conditions; (2) prepared in such a manner that the solvent selected shall have the least possible tendency to effect chemical change.

The operations described in the following articles must therefore be taken generally as applying only to solutions under these limitations.

## DETERMINATION OF MOLECULAR WEIGHTS

**49. Depression of Freezing Point.**—It is a well known fact that salt water does not freeze as readily as fresh water, and a similar observation has been extended to solutions in general, and has shown to have some connection with the molecular weight of the dissolved substance. But it was not until recently that, owing to the researches of Raoult and others, a definite quantitative relation has been established between the lowering of the freezing point of a solution and the molecular weight of the substance contained in the solution.

If 1 part of ether $C_4H_{10}O$ be dissolved in 100 parts of water, the freezing point of the mixture falls to .25° below zero; and if 2 parts of ether be dissolved, the depression is twice this. Calculated for the molecular weight in grams of ether (which is positively known from its vapor density), we have

$$.25 \times 74 = 18.5$$

In general if $d$ be the depression of the freezing point of water for a 1-per-cent. solution, and $M$ be the known molecular weight, then for water as solvent, $M.d$ is a value approximating very nearly to 18.9.

Similarly, other solvents may be used. Thus a 1-per-cent. solution of liquid nitrogen tetroxide depressed the freezing point of acetic acid .412°. The molecular weight of nitrogen tetroxide being 92,

$$M.d' = 37.9$$

A number of such determinations with bodies of known molecular weight shows that the effect of dissolving an amount equal to the molecular weight in grams in 100 c. c. of the solvent gives a depression for

Water = 18.9
Acetic acid = 38.8
Benzene = 49.0

Such determinations require small ranges of temperature to be measured with great accuracy; for, as the relation only holds for dilute solutions, a depression amounting very often to only a few tenths of a degree has to be measured.

A convenient apparatus, known as **Beckmann's apparatus,** is shown in Fig. 12. It consists of a stout wide glass tube $a$, to contain the solvent, furnished with a side tube $b$, by which the substance may be introduced. A thermometer *c*, graduated to .01 of 1° is inserted through a rubber stopper into the tube *a*. The lower part of tube *a* is enclosed in a thin outer tube *d*, to form an air jacket for the purpose of preventing too rapid changes of temperature. The whole is placed in the outer vessel *e*, which contains some kind of freezing mixture, and is provided with a stirring rod *f*. A known weight, say 20 grams, of the solvent is introduced and cooled a little below its freezing point, and then stirred with the platinum stirrer *g* until it commences to freeze. The thermometer will now rise and remain steady at the correct freezing point of the liquid, say $t^\circ$. The solvent is liquefied and cooled again, and a second experiment is performed; a weighed amount, say .2 gram of the substance being introduced by the side tube. When the freezing again takes place, the thermometer rises and remains steady at the temperature $t_1^\circ$. The depression of freezing point is $t^\circ - t_1^\circ$. This is for a 1-per-cent. solution, and if acetic acid, for instance, had been used,

$$M\,(t^\circ - t_1^\circ) = 38.8;$$

that is, the molecular weight

$$M = \frac{38.8}{t^\circ - t_1^\circ}$$

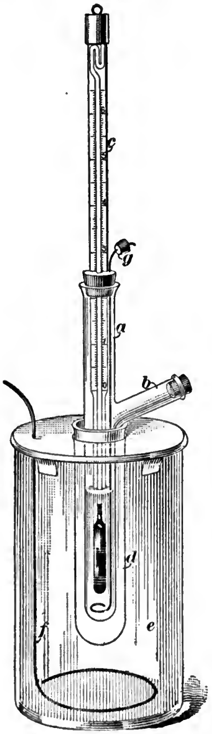


FIG. 12

Care should be taken to prevent the solvent from absorbing moisture from the air during the experiment, as this would naturally interfere with accurate results.

As it is sometimes impossible or inconvenient to use exactly a 1-per-cent. solution, we may adopt the general expression

$$M = \frac{rp \times 100}{dg},$$

where $M$ = molecular weight;
$r$ = constant (for water, 18.9);
(for acetic acid, 38.8);
(for benzene, 49.0);
$d$ = depression of freezing point;
$p$ = number of grams of substance dissolved;
$g$ = number of grams of solvent used.

The following experiment has been performed by the author for the instruction of the student:

The freezing point of 120 grams of benzene was found to be 6°; 6 grams of sulphur were dissolved in the benzene and the freezing point again determined; it was found to be 4.68°, that is to say a depression of 1.32° resulted. Using the formula given above,

$$M = \frac{rp \times 100}{dg},$$

and substituting the proper values,

$$M = \frac{49 \times 6 \times 100}{1.32 \times 120} = 185.6 \text{ was found}$$

Thus the molecular weight of solid sulphur is 185.6, a number sufficiently close to 192 to confirm the recent conclusion that the molecule of solid sulphur is $S_6$.

This method of determining molecular weights is known as the **cryoscopic method** or **Raoult's method.**

As further examples of the determination of molecular weight we may quote the following organic substances, the depression being that for a 1-per-cent. solution in water:

| Name | Formula | $d$ | $\frac{18.9}{d}$ | $M$ |
|---|---|---|---|---|
| Urea | $CON_2H_4$ | .287 | 65.9 | 60 |
| Tartaric acid | $C_4H_6O_6$ | .130 | 145.4 | 150 |
| Lactic acid | $C_3H_6O_3$ | .213 | 88.8 | 90 |
| Cane sugar | $C_{12}H_{22}O_{11}$ | .054 | 350.0 | 342 |

**GROUP OF ISOMORPHOUS SULPHATES**

| Name | Formula | $d$ | $\frac{18.9}{d}$ | $M$ |
|---|---|---|---|---|
| Magnesium sulphate | $MgSO_4,7H_2O$ | .072 | 262.5 | 245.6 |
| Ferrous sulphate... | $FeSO_4,7H_2O$ | .055 | 343.6 | 277.6 |
| Nickel sulphate.... | $NiSO_4,7H_2O$ | .055 | 343.6 | 280.0 |
| Copper sulphate.... | $CuSO_4,7H_2O$ | .065 | 290.8 | 284.9 |
| Zinc sulphate...... | $ZnSO_4,7H_2O$ | .058 | 325.8 | 286.8 |

**SALTS OF THE ALKALIES**

| Name | Formula | $d$ | $\frac{18.9}{d}$ | $M$ |
|---|---|---|---|---|
| Sodium chloride ... | $NaCl$ | .600 | 31.5 | 58.4 |
| Sodium bromide ... | $NaBr,4H_2O$ | .189 | 100.0 | 174.6 |
| Sodium iodide ..... | $NaI,4H_2O$ | .152 | 124.3 | 221.4 |
| Potassium chloride. | $KCl$ | :446 | 42.4 | 74.4 |
| Potassium bromide. | $KBr$ | .292 | 64.7 | 118.8 |
| Potassium iodide... | $KI$ | .212 | 89.1 | 165.6 |

It will be readily seen that in the first table there is a close agreement between the molecular weight in the solution as indicated under the column $\frac{18.9}{d}$, and that shown by the formula as given under $M$. But in the salts of the alkalies there is quite a considerable divergence, and the molecular weight as determined in solution is in each case little more than half that required by the formula; also in the second table the irregularities are considerable. With mineral acids, or strong bases or salts of complex structure, containing water of crystallization, there is usually a notable divergence; and this is doubtless due to the disturbing effect of chemical changes that ensue during solution, or to variable conditions of aggregation of the molecules. This view is supported by the fact that where an indifferent body, as benzene, can be used as a solvent, more consistent results are obtained. As to the behavior of the haloid salts of the alkalies, it is taken to indicate that they undergo partial dissociation in solution.

**50. Elevation of Boiling Point.**—It is likewise found that the elevation of boiling point, which is brought about in a liquid by dissolving a foreign substance in it, is also proportional to the molecular weight. In this case

$$M = \frac{Kp \times 100}{Eg}$$

where $g$ and $p$ have the same significance as before; $E$ is the observed elevation of boiling point; and $K$ is a constant that for water is 520; for acetic acid, 2,530; and for benzene, 2,670.

An apparatus used for this purpose is shown in Fig. 13. It consists essentially of a glass boiling tube *a*, through the orifice of which a thermometer graduated to .01 of 1° is fitted; this tube serves as the receptacle for the solvent. This is enclosed by a steam jacket *b* made of either glass or metal, the heating box *c* made of asbestos, the chimneys *s*, and the coolers *k*. The mode of operation is practically the same as that described for Beckmann's apparatus (see Fig. 12). The steam jacket *b* and the boiling tube *a* are partly filled with the solvent; the Bunsen burners beneath the apparatus are lighted; and after the expiration of from 30 to 60 minutes the solvent will be steadily boiling. The temperature is noted, and the substance to be

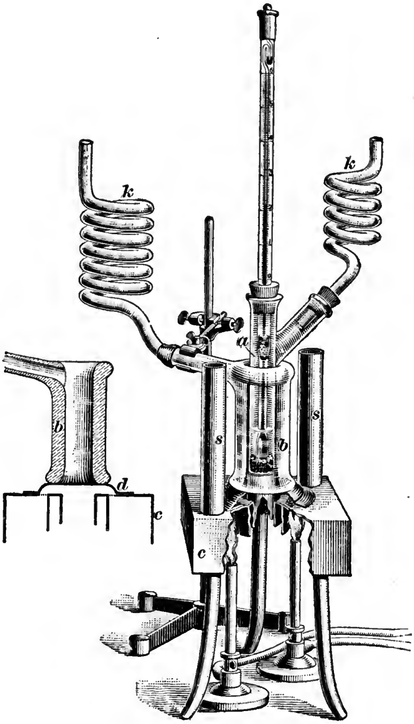


FIG. 13

dissolved is then added to the solvent in tube *a*. When the solution again boils and the thermometer shows a steady point, the new boiling temperature is read off. The calculation is made exactly in the same way as shown in Art. **49.**

**51. Osmotic Pressure.**—The pressure that a substance in solution exerts on the solvent is called the **osmotic pressure** of the solution, as it can only be rendered apparent and directly measured by taking advantage of the phenomenon of **osmosis.** It has been previously mentioned (see Art. **47**) that structureless substances, such as parchment, etc., will allow a much more rapid passage through them of some kinds of molecules than of other kinds. Several substances exist that will allow water molecules to pass through them almost infinitely faster than they allow many other kinds of molecules to pass. When a membrane made of one of these substances is immersed in an aqueous solution, it will generally happen that the water molecules will pass through the membrane very much faster than the molecules of the dissolved substance. This transition of molecules differs from that called diffusion in that it appears to depend rather upon the specific nature of the membrane than upon its porosity. The term **osmosis** is used to indicate this difference.

The method employed for studying the pressure exerted by a dissolved substance on the solvent, can be easily understood. A vessel is constructed of a material that permits the osmosis of the solvent molecules, but not the dissolved molecules. The solution whose osmotic pressure is to be studied, is introduced into this vessel, which is then immersed in a bath of the pure solvent. The solvent molecules will pass into the vessel and out of it, but since there are more of these molecules in unit volume outside the vessel than there are inside (on account of the presence of the dissolved molecules), more of the solvent will pass into it in unit time than will pass out, and equilibrium will only be established when a certain pressure, compensating for this difference between the number of solvent molecules in unit volume, has been established inside the vessel. This pressure is termed the *osmotic pressure of the solution*, and is attributed to the dissolved molecules; it can be measured by closing the vessel by an ordinary pressure gauge.

In practice, it is found necessary to support the *osmotic membrane*, which is to form the walls of the vessel, by depositing it on the surface of a porous vessel. The most successful method consists in depositing copper ferrocyanide (a material that behaves as an osmotic membrane to aqueous solutions) within the pores of a biscuit-porcelain battery cell (3 in. × 1 in.); for this purpose the cell is filled with a 3-per-cent. solution of copper sulphate and immersed in a 3-per-cent. solution of potassium ferrocyanide. The two solutions meet in the wall of the cell, and a continuous sheet of copper ferrocyanide is deposited therein. An inverted funnel is cemented in the mouth of the cell, and a **U**-shaped mercury gauge is sealed to the stem of the funnel. The cell is nearly filled with the aqueous solution whose osmotic pressure is to be measured, and is immersed in a bath of distilled water. The pressure of the air trapped between the gauge and the solution is measured by the variation in the height of the mercury in the gauge.

It is found that the same relationship exists between the osmotic pressure and the concentration of a gas. That is to say, the osmotic pressure is directly proportional to the weight of the dissolved substance in unit volume of the solution, just as the pressure of a gas is directly proportional to the weight of the gas in unit volume (according to Mariotte's law). Thus a 1-per-cent. sugar solution exerts an osmotic pressure equal to 535 mm. of mercury, while the osmotic pressure of a 2-per-cent. solution of sugar is equal to 1,070 mm., provided the temperature is the same in both cases.

Again, the osmotic pressure of a solution varies directly as the absolute temperature (thermometric temperature + 273) of the solution, just as the pressure of a gas varies directly with its absolute temperature (Gay-Lussac's law applied to solutions). Thus the 1-per-cent. solution of sugar shows an osmotic pressure of 544 mm. of mercury at 32° and of 512 mm. at 14.15° $\left(544 \times \frac{287.15}{305} = 512\right)$.

It seems, then, that the variations which occur in osmotic pressure of a dilute solution when the concentration of the solution is varied, are controlled by the same laws as those that govern the variations in the pressure of a gas when the concentration of the gas is varied. But the analogy between the osmotic pressure and the gaseous pressure is still closer than this; for it is found that *the osmotic pressure is identical with the gaseous pressure which the weight of dissolved substance would exert at the same temperature, if it were in the state of gas and occupied the volume filled by the solution.*

It is considered reasonable to deduce from this that the number of molecules of dissolved substances in a volume $v$ of a solution, having an osmotic pressure $p$ and a temperature $t$, is the same as the number of molecules in a volume $v$ of a gas at the pressure $p$ and the temperature $t$.

Thus, for instance, a 1-per-cent. solution of cane sugar $C_{12}H_{22}O_{11}$ at 0° exerts an osmotic pressure of 493 mm. Now, the molecular weight corresponding with the formula $C_{12}H_{22}O_{11}$ is 342, and, could the cane sugar be gasified, 342 grams of it would occupy 22.32 liters at 0° and 760 mm. pressure; that is to say, 342 grams of gaseous sugar in a volume of 22.32 liters at 0° would exert a pressure of 760 mm. The concentration of 342 grams in 22.32 liters is the same as a concentration of 15.32 grams in 1 liter; therefore, 15.32 grams of gaseous sugar in 1 liter at 0° should exert 760 mm. pressure. It follows that 10 grams in 1 liter at 0° should exert a pressure of 496 mm. This is practically identical with the osmotic pressure of a (1-per-cent.) sugar solution containing 10 grams per liter.

Gases of high concentration—that is, at high pressure—cease to obey the laws of Mariotte and Gay-Lussac. The same may be considered true for solutions at high concentration.

Since we know that the law of Avogadro is deducible mathematically from those of Mariotte and Gay-Lussac, and since dilute solutions appear to be controlled by the two laws last named, it seems probable that a law similar to Avogadro's should exist for dilute solutions. This was first pointed out by Van't Hoff, whose *law of osmotic pressure* is thus stated: *Equal volumes of different solutions, at the same temperature and osmotic pressure, contain equal numbers of molecules of dissolved substance.*

The similarity between this statement and that expressing Avogadro's law will be at once evident.

Solutions that exert equal osmotic pressures are said to be **isotonic.**

Just as the relation between the weight of the molecules of gases can be deduced from Avogadro's law, so can the relation between the weight of the molecules of two dissolved solids be deduced from Van't Hoff's law. For it follows from this law, that when equal volumes of two solutions are isotonic, and at the same temperature, the weight of the dissolved solid in the one is as much heavier than the weight of the dissolved solid in the other, as the molecular weight of the first solid is heavier than the molecular weight of the second.

**52. Determination of Molecular Weights of Nonvolatile Substances.**—The applicability of the measurement of osmotic pressure to the determination of molecular weights will now be easily understood. A solution of the solid whose molecular weight is unknown may be diluted or strengthened until its osmotic pressure is identical with that of a solution containing a known weight of a solid whose molecular weight is known. The ratio between the weights of the solids in 1 liter of each solution is then the ratio between the molecular weights of the solids.

For example, a solution of a substance of unknown molecular weight was diluted until its osmotic pressure was found to be identical with that of a solution of sugar in water (at the same temperature). The weight of solid in 1 liter of each solution was then determined; that in the sugar solution was 1 gram; that in the other solution was 1.5 grams.

By Van't Hoff's law these weights must have the same ratio to each other as have the molecular weights of the substances. Let $x$ be the unknown molecular weight; the molecular weight of sugar is 342; therefore,

$$342 : x = 1 : 1.5, \text{ or } x = 342 \times 1.5$$

The measurement of osmotic pressure is neither easy nor capable of great accuracy; it is not, therefore, as a rule well adapted for the determination of molecular weights.

## ULTIMATE ORGANIC ANALYSIS

**53.** The science of chemistry was originally divided into *inorganic* and *organic chemistry*, in order to distinguish the substances derived from the mineral kingdom from those originating from either vegetable or animal life. These latter compounds were considered unobtainable by synthesis until the never-ceasing and patient labor of the chemists of the second half of the 19th century succeeded in producing a large number of organic compounds from the elements obtainable from mineral sources, and it has become customary now to define organic chemistry as *the chemistry of the carbon compounds*, since this element is always present in these compounds.

Organic chemistry differs from inorganic chemistry in being chiefly concerned with compounds produced by the arrangement in different proportions and in different positions of the elements carbon, hydrogen, oxygen, and nitrogen, though other elements, such as the haloids, etc., also frequently enter into their composition.

The student's attention should be here drawn to the difference existing between *organic compounds* and *organized bodies*. Organic bodies, such as marsh gas, benzene, alcohol, sugar, morphine, etc., are definite chemical compounds; those that are solids can, as a rule, be crystallized, while those that are liquids exhibit a constant boiling point. Organized bodies, on the other hand, always consist of mixtures of several definite compounds. They never crystallize, but exhibit a fibrous or cellular structure, and cannot be reduced to the liquid or gaseous state without complete decomposition. Lastly they are organs, or parts of organs, which are essentially products of vitality, and there is not the slightest prospect of their ever being produced by artificial means.

The study of the composition and chemical relations of organized bodies belongs to a special department of the science, called Physiological Chemistry, and will not be considered in this nor the following Instruction Papers.

**54.** A useful and practical distinction between organic and inorganic compounds is afforded by their behavior when heated. An organic substance is either converted into vapor when moderately heated, or is decomposed into volatile products, generally leaving a residue of charcoal that burns away when heated in air.

Upon this fact is based the so called *ultimate organic analysis*, the *making a combustion*, as it is technically known, which is performed in order to ascertain the relative proportions of elements composing an organic compound.

This process consists in burning the organic compound so as to convert its carbon into $CO_2$ and its hydrogen into $H_2O$; from the weight of these compounds the proportions of the two elements in question can be readily obtained by simple calculations.

A complete apparatus used for the purpose of making a combustion is shown in Fig. 14.

The organic substance to be analyzed, having been carefully dried beforehand and a certain amount—5 grams, for instance—of it weighed out, is placed in a small boat-shaped tray of either platinum or porcelain, and introduced into one end of the combustion tube *d e*, Fig. 14. This combustion tube is made of hard German or Bohemian glass, about 30 inches long and $\frac{5}{8}$ to $\frac{3}{4}$ of an inch inside diameter, of which about 24 inches are filled with small pieces of thoroughly dried cupric oxide. The end *d* where the boat is placed, is connected with an apparatus *a* for transmitting oxygen or

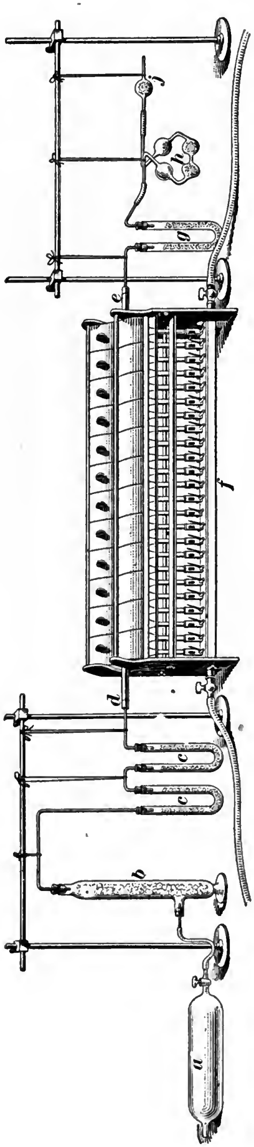


FIG. 14

air, which has been purified from $CO_2$ by passing through a jar *b* containing potash, and from $H_2O$ by passing through 2 **U** tubes *c*, *c* containing calcium chloride. A **U** tube *g* previously weighed and filled with small pieces of calcium chloride, to absorb $H_2O$, is attached to the other end *e* of the combustion tube. To this **U** tube is joined by a short rubber tubing, a bulb apparatus *h*, which contains potash to absorb $CO_2$, and a small guard tube *j* with calcium chloride, to prevent the loss of water from the potash. The combustion tube is supported in the gas furnace *f*, and the portion of the combustion tube that contains the $CuO$ is heated to redness. The end containing the boat is then gradually heated, so that the organic substance is slowly vaporized or decomposed. The vapor or the products of the decomposition in passing over the red-hot cupric oxide, will acquire the oxygen necessary to convert the $C$ into $CO_2$ and the $H$ into $H_2O$, and these are absorbed in the potash bulb and calcium chloride tube. At the end of the process, which usually occupies about 50 to 60 minutes, a slow stream of either pure air or oxygen is passed through, while the entire tube is red hot, in order to burn any charcoal that may remain in the boat, and carry forward all the $CO_2$ and $H_2O$ into the absorption apparatus. The weight of the $CO_2$ is given by the increase in weight of the potash bulbs *h*, and that of the $H_2O$ by the increase in weight of the calcium chloride tube *g*.

**55.** In some cases it is preferable to mix the substance to be analyzed with a large quantity of powdered cupric oxide, so that the mixture may occupy about 12 inches of an 18-inch tube with a layer of 3 inches of cupric oxide on each end. The one end of the tube is then often drawn out and sealed, the point being broken off when the combustion is finished, and a slow stream of air drawn through it by gentle suction at the opening of the potash bulbs. In case of substances difficult of combustion, the cupric oxide is usually replaced by lead chromate $PbCrO_4$, which evolves oxygen when heated.

**56.** When nitrogen is present in the substance it may be partly converted into $N_2O_4$, which would increase the weight of the absorption apparatus. To avoid this, 3 or 4 inches of the front end of the combustion tube are filled with metallic copper, which, being heated to redness, absorbs the $O$ from the $N_2O_4$, leaving $N$, which passes through the absorption apparatus and escapes. When it is desired to make a *determination of the nitrogen* the combustion tube is arranged in the same way, but the absorption apparatus is replaced by a bent tube to allow the collection of the gas in a measured tube filled with strong potash. Before commencing the combustion, the air is swept out of the tube by a current of pure $CO_2$, which is continued during the combustion, and is absorbed by the potash, the nitrogen being collected and measured.

Another method of estimating nitrogen in organic compounds that is quite frequently employed, consists in heating them with soda lime, when the $N$ is evolved as $NH_3$, which is absorbed by hydrochloric acid in the absorption bulb shown in Fig. 15, and precipitated by platinic chloride, the weight of $N$ being calculated from that of $PtCl_4,2NH_4Cl$ obtained; or the $NH_3$ is absorbed in a known quantity of acid, which is afterwards titrated with a normal alkaline standard solution, and the quantity that has been neutralized by the evolved ammonia is thus determined.

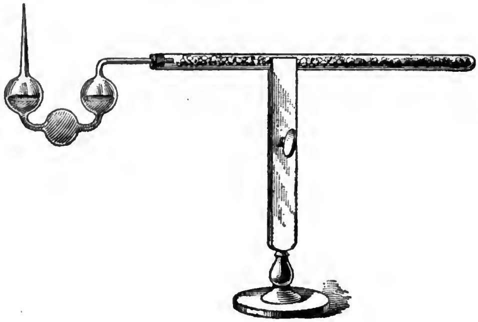


FIG. 15

**57.** *Sulphur* and *phosphorus* are estimated in organic compounds by converting them into sulphuric and phosphoric acids, respectively, by the action of oxidizing agents (nitric acid, bromine, etc.) and determining those acids by the usual methods. The *halogens* are determined by oxidizing the substance by heating with $HNO_3$ under pressure, whereby the halogen is converted into its hydrogen compound and may be precipitated by $AgNO_3$ and weighed as silver halide.

**58. Determination of Oxygen.**—The proportion of oxygen in an organic compound is mostly determined by difference; that means, by deducting the sum of the weights of all the other elements from the original weight of the substance.

As an example of the general proceedings of an ultimate analysis of an organic compound and the calculations connected with it, that of alcohol is given below.

(Volatile substances, such as alcohol, ether, etc., are weighed in a small glass bulb with a thin stem, the end of which is sealed for weighing, and broken off when the bulb is introduced into the combustion tube.)

.5 gram of alcohol burned with cupric oxide gave .9565 gram $CO_2$ and .5869 gram $H_2O$.

Since 44 grams of $CO_2$ contain 12 grams of $C$, $\frac{12}{44}$ of .9565, or .2608, is the weight of $C$ found.

Since 18 grams of $H_2O$ contain 2 grams of $H$, $\frac{2}{18}$ of .5869, or .0652, is the weight of $H$ found.

The sum of the weights of $C + H = .2608 + .0652 = .3260$. Deducting this from .5 gram alcohol (original weight), we have 0.174 gram of $O$.

So that .5 gram of alcohol contains .2608 gram $C$, .0652 gram $H$, and .174 gram $O$; or, as the report of the analysis would be written, 52.16 per cent. of carbon, 13.04 per cent. of hydrogen, and 34.80 per cent. of oxygen.

The result of such an analysis is, as a rule, expressed in an empirical formula, which may be defined as *a formula denoting the relative numbers of atoms of the elements contained in the compound.*

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### CALCULATION OF FORMULAS

**59. Deduction of the Empirical Formula From the Percentage Composition.**—The simplest way to deduce the empirical formula of a compound from its percentage composition consists in dividing the percentage of each element by its atomic weight, and expressing the resulting quotient in the ratio of its lowest terms, thus:

52.16 divided by 12, atomic weight of carbon = 4.34
13.04 divided by 1, atomic weight of hydrogen = 13.04
34.80 divided by 16, atomic weight of oxygen = 2.17

If the ratio 4.34 : 13.04 : 2.17 is expressed in its lowest terms it becomes 2 : 6 : 1, giving the empirical formula $C_2H_6O$.

In some cases the result of such division is that one quotient contains .5, or .33, etc., i. e., one atom of an element to a proportion of 1.5, etc. of another; the number of atoms in the molecule is then obtained by multiplying every number, so as to obtain the lowest ratio in figures without fractions.

It remains now to determine whether this formula is a true representation of the alcohol molecule, or whether the molecule should be written $C_4H_{12}O_2$ or $C_6H_{18}O_3$, or in any other form that will preserve the ratio established beyond doubt by the above analysis.

To do this we must deduce the *molecular formula* from the empirical formula.

A molecular formula may be defined as *a formula denoting the absolute number of atoms in one molecule.*

**60. Deduction of the Molecular Formula of a Compound From Its Empirical Formula.**—In order to deduce the molecular formula of a compound from its empirical formula, it is necessary to determine the molecular weight of the compound, for it is evident that the formula $C_2H_6O$ represents 2 atoms of $C$ weighing $12 \times 2$, 6 atoms of $H$ weighing $6 \times 1$, and 1 atom of $O$ weighing 16; 46, the sum of these numbers, would be the weight of a molecule of alcohol represented by $C_2H_6O$, whereas the formula $C_4H_{12}O_2$ would express $46 \times 2$ parts by weight, $C_6H_{18}O_3$ would represent $46 \times 3$ parts by weight of alcohol, etc.

The method of determining the molecular weight of a volatile compound, as perfected by Victor Meyer, has been already described.

In the case of a substance that cannot be converted into vapor without suffering decomposition, the molecular weight is determined by the cryoscopic method (see Art. **49**), or is inferred from a consideration of the chemical relations of the substance, and its determination then very often becomes a rather difficult and complicated matter. The general character of this latter method will be seen and readily understood from the following examples.

**61. Determination of the Molecular Formula of an Acid.**—An acid that was submitted to ultimate analysis yielded on combustion with cupric oxide, in 100 parts, 40 per cent. of carbon, 6.66 per cent. of hydrogen, and 53.33 per cent. of oxygen; the empirical formula of the substance consequently was $CH_2O$.

The acid was found to give only one class of salts with $K$ and $Na$, showing that it only contained one atom of $H$ replaceable by a metal, or that it was monobasic.

By neutralizing the acid with ammonia and stirring with a solution of silver nitrate, a crystalline silver salt was obtained that was purified by recrystallization from hot water, dried, weighed in a porcelain crucible of known weight, and gradually heated to redness. On again weighing the crucible after cooling, it was found to contain a quantity of metallic silver amounting to 64.66 per cent. of the weight of the salt. Now, generally a silver salt is formed from an acid by displacement of an atom of hydrogen by an atom of silver; so that what remains of the silver salt, after deducting the silver, represents the acid itself, minus a quantity of hydrogen equivalent to the silver.

| | |
|---|---|
| From the silver salt.................. | 100.00 |
| Deduct the silver.................... | 64.66 |
| Acid residue.................... | 35.34 |

Then,

$$64.66Ag : 108 \left\{ \begin{matrix} Ag \text{ in one mole-} \\ \text{cule of the salt} \end{matrix} \right\} = 35.34 : 59 \left\{ \begin{matrix} \text{acid resi-} \\ \text{due in one} \\ \text{molecule} \end{matrix} \right.$$

| | |
|---|---|
| To the acid residue ........................... | 59 |
| Add the hydrogen equivalent to 1 atom of $Ag$.. | 1 |
| Molecular weight of the acid.............. | 60 |

The formula $CH_2O$ represents $12+2+16=30$, but as the molecular weight is 60, the molecular formula of the acid must be $C_2H_4O_2$ and that of the salt $C_2H_3AgO_2$.

**62. Determination of the Molecular Formula of an Organic Base.**—The substance yielded on combustion with cupric oxide, in 100 parts, 77.42 per cent. of carbon, 7.53 per cent. of hydrogen; a determination of nitrogen showed 15.05 per cent. of this element, so that there was no oxygen. These numbers lead to $C_6H_7N$ as the empirical formula of the base. By dissolving the base in hydrochloric acid and adding platinic chloride, a yellow crystalline precipitate was obtained, resembling the ammonio-platinic chloride formed when ammonia is treated the same way. This precipitate was washed with alcohol, dried, weighed in a porcelain crucible, and heated to redness, when it left a residue of metallic platinum which amounted to 32.72 per cent. of the weight of the salt. As a general rule, a platinum chloride salt is formed by the combination of $PtCl_4$ with two molecules of the hydrochloride of the base; in the case of the ammonio-platinic chloride, the formula is $PtCl_4,2NH_4Cl$; so that what remains of a platinum salt after deducting the platinum represents 2 molecules of the base + 2 molecules of $HCl$ + 4 atoms of $Cl$.

| | |
|---|---|
| From the platinum salt............... | 100.00 |
| Deduct the metallic platinum obtained. | 32.72 |
| Remainder...................... | 67.28 |

Then,

$$32.72Pt : 195 \left\{ \begin{matrix} Pt \text{ in one mole-} \\ \text{cule of the salt} \end{matrix} \right\} = 67.28 : 400.9$$

| | |
|---|---|
| Deduct $2HCl + Cl_4$............. = | 215.0 |
| Weight of 2 molecules of the base = | 185.9 |

The molecular weight of the base, therefore, is 92.9. The formula $C_6H_7N$ represents $72 + 7 + 14 = 93$. This is, therefore, the molecular formula.

**63.** The law of even numbers is sometimes a useful guide in fixing molecular formulas. Since carbon behaves as a quadrivalent element, the atom-fixing power of any group of carbon atoms must be represented by an even number. Thus, a single carbon atom would be $C^{iv}$, indicating its power of attaching to itself 4 atoms of hydrogen. A *chain* of 2 carbon atoms would be $C_2^{vi}$, if the 2 atoms were singly linked or united by one atom-fixing power belonging to each, because the total number of the bonds of 2 separate quadrivalent carbon atoms would be $4 + 4$, and if one bond of each is employed in linking them together, the atom-fixing power of the chain would be $(4-1)+(4-1) = 6$.

If the 2 atoms were doubly linked, or united by 2 bonds belonging to each, the atom-fixing power of the chain would be $(4-2)+(4-2) = 4$, expressed by $C_2^{iv}$.

Again, if the atom were trebly linked, the atom-fixing power would be $(4-3)+(4-3) = 2$, expressed by $C_2''$.

So it is evident that each atom of carbon added to the chain can only increase the atom-fixing power of the chain itself by 2, for, although the added atom of carbon has an atom-fixing power of 4, one of these must be used up in attaching it to the chain, and one of the atom-fixing powers of the chain must be used up in attaching the chain to the added carbon atom.

From these considerations it follows that *the total number of atoms of univalent or trivalent elements united with carbon in an organic compound must be an even number*, because the atom-fixing power of the chain is always a multiple of 2, and no odd number of univalent or trivalent elements could satisfy such an atom-fixing power.

EXAMPLE.—Ultimate analysis shows $CH_3O$ to be the empirical formula for glycol, which, however, is evidently an impossible formula, since the atom-fixing powers are 4 belonging to the carbon, 3 belonging to the hydrogen, and 2 belonging to the oxygen. The molecular formula of glycol is $C_2H_6O_2$ where the hydrogen atoms are an even number, the 2 carbon atoms being singly linked, $C_2^{iv}$, 4 of the 6 otherwise available atom-fixing powers being used for the attachment of 4 of the hydrogen atoms, and the other two for each of the oxygen atoms, the second atom-fixing power of each (diad) oxygen atom being used for the attachment of the remaining hydrogen atoms.

**64.** The ultimate analysis of an organic compound serves, as we have seen, to decide its empirical formula, from which, after determining, in some way or other, the molecular weight of the compound in question, the molecular formula is readily derived. We have, however, in organic chemistry especially, to consider also the rational, or structural, formula; this formula may be defined as *a formula denoting the mode of arrangement of the atoms in the molecule;* because with this aid we are able to trace the existence of compound radicals (unsaturated groups of atoms), which play an important part in the formation of organic compounds. Furthermore it becomes necessary to provide some working hypothesis that will account for the fact that many substances exist, which, though they have the same ultimate composition and the same molecular formula, possess different properties; such cases are included under the term *isomerism*, which will shortly receive close attention. The necessary hypothesis is supplied by supposing the atoms in the compound to be linked together by *bonds* in such a way that this linkage can be represented by a graphic formula.

For example, to determine the rational or structural formula for alcohol: When sodium is placed in alcohol, it is dissolved with the evolution of hydrogen, and the alcohol is converted into a crystalline substance known as *sodium ethyl* or *ethylate*, having the composition $C_2H_5ONa$. Comparing this with the formula of alcohol, it is seen that one atom of $H$ has been replaced by $Na$. Since the compound still contains $H_5$, it might be supposed that by the use of an excess of $Na$ still more $H$ might be replaced, producing ultimately a compound $C_2Na_6O$. This, however, is not the case; only one of the six atoms of hydrogen in alcohol can be replaced by $Na$ in this way; hence, it is seen that one atom of the six is on a different footing from the other five. This would be expressed by writing the formula for alcohol $C_2H_5OH$. Again, when alcohol is acted on by hydrochloric-acid gas, and distilled at a low temperature, it yields water and a very volatile liquid, known as *ethyl chloride*, having the composition $C_2H_5Cl$. This decomposition would be expressed by the equation:

$$C_2H_5OH + HCl = C_2H_5Cl + HOH$$

from which it is evident that the $Cl$ of the $HCl$ has been exchanged for $OH$ in the alcohol, leading to the conclusion that alcohol is made up of at least two separate groups, and that one way of writing its rational formula is $C_2H_5OH$.

# ORGANIC CHEMISTRY

## (PART 2)

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## ORGANIC COMPOUNDS

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### CLASSIFICATION OF ORGANIC COMPOUNDS

**65.** Organic compounds may generally be assigned to one of the following divisions: (1) hydrocarbons, (2) alcohols, (3) aldehydes, (4) acids, (5) ketones, (6) ethers, (7) haloid compounds, (8) ethereal salts, (9) ammonia derivatives, (10) cyanogen compounds, (11) phenols, (12) quinones, (13) organo-mineral compounds, (14) carbohydrates, (15) glucosides, (16) albuminoids or gelatinoids.

**66.** 1. *Hydrocarbons* are composed of carbon and hydrogen only, and constitute the most extensive class of organic compounds, of which ethane $C_2H_5 \cdot H$, and dimyricyl $C_{60}H_{122}$ are examples. Hydrocarbons from which hydrogen has been removed give rise to *hydrocarbon radicals;* thus $C_2H_5$ is the radical *ethyl* from ethane. They are incapable of existing in the free state. These behave toward other radicals analogously to the behavior of metals toward non-metals, and are frequently termed *positive radicals*, while such compound radicals as $OH$, $COOH$, etc. are termed *negative*.

2. *Alcohols* are compounds of carbon, hydrogen, and oxygen, constructed on the model of water, in which half of the hydrogen is replaced by a radical, which is generally composed of carbon and hydrogen. Thus, methyl alcohol $H_3C \cdot OH$ may be considered as water in which one atom of $H$ is replaced by the radical $H_3C^{IV}$ (methyl).

The group or radical $OH$ is termed hydroxyl, and is evidently univalent, because one of the two bonds of the divalent oxygen is satisfied by the univalent hydrogen atom, thus, $H—O—$, leaving one bond available for the attachment of another element or group.

Methyl alcohol $H_3C \cdot OH$ is derived from methyl hydride $H_3C \cdot H$ by the substitution of hydroxyl $HO$ for hydrogen. This substitution is effected by two operations, as is seen from the following equations:

$$(1) \qquad \underset{\substack{\text{methyl}\\\text{hydride}}}{H_3CH} + Cl_2 = \underset{\substack{\text{methyl}\\\text{chloride}}}{H_3CCl} + HCl$$

$$(2) \qquad H_3CCl + \underset{\substack{\text{potassium}\\\text{hydrate}}}{KOH} = KCl + \underset{\substack{\text{methyl}\\\text{alcohol}}}{H_3C \cdot OH}$$

3. The *aldehydes*, or dehydrogenized alcohols, are products of oxidation of the alcohols, whereby hydrogen has been removed. Thus,

$$H_3C \cdot OH + O = H_2O + \underset{\substack{\text{methyl}\\\text{aldehyde}}}{H_2CO}$$

In the methyl aldehyde, two bonds of the carbon atom are united to the bivalent oxygen atom, and the other two bonds to the two hydrogen atoms; thus, $\begin{smallmatrix}H\\H\end{smallmatrix}\!>C^{\text{iv}}==O''$.

4. The *acids* result from a further oxidation of the alcohols, by which not only is hydrogen removed, but oxygen placed into the vacancy thus created, as is seen from the following equation:

$$H_3C \cdot OH + O_2 = H_2O + \underset{\substack{\text{formic}\\\text{acid}}}{OC\!<\!\begin{smallmatrix}OH\\H\end{smallmatrix}}$$

The organic acids contain the group $OC \cdot OH$, known as *carboxyl* or *oxatyl*. This group is monovalent, as is seen from the following graphical representation $O = C\!<^{OH}$. Two of the bonds of the quadrivalent carbon are satisfied by the bivalent oxygen, a third by the univalent group $(OH)'$, thus leaving the fourth bond free for the attachment of another element or compound radical.

5. The *ketones* are derived from the acids by the substitution of a hydrocarbon radical for hydroxyl.

$$\text{Acetic acid } OC<\begin{matrix}OH\\CH_3\end{matrix} \qquad \begin{matrix}\text{acetic ketone}\\\text{(acetone)}\end{matrix} \quad OC<\begin{matrix}CH_3\\CH_3\end{matrix}$$

Hence the ketones contain the bivalent group carbonyl $OC''$, combined with two hydrocarbon radicals.

6. The *ethers* are derived from the alcohols by the substitution of a compound radical for the hydrogen in the hydroxyl group.

For instance:

Methyl alcohol, $H_3C\cdot OH$
Methyl ether, $H_3C\cdot O\cdot CH_3$

One method of converting an alcohol into an ether is shown in the following equations:

$$(1) \qquad \underset{\substack{\text{methyl}\\\text{hydrate}}}{H_3C\cdot OH} + Na = \underset{\substack{\text{sodium}\\\text{methylate}}}{H_3C\cdot ONa} + H$$

$$(2) \qquad H_3C\cdot ONa + \underset{\substack{\text{methyl}\\\text{iodide}}}{H_3CI} = NaI + \underset{\substack{\text{methyl}\\\text{ether}}}{H_3C\cdot O\cdot CH_3}$$

7. *Haloid compounds* are formed from the foregoing groups by the substitution of a halogen radical for either hydrogen or hydroxyl.

8. *Ethereal salts* (or esters) are formed from the acids by the substitution of a hydrocarbon radical for the hydrogen in the carboxyl radical $CO_2H$.

9. The *ammonia derivatives* are formed from ammonia by the substitution of a compound radical for hydrogen; for instance, ammonia $NH_3$, methylamine $NH_2\cdot CH_3$, dimethylamine $NH:(CH_3)_2$, trimethylamine $N\vdots(CH_3)_3$.

10. *Cyanogen compounds* are those that contain the radical $CN'$, which is univalent, because only three bonds of the quadrivalent carbon are satisfied by the trivalent

nitrogen; $H\cdot CN$, hydrocyanic acid, is an example of this class of compounds.

11. *Phenols* resemble the alcohols in composition by containing the hydroxyl group, but also resemble the acids in some of their properties, but do not yield aldehydes when partially oxidized.

12. *Quinones* are formed from hydrocarbons by the substitution of a group of two oxygen atoms for two hydrogen atoms; as, for instance, quinone $C_6H_4(O_2)$, which is obtained from benzene $C_6H_6$.

13. *Organo-mineral compounds* are formed upon the type of the chlorides of metals or non-metals, by the substitution of hydrocarbon radicals for the chlorine; as, for instance, zinc ethide $Zn(C_2H_5)_2$.

In cases where sufficient evidence has not been obtained as to the rational formulas of compounds, they are classified according to their similarity in properties, or in ultimate composition, or in products of decomposition. The following are the most important of such classes:

14. *Carbohydrates*, or compounds that contain six, or some multiple of six, atoms of carbon, together with some multiple of the group $H_2O$; as, for instance, starch $C_6H_{10}O_5$, glucose $C_6H_{12}O_6$, sugar $C_{12}H_{22}O_{11}$, etc.

15. *Glucosides*, or compounds that yield glucose as one of their products of decomposition.

16. *Albuminoids* and *gelatinoids*, or compounds containing $C$, $H$, $N$, and $O$, often with small quantities of $S$ and sometimes of $P$, distinguished by their tendency to putrefy when moist; of such, albumin, fibrin, and casein are examples.

## HYDROCARBONS

**67.** One of the characteristic properties of carbon, to which the attention of the student has not yet been drawn, is its capability of combining with itself. While studying inorganic compounds, the student has met with compounds that contain as many as 6 atoms of one element alone in one molecule of the compound. Among the carbon compounds, however, 6 atoms of carbon is quite a common occurrence, and the molecular formulas that are assigned to many organic compounds contain a considerably greater number of carbon atoms than six. It is this property of carbon that gives rise to the existence of a much larger number of compounds of this element than of any other element known.

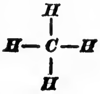
## SATURATED HYDROCARBONS

### PARAFFIN SERIES OF HYDROCARBONS

**68.** Only one hydrocarbon, containing but 1 atom of $C$, is known; namely, *marsh gas*, or *methane*, $CH_4$ (sometimes known as *firedamp*), the chief properties of which have been described already.

We have further seen that when $CH_4$ undergoes metalepsis with chlorine, one of its $H$ atoms is replaced by $Cl$, the compound $CH_3Cl$ being produced by the reaction $CH_4 + Cl_2 = CH_3Cl + HCl$. Although there are various ways of producing a compound of this formula, the product obtained always possesses the same properties, which decisively shows that only one compound of the formula $CH_3Cl$ is in existence. It is contrary to experience acquired in other cases to suppose that all the methods of producing $CH_3Cl$ would result in the displacement of the same $H$ atom, and it may rightly be assumed that while the product of one method is $CHHHCl$, that of the second may be $CHHClH$, that of the third $CHClHH$, and that of a fourth $CClHHH$. But all these compounds are found to be one and the same substance. It is consequently assumed that the four $H$ atoms in methane have an equal position with regard to the carbon atom, so that whichever is replaced, the center of gravity of the molecule will remain the same.

In order to explain this equality of position of the hydrogen atoms in relation to the carbon atom, these hydrogen atoms are represented as being symmetrically arranged around the central carbon atom (see Fig. 16). It is evident from this graphical representation that, whichever $H$ atom is replaced by the $Cl$ atom, the figure has only to be turned round in order to appear the same.

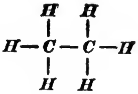


$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

FIG. 16

Graphically, the atoms are necessarily shown on the same plane, but it is not supposed that this represents their true arrangement in the molecule, and although we have at present no satisfactory knowledge of the shapes of molecules, we are obliged to think of them as having three dimensions. The most fruitful hypothesis as to the structure of the methane molecule is that the carbon atom occupies the center of a regular tetrahedron, the hydrogen atoms being attached to the four angles thereof.

As methane has the formula $CH_4$, which is graphically expressed as shown in Fig. 16, it must necessarily be regarded as a *saturated compound*, devoid of any residual affinity such as would be possessed, for instance, by a compound having the formula $CO$. In the case of all other hydrocarbons it is assumed that the carbon atoms are directly united together, since it does not appear to be possible for $H$ to act in any other way than as a monad, so that there cannot be any reason to assume that it acts as an intermediary, and a compound graphically expressed $C—H—C$ would be an impossibility. Of those hydrocarbons that have two carbon atoms, or, as it is sometimes expressed, a *two-carbon nucleus*, there are at least three, of which two, *ethylene*, *olefiant gas*, or *heavy carbureted hydrogen* $C_2H_4$ and *acetylene* $C_2H_2$, now largely used as an illuminating gas, have been already treated upon and will be referred to again. The third, which has the formula $C_2H_6$ and which, in general, is graphically represented as shown in Fig. 17, but which is equally well written $H_3C \cdot CH_3$, is known as *ethane*.



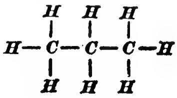
$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & H & \end{array}$$

FIG. 17

The evidence for this formula is of a similar character to that for the methane formula, only one compound, namely $C_2H_5Cl$, being obtainable. If two regular tetrahedrons are placed with one solid angle of each in contact, a two-carbon nucleus will be represented, in which each carbon is the center of a tetrahedron, the six $H$ atoms being at the remaining three angles of each tetrahedron (see Fig. 26).

**69.** Owing to the fact that all the bonds of the two carbon atoms of ethane are linked, this compound is also necessarily considered a saturated hydrocarbon. Turning our attention to the next group—that is, to those compounds that contain three carbon atoms, or a three-carbon nucleus—we find that the saturated compound, i. e., the compound that contains the highest number of hydrogen atoms, is $C_3H_8$, called *propane*, and is represented as shown in Fig. 18, or more simply as $CH_3 \cdot CH_2 \cdot CH_3$.

The evidence of this formula is derived from the methods by which propane is prepared, and will be more fully appreciated when these are described in the future articles. The reasoning applied to methane will not serve in this case, for two compounds of the formula $C_3H_7Cl$ are known, as will be explained later.



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

FIG. 18

**70.** A comparison of these three hydrocarbons will show that ethane may be regarded as derived from methane, and propane from ethane, by substituting $CH_3$ for $H$. By continuing this process a whole series of hydrocarbons is obtained, each of which is saturated and differs from the one preceding it by $CH_2$. Thus, butane, the next member of the series, is $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$, pentane is $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$, and so on. Any series of carbon compounds, each member of which differs from the one preceding it by a constant quantity, as $CH_2$, is called an *homologous series*, and the compounds are homologues of each other.

A little consideration will readily show that in the homologous series in question, the number of hydrogen atoms must always exceed twice the number of carbon atoms by 2, a fact which may be expressed by the general formula for the series, $C_nH_{2n+2}$, and as every terminal carbon atom has, as we have previously seen, 3 hydrogen atoms attached to it, the general formula $C_nH_{2n+2}$ may be extended to $H_3C \cdot C_nH_{2n} \cdot CH_3$. It has been already mentioned that hydrocarbons that conform to this general formula are termed *saturated*, because they cannot possess any free affinities by which other elements can attach themselves to the molecule. The term "saturated" is not merely a theoretical or speculative one—it is a term derived from and based on actual experience, as it has been found that it is entirely impossible to produce a new compound from any of these hydrocarbons except by substitution. No chlorine compound, for instance, can be obtained from methane, except by substituting one or more chlorine atoms for one or more $H$ atoms.

On account of this inactivity the series has been called the *paraffin series of hydrocarbons;* the name paraffin is derived from the Latin words *parum*, meaning "little," and *affinis*, meaning "affinity," and was originally bestowed on the wax-like substance obtained in the distillation of coal and peat, because of its resistance to chemical reagents, and this solid was subsequently shown to consist mainly of saturated hydrocarbons.

The paraffin hydrocarbons may be regarded as the hydrides of positive radicals of the general formula $C_nH_{2n+1}$, the formula for the hydrocarbons being $C_nH_{2n+1}H$. These radicals have been termed *alkyl radicals*, and they are necessarily monovalent. They are designated similarly to the hydrocarbons, which constitute their hydrides, the suffix *yl* being substituted for *ane*.

**71.** The natural source of the paraffin hydrocarbons is the mineral product known as *petroleum*, *rock oil*, or *naphtha*, which is found native in nearly all countries. It should, however, be mentioned, that the Russian petroleum consists largely of hydrocarbons (naphthenes) belonging to the aromatic series, while that of Pennsylvania consists almost exclusively of a mixture of paraffin hydrocarbons.

The oil wells of Pennsylvania evolve large volumes of a gas mixture consisting of $H$, $CH_4$, and $C_2H_6$ (ethane), which are frequently used for lighting as well as heating purposes in the surrounding districts. The liquid pumped out of the well still retains a considerable quantity of ethane in solution, and consists chiefly of members of the paraffin series, of which a list is given below in Table VIII.

### TABLE VIII

| Name | Composition | Characteristic | Name | Composition | Characteristic |
|---|---|---|---|---|---|
| Methane . . . | $CH_4$ | Gas | | | Boils at |
| Ethane. . . . . | $C_2H_6$ | Gas | Heptane . . . | $C_7H_{16}$ | 98° |
| Propane. . . . | $C_3H_8$ | Gas | Octane. . . . . | $C_8H_{18}$ | 125° |
| Butane. . . . . | $C_4H_{10}$ | Gas | Nonane . . . . | $C_9H_{20}$ | 149° |
| | | Boils at | Decane. . . . . | $C_{10}H_{22}$ | 173° |
| Pentane. . . . | $C_5H_{12}$ | 37° | Dodecane . . | $C_{12}H_{26}$ | 214° |
| Hexane . . . . | $C_6H_{14}$ | 69° | Hexadecane | $C_{16}H_{34}$ | 287° |

The liquid constituents of the petroleum are separated by the process known as *fractional distillation*, which depends on the difference in their boiling points.

When the petroleum is heated, the hydrocarbons ethane, propane, and butane are evolved in the gaseous state; these are collected and subjected to the action of a condensing pump, which liquefies a portion of them, yielding the liquid sold as *cymogene*, which has a specific gravity of .59, and is used in freezing machines on account of its rapid evaporation, producing a great cold. The chief constituent of cymogene is *butane* $C_4H_{10}$.

The portion that first distils over, and which boils at 18°, requires special condensation. It contains a considerable proportion of pentane $C_5H_{12}$ and is commercially known as *rhigolene*. It has a specific gravity of .62, and finds employment in the arts as a standard of light and in medicine as an anesthetic. The next portion, that distils over at about 60°, consists nearly entirely of hexane $C_6H_{14}$; it is known commercially as *petroleum ether*, *petroleum spirits*, and *gasolene*. It has a specific gravity of .66, and is used in various industries as a solvent of india rubber, etc. The next fraction consists mainly of heptane $C_7H_{16}$, and is collected until the temperature rises to about 110°; its specific gravity is .7; it is known commercially as *naphtha*, *ligroin*, and *benzoline*. It is used as a burning oil in some kinds of lamps, and serves as a solvent in a number of manufacturing processes. The next fraction of distillation is collected below 150° and is known as *benzine*, which has a specific gravity of .74, and should not be confounded with **benzene,** the coal-tar product. The *kerosene oil* so generally used for lighting purposes is the portion that distils between 150° and 300°. It is generally refined by agitation with about 2 per cent. of sulphuric acid, in order to remove the olefines contained in the oil, before being sent into the market. It is unsafe to use oils of low boiling point as illuminants in ordinary lamps, because they so easily evolve vapor, which forms an explosive mixture with air, and bursts the lamp.

The temperature at which the hydrocarbon evolves enough vapor to form an inflammable mixture with the air above is known as its *flashing point*. No so called paraffin oil should be considered safe for either lighting or cooking purposes that kindles from a flame brought near its surface when it is heated to 38° in an *open vessel;* a tea cup placed in a basin of hot water in which a thermometer is plunged, answers for a rough test. In a closed vessel, where the vapor more rapidly accumulates in sufficient quantity, the flashing point is much lower, and no oil is considered safe that kindles at or below 23° in a covered vessel when a flame is brought near its surface; a small beaker covered with a piece of tinplate having a small hole for the introduction of a match may be placed in warm water for the *closed test*.

The distillation of the petroleum is carried on until a tarry residue is left in the retort. The distillate above 300° consists of heavy lubricating oils containing paraffin wax, which melts at about 55°, and may, therefore, be separated from the oils by freezing; this wax contains the highest known homologues of the paraffin series. The softer varieties of paraffin are known as *vaseline* or *petrolatum.* All the oils mentioned above are colorless when quite pure, although the commercial products are frequently yellow or brown.

**72.** For the purpose of fractional distillation on a small scale, an apparatus as shown in Fig. 19 is usually employed.

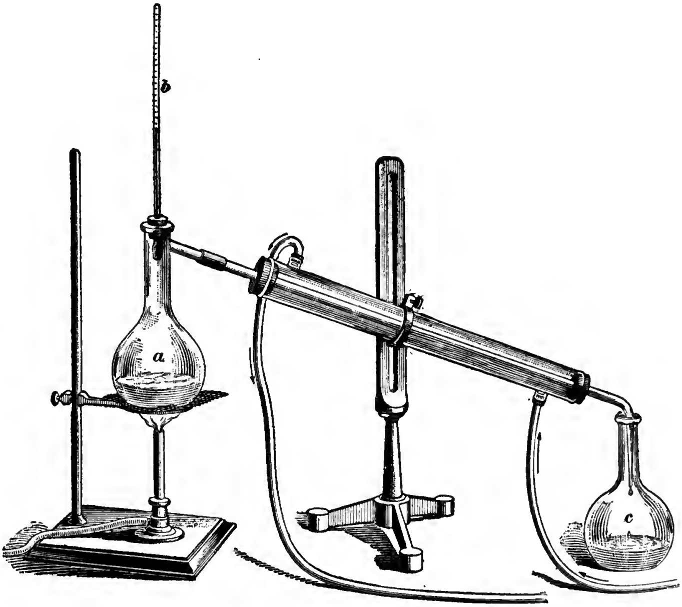


FIG. 19

It consists of a bottle *a* provided with a long neck through which a thermometer *b* passes to indicate the temperature at which the liquid in the flask *a* boils. The first portion that distils over will, of course, consist chiefly of the liquid that has the lowest boiling point, particularly if the neck of the flask consists of a series of bulbs, as shown in Fig. 20, and thus exposes a large surface to be cooled by the air;

if the receiver *c* is changed at stated intervals corresponding with a certain rise in the temperature, a series of liquids will be obtained, containing substances the boiling points of which lie within the limits of temperature between which the liquids were collected.

When these liquids are again distilled separately in the same way, a great part of each is generally found to distil over within a few degrees on either side of some particular temperature, which is the boiling point of the substance of which that liquid chiefly consists; and if the receivers are again changed at stated intervals, a second series of distillates will be obtained, the boiling points of which are comprised within a narrower range of temperature. It will be evident that, by repeated distillations, the original mixture will eventually be resolved into a number of liquids, each distilling over entirely at about one particular temperature, which is the boiling point of its chief constituent.

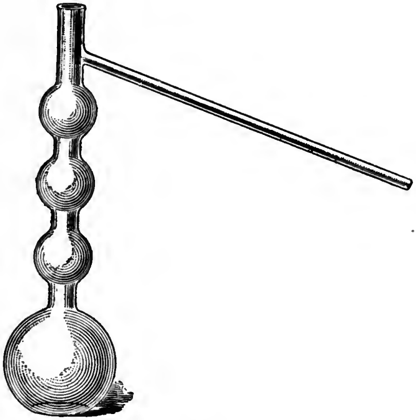


FIG. 20

**73. Methane, or Methyl Hydride.**—The occurrence, preparation, and properties of methane (also known as *marsh gas* and as *firedamp*) have been already treated upon to some extent. The following must now be added to these descriptions.

In order to prepare chemically pure methane, methyl iodide is dropped very slowly into a flask containing a copper-zinc* couple covered with dilute alcohol; the reaction

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*This is a special preparation of zinc coated with copper precipitated from a solution of copper sulphate, which acts much more energetically than zinc alone.

that takes place may be expressed by the subjoined equation:

$$CH_3I + HOH + Zn = CH_3H + ZnIOH$$

It may also be obtained by the decomposition of zinc methide by water:

$$Zn(CH_3)_2 + 2HOH = Zn(OH)_2 + 2CH_4$$

or by the action of sodium amalgam and water (to supply $H$) on carbon tetrachloride:

$$CCl_4 + 4H_2 = CH_4 + 4HCl$$

and by passing a mixture of $CS_2$ vapor and $H_2S$ over red-hot copper:

$$CS_2 + 2H_2S + 4Cu_2 = 4Cu_2S + CH_4$$

These last two methods are especially remarkable, since they represent the preparation of the gas from its elements, and, therefore, the synthesis of the paraffin hydrocarbons in general, for the majority of these can be built up from marsh gas by the aid of a few elements, which are necessary to act as intermediaries.

Methane has a specific gravity of .56. Water dissolves approximately 5 per cent. and alcohol 50 per cent. of the gas. It boils at −160°, but is liquid at −11° under 180 atmospheres of pressure; the specific gravity of the liquid is .415 at −164°.

When methane is mixed with chlorine and exposed to sunlight, a violent reaction resembling an explosion occurs, $HCl$ being formed and $C$ separated, but when the $Cl$ is diluted with $CO_2$ and allowed to act gradually, so called *chlorine substitution products* are formed; viz.:

$$CH_4 + Cl_2 = HCl + CH_3Cl \text{ (monochloromethane)}$$
$$CH_4 + 2Cl_2 = 2HCl + CH_2Cl_2 \text{ (dichloromethane)}$$
$$CH_4 + 3Cl_2 = 3HCl + CHCl_3 \left\{ \begin{array}{l} \text{(trichloromethane, or} \\ \quad \text{chloroform)} \end{array} \right.$$
$$CH_4 + 4Cl_2 = 4HCl + CCl_4 \text{ (tetrachloromethane)}$$

The chlorine in these compounds is not precipitated by silver nitrate, like the $Cl$ in $HCl$ and the chlorides of the metals.

**74. Ethane, or Ethyl Hydride.**—Ethane $C_2H_6$ is obtained by treating zinc ethyl with water:

$$\underset{\text{zinc ethyl}}{Zn(C_2H_5)_2} + 2H_2O = \underset{\text{ethane}}{2C_2H_6} + \underset{\text{zinc hydrate}}{Zn(OH)_2}$$

It is likewise formed when methyl iodide is heated with sodium in a closed tube:

$$2CH_3I + 2Na = C_2H_6 + 2NaI$$

Ethane is a colorless gas, resembling methane in most of its properties, but is more easily liquefied; it is about twice as soluble in alcohol as methane.

**75. Propane, or Propyl Hydride.**—Propane $C_3H_8$ is obtained by the action of nascent hydrogen on propyl iodide; according to the equation:

$$C_3H_7I + H_2 = C_3H_8 + HI$$

It is also obtained when a mixture of ethyl iodide and methyl iodide is heated with zinc:

$$\underset{\substack{\text{ethyl}\\ \text{iodide}}}{C_2H_5I} + \underset{\substack{\text{methyl}\\ \text{iodide}}}{CH_3I} + Zn = C_3H_8 + ZnI_2$$

or $CH_3, CH_2, I + CH_3I + Zn = CH_3, CH_2, CH_3 + ZnI_2$

The reaction is of importance, as it confirms the constitution of propane (see Fig. 18), showing that the hydrocarbon is formed by the combination of methyl with ethyl.

Propane is a colorless gas which boils at −20°.

The student will have noticed that similar methods serve for the preparation of the three compounds, methane, ethane, and propane, which clearly illustrates the fact that the members of an homologous series of carbon compounds can be prepared from the members of another homologous series by the same reaction; thus, the series of *alkyl iodides* $CH_3I$, $C_2H_5I$, $C_3H_7I$, etc. will yield the corresponding series of *alkyl hydrides* (hydrocarbons) by metalepsis with nascent hydrogen. For each series of carbon compounds, therefore, there is a number of general methods of formation.

In case of the paraffin hydrocarbons the following general methods of formation may be distinguished: In the equations $R$ = any alkyl radical. (1) The action of nascent hydrogen on alkyl halides:

$$RCl + 2H = RH + HCl$$

(2) The action of sodium on the alkyl iodides:

$2RI + 2Na = R \cdot R + 2NaI$, or $RI + R'I + Na_2 = R \cdot R' + 2NaI$

(3) Heating the alkali salt of an acid of the acetic series with an alkali:

$$R\cdot COONa + NaOH = RH + NaO\cdot COONa$$

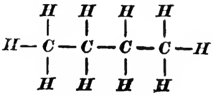
(4) The interaction of the alkyl iodides with the zinc alkyl compound:

$$2RI + ZnR_2 = 2(R\cdot R) + ZnI_2$$

**76. Butane.**—Butane $C_4H_{10}$ is prepared by heating ethyl iodide and zinc in a sealed tube to 150°:

$$2C_2H_5I + Zn = ZnI_2 + C_4H_{10}$$

Butane is much more readily condensed to a liquid than any other of the hydrocarbons treated upon so far; the liquid boils at 0° and has a specific gravity of .6. Since butane is prepared from ethyl iodide, it may be regarded as diethyl in the same sense that ethane is dimethyl, and we can justly write its formula: $CH_3\cdot CH_2\cdot CH_2\cdot CH_3$, or we can represent it graphically as shown in Fig. 21.



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

FIG. 21

Ethyl iodide is the iodine substitution product of ethane $CH_3\cdot CH_3$, and its formula is $CH_3\cdot CH_2I$. When the diad zinc acts upon this, it must take the $I_2$, which it requires to form zinc iodide, from two molecules of ethyl iodide, leaving the residues to combine and produce butane, thus:

$$CH_3\cdot CH_2I + Zn + ICH_2\cdot CH_3 = ZnI_2 + CH_3\cdot CH_2\cdot CH_2\cdot CH_3$$

A second hydrocarbon, having the same formula $C_4H_{10}$ is, however, in existence. It is obtained when nascent hydrogen acts upon the compound known as *tertiary butyl iodide*, which has the formula $C_4H_9I$. This second compound might be taken for butane, but for the fact that it is much more difficult to liquefy (a temperature of −17° being required) than butane. This compound is generally known as *secondary butane*, or *isobutane*, while the first product is termed *normal butane*, being the product of the usual general methods of formation of the paraffins, and possessing the physical properties that the hydrocarbon $C_4H_{10}$ should and must possess from its position in the homologous series of paraffins—that is, a boiling point about 30° lower than the next higher member in the series. In order to explain the existence of this secondary butane, we must take recourse to the assumption that the four carbon atoms in the secondary butane molecule are arranged in a different manner than are those in the normal butane molecule. The only possible second method of arrangement is shown in Fig. 22, in which the fourth $C$ atom is attached to the central $C$ atom of the propane formula. The same arrangement may be expressed by writing its formula as $CH_3\cdot C(CH_3)H\cdot CH_3$, or as $(CH_3)_2\cdot CH\cdot CH_3$, and may be described as consisting of methane in which 3 atoms of $H$ have been replaced by methyl, or *trimethylmethane.*

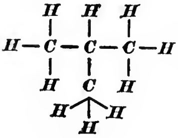
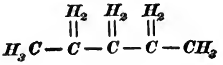


FIG. 22

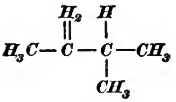
**77. Pentane.**—Three hydrocarbons having the formula $C_5H_{12}$ exist. That compound which is prepared by the regular methods and which is consequently known as *normal pentane*, is a colorless liquid which boils at 36°; *secondary pentane*, or *isopentane*, boils at 30°; and *tertiary pentane*, or *tetramethylmethane*, at 9.5°.

In order to account for the existence of these three hydrocarbons, it becomes necessary to assume that the five carbon atoms are arranged in three different ways; this will be found to be possible, the results being shown in Figs. 23, 24, and 25.



$H_3C-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-CH_3$

FIG. 23



$H_3C-\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}-CH_3$

FIG. 24

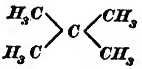


FIG. 25

Fig. 23 shows the atom arrangement of normal pentane to which we may assign the formula $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$. Fig. 24 shows the arrangement of isopentane, which will have the formula $CH_3\cdot CH_2\cdot C(CH_3)H\cdot CH_3$; and, lastly, Fig. 25 shows the arrangement of tertiary pentane, which accordingly has the formula $C(CH_3)_4$.

Should it be possible to arrange the five carbon atoms in a way essentially different from any of these three, a fourth variety of pentane might reasonably be expected to exist.

It will be evident that the greater the number of carbon atoms in the hydrocarbon, the greater the variety of arrangement, and, therefore, the greater the number of possible *isomerides;* thus, for instance, there exist theoretically 802 compounds having the formula $C_{13}H_{28}$.

The term *isomerides* has been used above; these may be defined as those compounds that, although they possess the same percentage composition, and the same molecular weights, differ in their properties. Isomerism is a frequent occurrence with carbon compounds; attempts have been made to explain all these cases by referring to the arrangement of the atoms of the compounds in space although in some cases special difficulty is experienced; these will be referred to later on.

*Polymerides* may be defined as compounds having the same percentage composition, but different molecular weights; thus, for example, $C_2H_2$ and $C_6H_6$, $CH_2O$ and $C_6H_{12}O_6$, etc.

**78.** As carbon is always a tetrad, there can only be three different modes in which the carbon atoms can be linked to each other, giving rise to three main classes of isomerides, which are illustrated by the three classes of paraffin hydrocarbons.

*Normal paraffins* are those in which all the carbon atoms are united in a single chain without branches, so that the formula begins with $CH_3$ and ends with $CH_3$, every other link being $CH_2$ (compare Fig. 23).

*Secondary paraffins*, or *isoparaffins*, have at least one branch; that is, at least one carbon atom is united with three other carbon atoms, as is shown in Fig. 24.

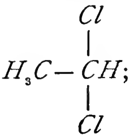
*Tertiary paraffins*, or *neoparaffins*, have at least one carbon atom linked to four other carbon atoms, as is seen in Fig. 25.

## UNSATURATED HYDROCARBONS

**79.** It has been found, experimentally, that all those hydrocarbons whose formulas do not correspond with the general formula $C_nH_{2n+2}$ are able to combine with the halogens without exchanging hydrogen for them. Those compounds are consequently termed *unsaturated hydrocarbons.* No hydrocarbon has so far been discovered that contains an uneven number of hydrogen atoms, nor is an unsaturated hydrocarbon known that contains only one atom of carbon. In order to get an explanation of these facts, it is assumed that all unsaturated hydrocarbons contain at least two carbon atoms which are linked together by two or three bonds; thus,

$$\begin{matrix}H\\H\end{matrix}\!>C=C<\!\begin{matrix}H\\H\end{matrix};\text{ or, thus, }H-C\equiv C-H$$

It may be said that the existence of an unsaturated carbon atom in a hydrocarbon is impossible; because, if there are not sufficient atoms of other elements to saturate the carbon atom, it will combine by means of all its free bonds with another carbon atom. The fact that no such hydrocarbon as $H_3C-\underset{|}{CH_2}$ exists, or, at least, is known at present, supports this theory. Of these two carbon atoms, the unsaturated one will take up a bond of the saturated carbon atom, at the expense of one of the hydrogen atoms united to this latter, forming $H_2C=CH_2$, in which neither carbon atom can be said to be unsaturated. Treatment of this compound with chlorine will open up the double linking, yielding $\underset{\underset{Cl}{|}}{H_2C}-\underset{\underset{Cl}{|}}{CH_2}$. If the compound were represented by the formula $\underset{|}{H_2C}-\underset{|}{CH_2}$, there would be no apparent reason why, when the compound is mixed with the proper quantity of chlorine, one carbon atom alone should not combine with $Cl$, yielding a compound having the formula $\underset{|}{H_2C}-\underset{\underset{Cl}{|}}{CH_2}$, a result which, however, has never yet been obtained. Another method of representing this hydrocarbon may be conceived, namely, as $H_3C-\overset{|}{\underset{|}{CH}}$, but the objection to this formula is that it represents an unsaturated carbon atom, which, as has been previously stated, never seems to occur in a hydrocarbon; moreover, if this formula were correct, the addition of chlorine to the hydrocarbon might be expected to produce



$$H_3C-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{CH}}$$

; whereas there is evidence to show that the two chlorine atoms in the compound resulting from the addition of chlorine to $C_2H_4$ are attached to different carbon atoms.

A similar reasoning will serve for supporting the formula $HC \equiv CH$ for the hydrocarbon $C_2H_2$.

If two regular tetrahedra be placed with one edge of each coincident, there will be two solid angles of each tetrahedron left unattached. Such an arrangement may be supposed to represent the structure of the hydrocarbon $C_2H_4$ in space; each carbon atom would occupy the center of a tetrahedron, and each hydrogen atom would be attached to a free solid angle. By placing the two tetrahedra with one face of each coincident, the structure of the hydrocarbon $C_2H_2$ may be represented.

The following figures will represent hydrocarbons containing singly linked, doubly linked, and trebly linked carbon atoms, respectively:

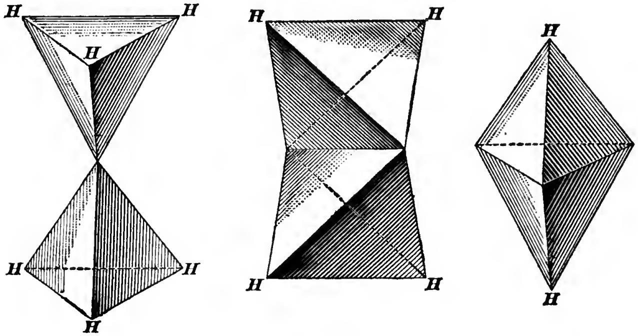


FIG. 26

### OLEFINE SERIES OF HYDROCARBONS

**80.** The olefine hydrocarbons are unsaturated hydrocarbons containing a pair of doubly linked carbon atoms. Their composition may be expressed by the general formula $C_nH_{2n}$. The lowest three members of the series are:

Ethylene $C_2H_4$, or $H_2C:CH_2$;
Propylene $C_3H_6$, or $H_2C:CH\cdot CH_3$;
Butylene $C_4H_8$, or $H_2C:CH\cdot CH_2\cdot CH_3$.

The attention of the student is here drawn to the fact that the nomenclature adopted differs from that for the paraffins by the substitution of the suffix *ylene* for *ane*.

The olefines are found in petroleum oil as well as in the products of the destructive distillation of wood, coal, etc. The above mentioned members are gases, while the remainder are colorless liquids, with the exception of a few of the highest members, which are solids. A gradation of boiling points and melting points is observed similar to that existing in the paraffin series. The properties of ethylene described in the following article may be regarded as typical of all other members of this group of hydrocarbons.

**81. Ethylene, or Olefiant Gas.**—Ethylene, olefiant gas, or ethene, which is one of the most important constituents of illuminating gas, is formed when certain organic substances are subjected to dry distillation. The two principal reactions that yield it are:

1. The action of an alcoholic solution of a caustic alkali on either ethyl chloride, bromide, or iodide, according to the equation:

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

2. The action of sulphuric acid or other dehydrating agents on alcohol:

$$C_2H_5\cdot OH = C_2H_4 + HOH$$

Ethylene is a colorless gas with a faint ethereal odor and a specific gravity of .97. It is slightly soluble in water, more soluble in alcohol, and burns with a bright luminous flame.

When mixed with three volumes of oxygen and then ignited, it produces a violent explosion. It is liquefied by a pressure of 60 atmospheres at 10°, and the evaporation of the liquid under reduced pressure affords a valuable means of attaining very low temperatures. When mixed with chlorine, ethylene combines with it to form a fragrant liquid which is known as *ethylene chloride* or *Dutch liquid* $ClH_2C \cdot CH_2Cl$. Bromine forms a similar compound with it. Sulphuric acid slowly absorbs ethylene, forming *sulphethylic* or *ethylsulphuric acid* $C_2H_5HSO_4$, which is also known as *ethyl hydrogen sulphate*, from which alcohol may be obtained by distillation with water:

$$C_2H_5HSO_4 + HOH = \underset{\text{alcohol}}{C_2H_5OH} + H_2SO_4$$

Sulphuric oxide $SO_3$ absorbs ethylene much more easily, and a strong solution of $SO_3$ in $H_2SO_4$ (fuming sulphuric acid) is employed for its absorption in the analysis of coal gas. The compound formed by $SO_3$ with ethylene is crystalline, and is known as *carbyl sulphate* or *ethionic anhydride* $C_2H_4(SO_3)_2$. In contact with water this forms *ethionic acid*, $CH_2(OSO_3H) \cdot CH_2(SO_3H)$, and when this is boiled with water it yields *isethionic acid* $CH_2(OH) \cdot CH_2(SO_3H)$ according to the equation:

$$H_2C_2H_4S_2O_7 + H_2O = H_2SO_4 + CH_2(OH) \cdot CH_2(SO_3H)$$

It will be noticed that isethionic acid has the same composition as ethyl hydrogen sulphate, but it is a much more stable compound.

In presence of platinum black, ethylene combines with hydrogen to form *ethane* $C_2H_6$. With $HBr$ and $HI$ it combines to form *ethyl bromide* $C_2H_5Br$ and *ethyl iodide* $C_2H_5I$, respectively.

Oxidizing agents, such as nitric and chromic acids, convert ethane into oxidized bodies containing two carbon atoms, as, for instance, oxalic acid $C_2H_2O_4$, aldehyde $C_2H_4O$, and acetic acid $C_2H_4O_2$.

From the given description of the properties of ethylene, the student will notice the wide difference between this gas and methane and the other paraffins, in the readiness with which it combines with other bodies, especially bromine, chlorine, and sulphuric oxide, forming *addition products* instead of *substitution products.*

**82. Propylene.**—Propylene $C_3H_6$ or $CH_3 \cdot CH{:}CH_2$ occurs in small quantities in coal gas, being one of the illuminants. It is prepared by heating allyl iodide with mercury and concentrate hydrochloric acid:

$$2C_3H_5I + 4Hg + 2HCl = Hg_2Cl_2 + Hg_2I_2 + 2C_3H_6$$

Propylene is a colorless gas, having a feeble, alliaceous odor. It is readily absorbed by sulphuric acid and closely resembles ethylene.

**83. Butylene.**—Butylene $C_4H_8$ or $CH_3 \cdot CH_2 \cdot CH{:}CH_2$ occurs largely in illuminating gases obtained by distilling vegetable and animal oils. Its boiling point is $-6°$.

A careful scrutiny of the formula of butylene will show that three isomerides of this compound can exist; namely, $\alpha$ or *normal butylene* $CH_3 \cdot CH_2 \cdot CH{:}CH_2$, $\beta$ or *isobutylene* $CH_3 \cdot CH{:}CH \cdot CH_3$, and, lastly, $\gamma$ *butylene* $(CH_3)_2C{:}CH_2$. The butylene described above is the normal compound.

**84. Amylene, or Pentylene.**—Amylene or pentylene $C_5H_{10}$ or $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH{:}CH_2$ can exist in five isomeric forms. They occur in petroleum and paraffin oil. Normal amylene, the formula of which is given above, boils at 40°.

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### ACETYLENE SERIES OF HYDROCARBONS

**85.** The *acetylene hydrocarbons* are unsaturated hydrocarbons containing a pair of trebly linked carbon atoms, and correspond in composition with the general formula $C_nH_{2n-2}$. The first two members of the series, *acetylene* $HC \vdots CH$ and *allylene* $H_3C \cdot C \vdots CH$, are gaseous under ordinary conditions, while nearly all other members of the series are colorless liquids at ordinary temperatures and pressures.

It will be seen that the hydrocarbon $C_3H_4$ is capable of being represented by the formulas $CH_3 \cdot C \vdots CH$, and

$CH_2{:}C{:}CH_2$, so that two modifications of this compound may be expected. These have been prepared, the former being called *allylene* and the latter *allene*. For every true acetylene (a hydrocarbon containing a pair of trebly linked carbon atoms) there may also be a hydrocarbon containing two pairs of doubly linked carbon atoms. These *diolefines* differ considerably in properties from the acetylenes. They are of no importance, and will not be considered here.

**86. Acetylene, or Ethine.**—Acetylene $C_2H_2$ is the only hydrocarbon which can be obtained by the direct union of its component elements. Although the preparation (by the action of water on calcium carbide) and properties of acetylene have been already treated, a few details concerning the properties of this gas will be here added. Acetylene has a specific gravity of .91. Water at 18° dissolves its own volume of the gas; hence, it can only be collected over water with some loss. It burns with a brighter flame than olefiant gas, but emits smoke. In the presence of platinum black (which by contact promotes the reaction), it combines with hydrogen to form ethene $C_2H_4$. Strong sulphuric acid absorbs acetylene slowly, as it does ethene; but when the solution is mixed with water and distilled, it yields, not alcohol as with ethene, but *croton-aldehyde* $C_3H_5 \cdot CHO$:

$$2C_2H_2 + H_2O = C_4H_6O$$

Chromic acid oxidizes acetylene to acetic acid, while potassium permanganate converts it into oxalic acid.

One of the most remarkable features of acetylene is the facility with which its hydrogen is displaced by metals. If sodium is heated in acetylene, *monosodium acetylide* $C_2HNa$ and *disodium acetylide* $C_2Na_2$ are obtained. *Cuprous acetylide* $C_2Cu_2, H_2O$ is formed when acetylene acts upon a cuprous compound in the presence of ammonia; thus, if acetylene is passed into an ammoniacal solution of cuprous chloride:

$$Cu_2Cl_2 + 2NH_3 + C_2H_2 = C_2Cu_2 + 2NH_4Cl$$

The cuprous acetylide forms a bright red precipitate, the production of which forms a characteristic test for acetylene. *Silver acetylide* $C_2Ag_2, H_2O$ is obtained as a white precipitate when acetylene is passed into silver nitrate. Silver acetylide, like cuprous acetylide, is a highly explosive compound.

Acetylene inflames at once in contact with chlorine in daylight, yielding $HCl$ and finely divided carbon; but if acetylene is passed into antimonic chloride and kept cool, crystals of $C_2H_2Cl_2 \cdot SbCl_3$ are formed, which, on heating, yield the *acetylene dichloride* $C_2H_2Cl_2$, a liquid having the characteristic smell of chloroform and boiling at 55°. *Acetylene tetrachloride* $C_2H_2Cl_4$ and *monochloracetylene* $C_2HCl$ have also been prepared.

When heated in a sealed tube, acetylene is partially converted into a mixture of two liquids, namely *benzene* $C_6H_6$ and *styrolene* $C_8H_8$. By passing electric sparks through a mixture of acetylene and nitrogen, *hydrocyanic acid* is produced: $C_2H_2 + N_2 = 2HCN$. Hence, this acid, from which a large number of organic bodies may be derived, has been synthesized from its elementary constituents. Cuprous acetylide, in contact with zinc and solution of ammonia, yields ethylene, which is convertible into alcohol, and from this a very large number of organic compounds may also be obtained.

Acetylene is regarded as one of the most important intermediate bodies in the synthesis of organic compounds from their elements.

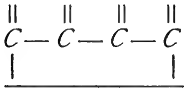
**87. Allylene, or Propine.**—Allylene $C_3H_4$ or $CH_3 \cdot C \vdots CH$ can be prepared from propylene bromide $C_3H_6Br_2$. It resembles acetylene, but its cuprous compound has a yellow instead of a red color.

**Butine** $C_4H_6$ exists in two forms, each of which will have a pair of trebly linked carbon atoms; namely, *ethylacetylene* $CH_3 \cdot CH_2 \cdot C \vdots CH$, and *crotonylene* or *dimethylacetylene* $CH_3 \cdot C \vdots C \cdot CH_3$.

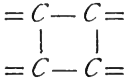
**Crotonylene** is a liquid which boils at 27°; its vapor is one of the illuminating hydrocarbons of coal gas. It does not form any metallic derivatives, and this seems to be generally the case with those acetylenes which have not the group $C \vdots CH$ in their composition.

The other members of the group appear to be of little practical importance so far, and need not be treated upon here.

**88.** The carbon atoms of the paraffins, olefines, and acetylenes are supposed to be linked together as an *open chain*, which means that they are connected in such a way that there are terminal carbon atoms, each of which is attached to only one carbon atom. The student will see from the following that there is good reason to believe that a large number of hydrocarbons exist in which no carbon atom is attached to only one of the other carbon atoms. This can only be the case if it is assumed that the terminal carbon atoms are attached to each other; thus,

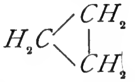


Such hydrocarbons are termed *closed-chain hydrocarbons* or *ring hydrocarbons*, since the arrangement of the carbon atoms in the form of a ring is the most convenient graphical way to show it; e. g.,

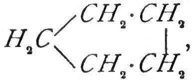


Besides the three open-chain series previously mentioned, there are those corresponding with the general formulas, $C_nH_{2n-4}$ and $C_nH_{2n-6}$. The hydrocarbons of the former series must have either one pair of trebly and one pair of doubly linked carbon atoms, as in the formula $CH_3 \cdot CH : CH \cdot C \vdots CH$, or three pairs of doubly linked carbon atoms, as in the formula $CH_3 \cdot CH : C : C : CH_2$. The hydrocarbons of this series are distinguished by the suffix *one*, as for instance: *hexone* $C_6H_8$. The $C_nH_{2n-6}$ open-chain hydrocarbons must contain either two trebly linked or four doubly linked carbon atoms. The treble linking is the more common; for instance, *diacetylene* $CH \vdots C \cdot C \vdots CH$, and *dipropargyl hexadiine* $CH \vdots C \cdot CH_2 \cdot CH_2 \cdot C \vdots CH$, which is isomeric with benzene. Both these hydrocarbons form copper and silver compounds like acetylene.

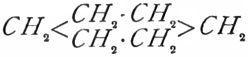
**89. Closed-Chain Hydrocarbons.** — The simplest closed-chain hydrocarbon is the gas *trimethylene**



which is an isomeride of propylene. Pentamethylene,



hexamethylene†



$CH_2 < \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} > CH_2$, and heptamethylene are also known, but up to the present time these hydrocarbons are of little practical importance. The arguments in favor of closed-chain structure for them are similar to those in favor of the closed-chain structure of benzene.

### BENZENE SERIES OF HYDROCARBONS

**90.** The general formula of this series is $C_nH_{2n-6}$, where $n$ is any whole number not less than 6. This series was originally called the *aromatic series*, owing to the fact that the first hydrocarbons discovered were obtained from aromatic balsams and resins. *Benzene* has the formula $C_6H_6$, and its homologues are formed from it by the replacement of hydrogen by the group $CH_3$; thus, *toluene* $C_6H_5 \cdot CH_3$, *xylene* $C_6H_4(CH_3)_2$, etc. Before we consider the structure of these hydrocarbons, it seems advisable to study some of their properties.

**91. Benzene.**—Benzene $C_6H_6$ is prepared from the *light oil* obtained in the distillation of coal tar. It may also be

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* The group $CH_2$ is termed *methylene*.

† Identical with benzene hexahydride; it is also called cyclo-hexane and naphthene, and is a constituent of the Russian petroleum.

prepared by heating benzoic acid with lime, when the acid breaks up into carbon dioxide and benzene:

$$C_7H_6O_2 = C_6H_6 + CO_2$$

or by simply heating acetylene:

$$3C_2H_2 = C_6H_6$$

Benzene is a colorless ethereal liquid of specific gravity .899 at 0°. It has a peculiar, pleasant odor, and boils at 80°. It is very inflammable, and burns with a red, smoky flame; but its vapor, when mixed with either hydrogen or air, as in coal gas, burns with a bright white flame. It is insoluble in water, but dissolves in alcohol and ether. It is used for dissolving caoutchouc, fats, etc. If benzene is dropped into strong nitric acid, or into a mixture of ordinary concentrated nitric acid with an equal volume of strong sulphuric acid, a violent action occurs, red fumes are evolved, and the liquid becomes red. On pouring it into several times its volume of water, a heavy, oily liquid falls, which is *nitrobenzene* $C_6H_5NO_2$, according to the equation

$$C_6H_6 + NO_2 \cdot OH = C_6H_5NO_2 + H_2O$$

The red fumes originate from a secondary reaction not expressed in the above equation. The sulphuric acid is used to combine with the water, since weak nitric acid does not act on benzene. Nitrobenzene has an exceedingly strong flavor of almonds, and is sold, dissolved in alcohol, as *mirbane essence* to the manufacturers of perfumery, etc. It is a poisonous substance when employed in large doses. Nitrobenzene is also employed for the preparation of aniline. This liquid has a specific gravity of 1.2 at 0°, and boils at 206°.

If the mixture of nitric and sulphuric acids mentioned above is boiled with benzene, the liquid, on cooling, deposits a yellowish-colored crystalline solid known as *dinitrobenzene* $C_6H_4(NO_2)_2$, a compound used in the manufacture of some explosives:

$$C_6H_6 + 2(NO_2OH) = C_6H_4(NO_2)_2 + 2H_2O$$

Strong sulphuric acid also oxidizes part of the hydrogen in benzene, when heated with it, leaving in its place the *sulphonic group*, or *sulphuric-acid residue* $SO_2 \cdot OH$, which bears the same relation to sulphuric acid $SO_2(OH)_2$ as nitryl $NO_2$ bears to nitric acid $NO_2 \cdot OH$; thus, $C_6H_6 + SO_2(OH)_2 = H_2O + C_6H_5 \cdot SO_2 \cdot OH$ (*benzene sulphonic acid*). If fuming sulphuric acid be used, a second atom of hydrogen may be replaced; thus, $C_6H_6 + 2SO_2(OH)_2 = 2H_2O + C_6H_4(SO_2 \cdot OH_2)_2$ (*benzene disulphonic acid*).

When chlorine is passed into benzene, to which, in order to facilitate and accelerate the reaction, some iodine has been added, *monochlorobenzene* $C_6H_5Cl$ is obtained; this is a liquid possessing a strong smell of almonds, and a boiling point of 132°. It is not decomposed by caustic alkalies, but is reconverted into benzene by water and sodium amalgam. The further action of chlorine on benzene yields

| | |
|---|---|
| Dichlorobenzene $C_6H_4Cl_2$, | Tetrachlorobenzene $C_6H_2Cl_4$, |
| Trichlorobenzene $C_6H_3Cl_3$, | Pentachlorobenzene $C_6HCl_5$, |

Hexachlorobenzene $C_6Cl_6$

All these compounds are crystalline, solid bodies.

Besides these substitution products, benzene is capable of forming addition products with chlorine, such as *benzene dichloride* $C_6H_6Cl_2$, *benzene tetrachloride* $C_6H_6Cl_4$, *benzene hexachloride* $C_6H_6Cl_6$. These compounds do not possess the stability of the substitution products. Benzene hexachloride, for instance, yields trichlorobenzene $C_6H_3Cl_3$ when heated with potash dissolved in alcohol. The partial decomposition may be expressed by the equation:

$$C_6H_6Cl_6 + 3KOH = C_6H_3Cl_3 + 3KCl + 3H_2O$$

**92. Constitution of Benzene.**—A saturated hydrocarbon is a compound whose composition corresponds with the general formula $C_nH_{2n+2}$, from which it is evident that benzene must be an unsaturated hydrocarbon. In the case of the unsaturated hydrocarbons so far considered (ethylene, acetylene, etc.), it has been seen that they have been so termed because of their capability of uniting directly with chlorine or bromine, and it has also been noticed that the molecule of a hydrocarbon will combine with 2, 4, etc. atoms of either $Cl$ or $Br$ according to its degree of unsaturation, and that the final product of such combination is always a compound of the general type $C_nH_{2n-x}X_x$, where $X$ is either chlorine or bromine. This compound is a stable one, and does not combine with any more halogen. Moreover, this reaction between the unsaturated hydrocarbon and the halogen is the primary reaction between the two substances.

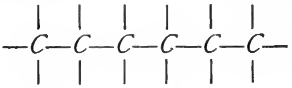
The reaction between benzene and a halogen is of a different nature from this. As has been previously stated, it is more easy to obtain halogen-substitution products—that is, those in which halogen is substituted for hydrogen—from benzene, than it is to obtain mere addition products, containing halogen added to the hydrocarbon.

It appears, then, that benzene resembles saturated as well as unsaturated hydrocarbons in its behavior towards halogens. It differs, however, from the former class in that it can form addition products with the halogens, and from the latter in that the most saturated derivative obtainable from it corresponds with the general formula $C_nX'_{2n}$ and not with $C_nX'_{2n+2}$. When benzene is heated with excess of hydriodic acid, it is converted into the hydrocarbon $C_6H_{12}$, according to the formula:

$$C_6H_6 + 6HI = C_6H_{12} + 3I_2$$

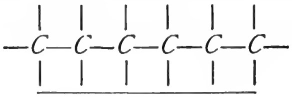
This compound, *benzene hexahydride*, is isomeric with the olefine hexylene, which, however, might be expected to become hexane $C_6H_{14}$ when heated with excess of hydriodic acid.

These facts with regard to benzene may be easily explained on the hypothesis that the six carbon atoms are united in such a way that there is no carbon atom which is not attached to two other carbon atoms—in fact, that the six carbon atoms form a closed chain. The student will readily see that all closed-chain compounds must contain a carbon nucleus that is possessed of two atom-fixing powers (or available bonds) less than the corresponding carbon nucleus in an open-chain compound has; for instance, the nucleus



$$\begin{array}{c} \;\;|\;\;\;\;\;|\;\;\;\;\;|\;\;\;\;\;|\;\;\;\;\;|\;\;\;\;\;| \\ -C-C-C-C-C-C- \\ \;\;|\;\;\;\;\;|\;\;\;\;\;|\;\;\;\;\;|\;\;\;\;\;|\;\;\;\;\;| \end{array}$$

has fourteen atom-fixing powers, while the nucleus



$$\underline{\begin{array}{c} \;\;|\;\;\;\;\;|\;\;\;\;\;|\;\;\;\;\;|\;\;\;\;\;|\;\;\;\;\;| \\ -C-C-C-C-C-C- \\ \;\;|\;\;\;\;\;|\;\;\;\;\;|\;\;\;\;\;|\;\;\;\;\;|\;\;\;\;\;| \end{array}}$$

has only twelve atom-fixing powers.

The closed-chain formula for benzene must contain three pairs of doubly linked carbon atoms, if all the affinities of each atom are to be represented as similarly satisfied as they are in open-chain compounds. Since, as will be shown, there is good reason to believe that the structure of the benzene molecule in space is symmetrical, it has become customary to represent these three double bonds symmetrically in the formula written in the form shown in Fig. 27, and known as *Kekulé's benzene ring.* The late Professor Doctor Kekulé, of Germany, one of the authorities on organic chemistry, was its originator.

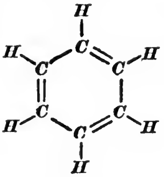


FIG. 27

Some support is lent to this formula by the fact that acetylene polymerizes into benzene when it is heated, $HC\vdots CH + HC\vdots CH + HC\vdots CH$ becoming $\underline{HC{:}CH\cdot HC{:}CH\cdot HC{:}CH}$. There are, however, objections to Kekulé's formula that will be noticed in the future articles.

**93.** Isomerides have already been defined in Art. **77** as compounds that, though they have the same percentage composition and molecular weight, possess different properties. The isomerism may be due to any one of the following causes:

1. The isomeric compounds may be composed of different radicals; as, for instance, the compounds $C_2H_5\cdot CO\cdot C_2H_5$ and $CH_3\cdot CO\cdot C_3H_7$ are isomeric. Such isomerides are sometimes termed *metamerides.*

2. The isomeric compounds may consist of the same radicals, but these may be attached to different carbon atoms; an example was met with in the case of pentane (see Art. **77**). Such isomerides may be termed *position-isomerides*.

3. The isomeric compounds may have the same radicals attached to the same carbon atoms, but differently situated in space with regard to each other, examples of which will be met hereafter (lactic acids). These isomerides are known as *stereo-isomerides*.

**94.** Position-isomerides that are mono-substitution derivatives of a hydrocarbon have only been found to exist in those cases where the carbon atoms in the nucleus are not all similarly united to each other. Thus, two monobromoethanes $C_2H_5Br$ have never been prepared, and it is concluded that more than one cannot exist, because, since there are only two carbon atoms in the nucleus, these must be similarly united to each other. There can, however, be two monobromopropanes $C_3H_7Br$, because the carbon nucleus contains three carbon atoms, one of which is united with two other carbon atoms and two hydrogen atoms, while each of the other two are only united to one other carbon atom and to three hydrogen atoms; thus, $H_3C{\cdot}CH_2{\cdot}CH_2Br$ and $H_3C{\cdot}CHBr{\cdot}CH_3$ may be expected to be different from each other, probably because the center of gravity of the molecule of each is not the same, owing to the difference in the point of attachment of the bromine atom. That these two compounds exist there is no doubt, and that they have the formulas ascribed to them is rendered highly probable from the methods of their formation, which will be presently discussed.

From what has been said, it will be understood that the fact that only one mono-substitution product of benzene can be found to exist, no matter what the substitution element or radical may be, is strong support in favor of similar linking between all the carbon atoms, and of the symmetrical structure of the molecule. Thus, monobromobenzene $C_6H_5Br$

can be prepared in different ways, but it always possesses exactly the same properties.

It can, of course, be assumed that, in the various methods of preparation, the $Br$ atom is always substituted for the same identical $H$ atom, and thus linked to the same carbon atom, and that if it were possible to attach it to some other one of the six $C$ atoms, a different monobromobenzene would result. The following line of argument, involving reactions which the student will fully comprehend later, refutes, however, this objection. Monobromobenzene is prepared by the direct action of bromine on benzene, and may have been formed by the substitution of $Br$ for any one of the six $H$ atoms in the benzene ring (see Fig. 27). Assume that $\overset{1}{H}$ has been replaced, so that the product may be represented as

$$C_6Br\overset{2}{H}\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$$

By treating this with $HNO_3$, the compound $C_6H_4Br\,(NO_2)$ is produced, and it is reasonable to admit that the second $H$ atom which has been replaced by the $NO_2$ cannot be the same $H$ atom as was replaced by the $Br$ beforehand. Assume that $\overset{2}{H}$ has been replaced by $NO_2$; the nitro-compound will then be

$$C_6Br(NO_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$$

By treating this compound with nascent hydrogen, two reactions take place, the chief one, for the present purpose, being the replacement of the bromine by hydrogen. In other words, $\overset{1}{H}$ is put back into the compound again, and we have

$$C_6\overset{1}{H}(NO_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$$

By means of two reactions which will be studied later on, it is a comparatively simple matter to replace the radical $NO_2$ by bromine; this done, we obtain

$$C_6\overset{1}{H}Br\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$$

or a monobromobenzene, in which the bromine certainly replaces a different hydrogen atom from that replaced by direct substitution. The products are, however, found to be identical, proving that whether $\overset{1}{H}$ or $\overset{2}{H}$ is replaced by $Br$, the same substance is produced.

**95.** The cases of position-isomerism among poly-substitution derivatives of hydrocarbons are very numerous. Two dibromo derivatives of ethane are known; namely, $CH_2Br \cdot CH_2Br$ and $CH_3 \cdot CHBr_2$. It has been found that there are four dibromopropanes $C_3H_6Br_2$, which it is assumed may be represented by the following four formulas: (1) $CH_2Br \cdot CH_2 \cdot CH_2Br$; (2) $CH_3 \cdot CHBr \cdot CH_2Br$; (3) $CH_3 \cdot CH_2 \cdot CHBr_2$; and (4) $CH_3 \cdot CBr_2 \cdot CH_3$. Only two other methods of writing this formula are possible; namely, (5) $CH_2Br \cdot CHBr \cdot CH_3$ and (6) $CHBr_2 \cdot CH_2 \cdot CH_3$; but on analyzing these last two formulas the student will readily perceive that in formula 5 the bromine atoms are attached to carbon atoms that are the same, so far as their linking to other atoms is concerned, as the carbon atoms to which the $Br$ atoms are attached in formula 2, and that there is the same similarity between formula 6 and formula 3. It is evident that if the number of carbon atoms in the open-chain hydrocarbon-nucleus, or the number of substituting bromine atoms, be increased, the number of ways in which the formula can be written, so that this is essentially different each time, will be increased. It has been supposed as many isomerides may exist as there are essential differences in the formulas which can be written for the compound. While many isomerides, thus theoretically constructed, have been actually prepared, the number undiscovered is large enough to cause some hesitancy in accepting the supposition.

**96.** In the case of benzene, the poly-substitution products have been thoroughly examined. Most of the di-substitution products are known in three isomeric forms, but no di-substitution product of benzene has been, so far, prepared in more than three isomeric forms.

Thus, although benzene yields only one mono-substitution product, it is capable of forming three di-substitution products, in each of which two atoms of hydrogen are replaced by either radicals or elements.

There exist, for instance, three dibromobenzenes, all having the formula $C_6H_4Br_2$, and are therefore strictly isomeric, and yet having different properties. There are also three dinitrobenzenes $C_6H_4(NO_2)_2$ as well as three benzene disulphonic acids $C_6H_4(SO_3H)_2$, and such compounds form perfectly distinct series, so that, if they be distinguished as *a*, *b*, and *c* compounds, *a-dibromobenzene* will yield *a-dinitrobenzene* and *a-benzene disulphonic acid*, while *b* and *c dibromobenzenes* will also yield their proper derivatives.

In order to obtain a reasonable explanation concerning the existence of these three isomeric di-substitution products, it becomes necessary to assume that different pairs of hydrogen atoms in benzene have different chemical values, and that the properties of the di-substitution products depend upon the particular pair of hydrogen atoms replaced by the substitution radical. In order to investigate this, it became necessary to *orient* (a term borrowed from the vocabulary of surveying) the plan of the benzene formula ; that is, to mark the situation or *bearing* of its different parts.

To effect this orientation of the benzene ring, it is necessary to distinguish the carbon atoms, for which purpose they are numbered consecutively, as on a watch face, and as shown in Fig. 28.

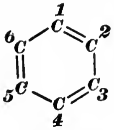


FIG. 28

The pairs of hydrogen atoms occupying places *1* and *2*, *2* and *3*, *3* and *4*, *4* and *5*, *5* and *6*, and *6* and *1*, bear the same relation to the figure, and are therefore of equal value, so that whichever pair is replaced by other radicals, the di-substitution products will be identical.

Again, *1* and *3*, *2* and *4*, *3* and *5*, *4* and *6*, *5* and *1*, *6* and *2*, being alternate atoms, bear the same relation to the figure, and their replacement would give rise to identical di-substitution products.

But consecutive atoms such as *1* and *2*, or *2* and *3*, have a different relation to the figure from that belonging to alternate atoms, such as *1* and *3*, *2* and *4*, so that the replacement of two consecutive atoms of hydrogen would give one kind of derivative (which we might call the *a* substitution product), and that of two alternate hydrogen atoms would produce another kind (which might be called the *b* substitution product).

Lastly, the pairs *1* and *4*, *2* and *5*, and *3* and *6* have the same relation to the figure, and when replaced by radicals would give identical products, but these would differ from the *a* as well as from the *b* products, and might, therefore, be called *c* products.

It will be seen that the above list exhausts all the possible pairs of hydrogen atoms, and that there can be positively only three di-substitution derivatives of benzene. It has become customary to employ the terms *ortho*, *meta*, and *para*, respectively, instead of the letters *a*, *b*, and *c* used above. That is to say, when *alternate* hydrogen atoms are replaced, the product is called a *meta compound;* when *opposite* hydrogen atoms are replaced, the product is termed a *para compound;* and when *adjacent* hydrogen atoms are replaced, the product is known as an *ortho compound.* This is sometimes denoted by figures appended to the formula ; thus dibromobenzene (1 : 2) is *orthodibromobenzene;* (1 : 3) is *metadibromobenzene;* and (1 : 4) is *paradibromobenzene*, all of which have the same formula, $C_6H_4Br_2$.

The fact that there are only three di-substitution products of benzene constitutes the main objection to Kekulé's formula. It is not in accord with experience obtained from the open-chain compounds, that a substitution derivative containing the substituent groups attached to carbon atoms doubly linked together should be identical with one that contains the groups attached to singly linked carbon atoms ; thus 1 : 2 dinitrobenzene should differ in properties from 6 : 1 dinitrobenzene, though, as a matter of fact, they are identical, and four di-substitution products are not known. Professor Kekulé got over these objections by assuming that the ring is in a state of constant vibration, the double and single links constantly changing places. Several other formulas have been proposed to overcome these difficulties, notably the so called *central formula* of Claus, the conception underlying which will be understood from Fig. 29.

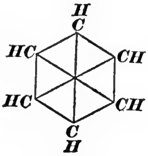


FIG. 29

An argument in support of this formula is the high resistance shown by benzene and some of its substitution products to direct oxidation (by alkaline permanganate, for instance), thus indicating that *ethylenic linking*—i. e., carbon doubly linked, as in ethylene—does not occur. On the other hand, many addition products of benzene, in which all the carbon atom-fixing powers are not satisfied, are so easily oxidized that ethylenic linking may be supposed to exist in them. Bäyer believes in the existence of ethylenic linking in some benzene compounds and of central or para-linking (as shown in Fig. 29) in others.

Pending a better knowledge as to the disposition of the fourth atom-linking power of each carbon atom, the majority of chemists prefer to represent benzene compounds as derived from a plain hexagon.

**97.** Tri-substitution derivatives of benzene, in which the same radical is substituted for all three atoms of hydrogen are found to exist in three isomeric forms; thus, there are three tribromobenzenes $C_6H_3Br_3$, distinguished as *adjacent* (1 : 2 : 3), *symmetrical* (1 : 3 : 5), and *asymmetrical* (1 : 2 : 4).

If the substituted radicals are of two different kinds—say, for instance, chlorine and bromine—six isomerides may be formed, and if three different radicals are introduced—say, chlorine, bromine, and $NO_2$—ten isomerides are possible.

Tetra-substitution derivatives of benzene may also be either adjacent (1:2:3:4), symmetrical (1:2:4:5), or asymmetrical (1:3:4:5). With a single substituted radical only these three isomerides are possible, but the number of compounds that may thus be formed increases rapidly with the number of different radicals substituted.

The experimental investigation of the orientation of a benzene derivative consists in attempting to introduce fresh substituents into the nucleus, or in replacing some substituent by hydrogen; how this settles the orientation will be readily seen from the following article.

**98.** By treating a dibromobenzene with bromine it is possible to convert it into tribromobenzene. It is found that the dibromobenzene which boils at 224° yields two tribromobenzenes, while that which boils at 219.5° yields three tribromobenzenes, and that which boils at 219° and melts at 89° (the others melt at about 1°) yields only one tribromobenzene. Now, an inspection of the formulas for the three dibromobenzenes, as written on the plane of the paper, will show the 1:2 dibromobenzene can only yield two tribromobenzenes; namely, 1:2:3 and 1:2:4, since 1:2:5 = 1:2:4 and 1:2:6 = 1:2:3. Again, it will be readily seen that the 1:3 dibromobenzene can yield three tribromobenzenes; namely, 1:2:3, 1:3:4, and 1:3:5 (1:3:6 = 1:3:4), while the 1:4 dibromobenzene can only yield one tribromobenzene; namely, 1:2:4 (or 1:3:4, or 1:4:5, or 1:4:6, all of these being identical with 1:2:4). The following diagram, marked Fig. 30, will make this more clear:

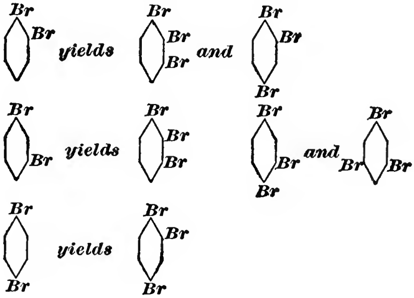


FIG. 30

It is evident, of the three known dibromobenzenes, that must be the 1:2 compound which yields two tribromo derivatives; that the 1:3 compound which yields three tribromo derivatives; and that the 1:4 compound which yields only one tribromo derivative.

**99.** The orientation of the tri-substitution derivatives may be similarly settled by replacing one of the substituents by hydrogen, and thus obtaining one or more di-derivatives. If the derivative is the 1:2:3 compound, it will yield two di-derivatives; namely, 1:2 and 1:3; if it be the 1:3:4 compound, it will yield all three derivatives; if it be the 1:3:5 compound, it can yield only one di-derivative.

The orientation of certain derivatives which may be termed standard derivatives, having been settled by investigations involving the principle stated above, the orientation of any new compound may be settled by converting it into one of these. Chief among these standards are the bromo-derivatives and the carboxylic acids (phthalic acid, etc.). Thus, the orientation of a newly discovered nitro-derivative could be settled by submitting it to a treatment (such as indicated in Art. **94**), that would replace the $NO_2$ groups by $Br$ atoms; a study of the properties of the bromo-derivatives thus produced would decide its orientation and therefore that of the original nitro-derivative.

**100.** It is to be noticed that a polyvalent element can never be substituted for several hydrogen atoms in the benzene nucleus; thus, a compound having, for instance, the composition $C_6H_4O$ is unknown.

The desire to foretell what compound will be produced when a benzene derivative is treated with a substituting agent, has led to the formulation of several rules. Thus, it has been laid down that, when in a compound $C_6H_5X$ in which $X$ is either $NO_2$, or $SO_2OH$, or $COOH$, any new radical entering into $C_6H_5X$ will take up the meta position to $X$. If $X$ is any other group, the newly entering substituent will generally produce the para derivative, but accompanied by a little of the ortho and sometimes of the meta derivative.

If $X$ is an element or radical that forms a compound $XH$, capable of direct oxidation to $HOX$, the newly entering substituent will take the meta position; if, on the other hand, it is not so capable of oxidation, the newly entering substituent will take up the ortho and para positions. Thus, the introduction of a substituent into $C_6H_5Cl$ will give ortho as well as para derivatives, because $HCl$ is incapable of direct oxidation to $HOCl$, while its introduction into $C_6H_5\cdot COOH$ will give a meta derivative, because $HCOOH$ is capable of direct oxidation to $HO\cdot COOH$.

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### HOMOLOGUES OF BENZENE

**101.** Homologues of benzene may be defined as derivatives of benzene containing alkyl radicals in place of hydrogen, such substituting radicals being known as *side chains*. *Methylbenzene* (*toluene*) $C_6H_5\cdot CH_3$, *dimethylbenzene* (*xylene*) $C_6H_4(CH_3)_2$, *trimethylbenzene* $C_6H_3(CH_3)_3$, and *tetramethylbenzene* $C_6H_2(CH_3)_4$, occur in coal tar; numerous others, such as *ethylbenzene* $C_6H_5\cdot CH_2\cdot CH_3$, *methylethylbenzene* $C_6H_4(CH_3)(CH_2\cdot CH_3)$, etc., have been prepared synthetically.

The residues of the benzene hydrocarbons, or *aromatic radicals*, are named similarly to the alkyl radicals; thus, corresponding with methyl, ethyl, and propyl, there are *phenyl* $C_6H_5$, *methylphenyl*, or *tolyl* $C_6H_4\cdot CH_3$, *dimethylphenyl*, or *xylyl* $C_6H_3\cdot(CH_3)_2$.

Toluene and xylene are the only compounds of any remarkably practical importance among the homologues. These hydrocarbons are extracted from the coal tar obtained by the distillation of coal in the process of manufacturing coal gas. A large quantity of the tar is distilled in an iron retort, when water passes over, holding salts of ammonia in solution, and accompanied by a brown, oily, offensive liquid that collects on the surface of the water. This is the light oil containing the benzene hydrocarbons. To purify it, it is shaken with caustic soda to dissolve carbolic acid (phenol), and afterwards with sulphuric acid, which removes aniline and other basic compounds. It is then subjected to a process of fractional distillation, similar to the process described in Art. **71.**

**102.** *Toluene* $C_6H_5\cdot CH_3$ was discovered in 1837 by Pelletier and Walter. H. Deville obtained it by distilling *balsam of tolu*, hence its name. It is always present in commercial benzene. It is a little heavier than benzene, which it resembles in odor, but it does not solidify even at −20°. It boils at 110°. Benzene may be converted into toluene by first obtaining bromobenzene $C_6H_5Br$ and treating this with methyl iodide and sodium, in the presence of ether:

$$C_6H_5Br + CH_3I + Na_2 = C_6H_5 \cdot CH_3 + NaBr + NaI$$

Toluene is chiefly used in the manufacture of aniline dyes and artificial oil of bitter almonds.

**103.** *Xylene* $C_6H_4(CH_3)_2$, being a di-substitution product, exists in three forms, but besides these there is a fourth hydrocarbon having the formula $C_8H_{10}$, namely ethylbenzene, which, however, is a metameride of xylene. The portion of the light oil that distils at from 136° to 141° contains about 70 per cent. of metaxylene, 20 per cent. of paraxylene, and 10 per cent. of orthoxylene. The mixture is used as a solvent.

By shaking the mixture with $H_2SO_4$ of 80-per-cent. strength, the metaxylene is dissolved out; by treating the residue with ordinary strong $H_2SO_4$, the orthoxylene is extracted, leaving the paraxylene. The action of the $H_2SO_4$ is to convert the xylene into a sulphonic acid $C_6H_3(CH_3)_2 \cdot SO_2OH$, from which the hydrocarbon can be obtained by dilution with water and distillation. *Orthoxylene* boils at from 140° to 141°; metaxylene at 137°, and paraxylene at 136°. By oxidation the methyl groups may be successively converted into $COOH$ groups, yielding *toluic acid* $C_6H_4(CH_3)(COOH)$ and *phthalic acid* $C_6H_4(COOH)_2$. Each of these acids exists in three forms, yielded, respectively, by ortho, meta, and para xylene.

*Mesitylene* is 1 : 3 : 5 trimethylbenzene $C_6H_3(CH_3)_3$ obtained by the action of sulphuric acid on acetone:

$$3(CH_3 \cdot CO \cdot CH_3) = C_6H_3(CH_3)_3 + 3H_2O$$

It is a liquid that boils at 163°, and is metameric with *cumene* or *isopropylbenzene* $C_6H_5 \cdot CH(CH_3)_2$. *Durene* is 1 : 2 : 4 : 5 *tetramethylbenzene* and possesses an odor resembling that of camphor; it is metameric with *cymene*, or *1:4 methylisopropylbenzene*, $C_6H_4(CH_3)\cdot CH(CH_3)_2$, which is found in oil of cummin and is a product of the dehydration of camphor.

**104.** The chief distinction between benzene hydrocarbons and open-chain hydrocarbons is the readiness with which the former may be converted into nitrosubstitution products by the action of strong nitric acid, and into sulphonic acids by the action of strong sulphuric acid. Moreover, the homologues of benzene easily undergo oxidation, resulting in the conversion of the side chains into the *carboxyl* group $COOH$ characteristic of acids.

The general methods employed in the preparation of *benzene hydrocarbons* are the following: (1) The distillation of the corresponding carboxylic acid with lime, which removes the $CO_2$ from the carboxyl group:

$$C_6H_4(CH_3)\cdot(COOH) = C_6H_5\cdot CH_3 + CO_2$$

(2) The interaction of the bromo-substitution derivative and an alkyl iodide with sodium in ether:

$$C_6H_5Br + C_2H_5\cdot I + Na_2 = C_6H_5\cdot C_2H_5 + NaI + NaBr$$

(3) The interaction of a benzene hydrocarbon with an alkyl iodide in the presence of $Al_2Cl_6$, the precise function of which is, however, not understood:

$$C_6H_5\cdot CH_3 + 2CH_3Cl = C_6H_3(CH_3)_3 + 2HCl$$

**105.** The above benzene hydrocarbons contain, as side chains, the residues of saturated open-chain hydrocarbons. There also exist hydrocarbons containing residues of olefine and acetylene hydrocarbons. The *olefine benzenes* correspond with the general formula $C_nH_{2n-10}$, and the *acetylene benzenes* correspond with the general formula $C_nH_{2n-12}$.

*Cinnamene*, *styrolene*, or *styrene* $C_6H_5\cdot CH:CH_2$ is *phenyl ethylene*. It is obtained by distilling cinnamic acid with lime:

$$C_6H_5\cdot CH:CH\cdot COOH + Ca(OH)_2 = C_8H_8 + CaCO_3 + H_2O$$

It can also be prepared by distilling balsam of storax, or by distilling the resin known as dragon's blood with zinc dust. Cinnamene is a fragrant liquid of specific gravity .924 and a boiling point of 145°. It resembles the olefine hydrocarbons in uniting directly with chlorine, bromine, and iodine. When heated in a sealed tube to 200°, it is converted into a transparent solid known as *metacinnamene* or *metastyrolene*, which is polymeric with cinnamene, into which it is reconverted by distillation. When heated with hydrochloric acid to 170°, cinnamene is converted into dicinnamene $C_{16}H_{16}$.

*Phenylacetylene* $C_6H_5 \cdot C \vdots CH$ is a liquid that boils at 142°; it yields the explosive silver and copper derivatives characteristic of true acetylenes.

## HYDROCARBONS CONTAINING MORE THAN ONE BENZENE NUCLEUS

**106.** Hydrocarbons containing more than one benzene nucleus may be divided into different groups; viz., (1) Hydrocarbons containing benzene nuclei directly united, as, for example, diphenyl $C_6H_5 \cdot C_6H_5$. (2) Hydrocarbons containing two or three nuclei united by one carbon atom, as in diphenyl methane $C_6H_5 \cdot CH_2 \cdot C_6H_5$ and triphenyl methane $CH(C_6H_5)_3$. (3) Those that contain two benzene nuclei united with two carbon atoms, like dibenzyl $C_6H_5CH_2CH_2C_6H_5$. (4) Those that contain condensed nuclei, as explained under naphthalene (see Art. **112**) and anthracene (see Art. **114**).

Many of the derivatives of these hydrocarbons are of importance in the arts, but with the exception of those from naphthalene and anthracene, the hydrocarbons are not used as raw material for preparing them.

**107.** *Diphenyl* $C_6H_5 \cdot C_6H_5$, also known as *phenyl phenyl*, is produced by passing benzene vapor through a red-hot tube containing fragments of pumice stone,

$$2C_6H_6 = (C_6H_5)_2 + H_2$$

which is the most convenient method of preparing it. It may also be obtained by treating bromo benzene with sodium:

$$2C_6H_5Br + 2Na = (C_6H_5)_2 + 2NaBr$$

It appears among the last products of the distillation of coal tar.

Diphenyl crystallizes from alcohol in iridescent scales, melts at about 70.5°, sublimes at a higher temperature, and boils at 254°. When dissolved in glacial acetic acid and treated with chromic acid, it oxidizes to benzoic acid $C_6H_5 \cdot CO_2H$.

Like benzene, it forms numerous substitution derivatives, and since it may be regarded as being itself nothing but a mono-substituted benzene containing phenyl in the place of $H$, its mono-substitution derivatives are really di-substituted benzenes and occur in three isomeric modifications. Its di-derivatives occur in many forms, for substitution may occur in each ring. The orientation is usually expressed as shown in Fig. 31.

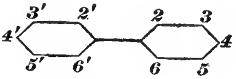
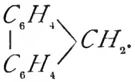


FIG. 31

*Phenyl tolyls* $C_6H_5 \cdot C_6H_4 \cdot (CH_3)$ and *phenyl ditolyls* $C_6H_4 \cdot (CH_3) \cdot C_6H_4 \cdot (CH_3)$ are examples of mono-substituted and di-substituted diphenyl; the 4 and 4 : 4′ derivatives are the most common.

**108.** *Diphenylmethane* $C_6H_5 \cdot CH_2 \cdot C_6H_5$ is obtained by heating a mixture of benzene (say 6 parts) and benzyl chloride (10 parts) with zinc dust (3 to 4 parts). It forms a colorless, crystalline mass, made up of needles, which possesses an odor resembling that of oranges; it melts at about 26° and boils at about 261°. It readily dissolves in alcohol and ether. Chromic acid oxidizes it to *diphenyl ketone* $CO(C_6H_5)_2$. Passed through a red-hot tube, it yields diphenylene methane:  $\left.\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\right\rangle CH_2$. *Diphenylene methane* is found in the last running in the distillation of coal tar (at from 300° to 305° C.). It crystallizes from alcohol with a beautiful blue fluorescence. Oxidation converts it into *diphenylene ketone.* Its melting point is 113° and its boiling point 295°.

**109.** *Triphenylmethane* $CH(C_6H_5)_3$ is obtained by heating benzal chloride with mercury diphenyl:

$$C_6H_5CHCl_2 + (C_6H_5)_2Hg = HgCl_2 + C_6H_5 \cdot CH \cdot (C_6H_5)_2$$

or it may also be obtained by the interaction of chloroform and benzene in the presence of $Al_2Cl_6$:

$$3C_6H_6 + CHCl_3 = CH(C_6H_5)_3 + 3HCl$$

It crystallizes in colorless, shining prisms. It dissolves in hot alcohol. Its melting point is 92° and its boiling point about 360°. The aniline dyes are derivatives of this hydrocarbon.

**110. Dibenzyl $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$.**—Toluene can give rise to two hydrocarbon residues or radicals; namely, tolyl $C_6H_4 \cdot CH_3$ and benzyl $C_6H_5 \cdot CH_2$. When the chloride of the latter radical $C_6H_5 \cdot CH_2Cl$ is treated with sodium, dibenzyl $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$ is produced, according to the equation:

$$2(C_6H_5 \cdot CH_2Cl) + Na_2 = C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5 + 2NaCl$$

Dibenzyl has a melting point of 52° and boils at about 284°; when subjected to oxidation it yields benzoic acid. *Diphenylethylene*, also known as *stilbene* and *toluylene* $C_6H_5 \cdot CH{:}CH \cdot C_6H_5$, is formed by treating benzal chloride with sodium, according to the equation:

$$2C_6H_5 \cdot CHCl_2 + Na_2 = C_6H_5 \cdot CH \cdot CH \cdot C_6H_5 + 2NaCl$$

or by partially oxidizing toluene or dibenzyl, by passing it over hot $PbO$. It crystallizes in prisms, melts at 125°, and is soluble in hot alcohol. It contains true ethylenic linking, for the first action of bromine on it is the formation of the dibromide $C_6H_5 \cdot CHBr \cdot CHBr \cdot C_6H_5$. *Diphenylacetylene*, or *tolane* $C_6H_5 \cdot C{\vdots}C \cdot C_6H_5$, is formed by boiling stilbene dibromide with alcoholic potash. It melts at 60° and behaves generally as an acetylene.

**111. Naphthalene.**—Naphthalene $C_{10}H_8$ was discovered by Garden in 1820, in coal tar. Its composition was determined by Faraday, and its properties and transformations were principally investigated by Laurent.

Naphthalene is a frequent product of the action of heat on organic matter rich in carbon. It is formed by passing the vapors of alcohol, ether, acetic acid, volatile oils, benzene, petroleum, etc. through red-hot tubes, and also by treating ethylene and acetylene in the same manner. It is found in coal tar, and sometimes occurs in pipes used for gas made by raising naphtha, gasoline, etc. to high temperatures. It has been prepared synthetically by conducting phenyl-butylene bromide over highly heated lime:

$$C_6H_5 \cdot C_4H_7Br = C_{10}H_8 + H_2 + 2HBr$$

and by conducting isobutyl benzene over lead oxide; viz.:

$$C_6H_5 \cdot C_4H_9 + 3O = C_{10}H_8 + 3H_2O$$

Naphthalene is prepared on a large scale from those portions of coal tar that boil between 180° to 220°. This material is treated with caustic soda and then with sulphuric acid, and distilled. Naphthalene is a transparent, crystalline body, possessing a pleasant, gas-like odor. It melts at 80°, is inflammable, and burns with a smoky flame. It sublimes readily. It is insoluble in water, but is soluble in boiling alcohol, benzene, and ether.

In its chemical relations, naphthalene is closely connected with benzene, but it shows a greater disposition to form addition products with chlorine and bromine, with which it also yields numerous substitution products. Naphthalene absorbs chlorine, forming a yellow liquid known as *naphthalene dichloride* $C_{10}H_8Cl_2$, and a crystalline solid, known as *naphthalene tetrachloride* $C_{10}H_8Cl_4$. The non-appearance of a compound having the formula $C_{10}H_8Cl_3$ is in accordance with the law of even numbers mentioned in Art. **63.**

Naphthalene is used for making phthalic acid, into which it is converted by oxidation; it is used for increasing the illuminating value of coal gas, and as an insecticide (as, for example, in the manufacture of moth balls). Many of its derivatives are used for making synthetic dyes.

**112. Constitution of Naphthalene.**—The similarity of the behavior of naphthalene and benzene strongly indicates an analogous structure for these two hydrocarbon compounds, and since by oxidation naphthalene yields a benzene dicarboxylic acid $C_6H_4(COOH)_2$, as seen from the following equation:

$$C_{10}H_8 + 9O = C_6H_4(COOH)_2 + 2CO_2 + H_2O$$

which contains the benzene residue $C_6H_4$, it must be taken for granted that $C_{10}H_8$ contains a benzene ring. In this way we are able to account for six of the ten carbon atoms this compound contains; further, two of the remaining four carbon atoms must be attached directly to two carbon atoms of the benzene ring, otherwise a dicarboxylic acid could not have resulted from the oxidation. Moreover, since the dicarboxylic acid thus obtained has been found to be phthalic acid, which is believed to have the carboxyl groups attached to adjacent carbon atoms of the ring, the two carbon atoms must be attached to the benzene ring in the ortho position. The two, so far, unaccounted carbon atoms are believed to form a closed chain with the two atoms just considered. Leaving, at present, the evidence for this belief aside, the formula to which it gives rise may be regarded as consisting of two benzene rings, which are condensed in such a manner that they possess two carbon atoms in common. Fig. 32 shows the construction of naphthalene for orientation; to avoid, however, the representation of ethylenic linking, it has become customary to represent the structure in the way shown in Fig. 33.

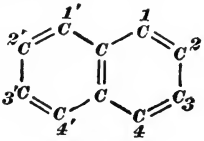


FIG. 32

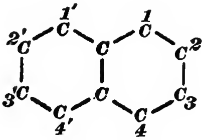


FIG. 33

That naphthalene consists of two benzene nuclei as represented by the formula is supported by the following facts: When nitronaphthalene $C_{10}H_7NO_2$ is oxidized, nitrophthalic acid is obtained according to the equation:

$$C_6H_3(NO_2)(C_2H_2)_2 + 9O = C_6H_3(NO_2)(COOH)_2 + H_2O + 2CO_2$$

From this reaction it is evident that the nitro group $NO_2$ in nitronaphthalene is in a benzene ring, whether there exists a second benzene ring or not, and we may assume that this nitro group occupies the position *1′* in the formula shown in Fig. 32. By reducing this same nitronaphthalene it becomes amidonaphthalene $C_6H_3(NH_2)(C_2H_2)_2$, which means that the amido group $NH_2$ now occupies the same position the nitro group $NO_2$ previously held. If we then oxidize this amidonaphthalene according to the equation:

$$C_6H_3(NH_2)(C_2H_2)_2+12O$$
$$=C_6H_4(COOH)_2+2CO_2+HNO_3+H_2O$$

we do not obtain amidophthalic acid, but simply phthalic acid $C_6H_4(COOH)_2$ by itself. Since an oxidizing action cannot replace $NH_2$ by $H$, it must be concluded that it is the ring in which the $NH_2$ group was situated that has been removed by the oxidation, and yet a benzene ring compound (phthalic acid) has been left, showing conclusively that naphthalene must have contained two of these benzene rings.

A little consideration will show that only two isomerides of every mono-substitution product exist; this is in accord with the formula, for it will be seen that while the carbon atoms 1, 1′, 4, and 4′ are similarly situated towards the whole molecule, they are differently situated from 2, 2′, 3, and 3′, which, however, are similarly situated towards the whole molecule. When a substituent takes up any of the first-named positions, it is termed an *a** *derivative*, while the other positions yield *β*† *derivatives*. It will be found that 10 di and 14 tri-derivatives are possible; all the mono, di, and tri-chloronaphthalenes are known and orientated, so that the orientation of a new derivative may be settled by its conversion into one of these.

The general formula for the naphthalene hydrocarbons is $C_nH_{2n-12}$.

**113.** Examples of members of the homologous series are *methyl naphthalene* $C_{10}H_7\cdot CH_3$ and ethyl naphthalene $C_{10}H_7\cdot C_2H_5$. These are liquid even at low temperatures,

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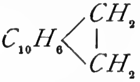
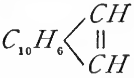
* *a*, called *alpha*, the Greek letter for our *a*.
† *β*, called *beta*, the Greek letter for our *b*.

and are constitutents of coal tar. *Ethene naphthalene*, also known as *acenaphthene*  $C_{10}H_6\left\langle\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\right.$ is formed by passing ethylnaphthalene through a red-hot tube, when hydrogen is separated. It also occurs in small quantity in coal tar. It crystallizes from fusion in flat prisms and from hot alcohol in long needles. It melts at 95° and boils at 277°. It is sparingly soluble in cold alcohol. Acenaphthene forms with picric acid the compound $C_{12}H_{10}, C_6H_2(NO_2)_3OH$, which crystallizes from alcohol in long needles, melting at about 161°. By oxidation with chromic acid, acenaphthene is converted into naphthalic acid. *Acetylene naphthalene*, or *acenaphthylene*,  $C_{10}H_6\left\langle\begin{matrix}CH\\ \|\\ CH\end{matrix}\right.$ is obtained as a fusible solid by passing the vapor of acenaphthene over gently heated lead oxide which removes $H_2$. It dissolves readily in alcohol, from which it crystallizes in yellow tablets. Its picric acid compound forms yellow needles. By chromic acid it is oxidized to naphthalic acid. *Dinaphthyl* $C_{10}H_7 \cdot C_{10}H_7$ is produced when vapor of naphthalene is passed through a red-hot tube:

$$2C_{10}H_8 = C_{20}H_{14} + H_2$$

It is also formed by the oxidizing action of $MnO_2$ with $H_2SO_4$ on naphthalene, and by decomposing bromo naphthalene with sodium. It forms scaly crystals that melt at 154°.

**114. Anthracene.**—Anthracene $C_{14}H_{10}$, which is a solid, is prepared in large quantity from those portions of coal tar that boil between 340° and 360°. The distillate is redistilled, and that which remains in the retort after the temperature has reached 350° is crystallized and sublimed. It is difficult to obtain it that way in a perfectly pure state. Anthracene has been prepared synthetically from benzene derivatives by the following different methods:

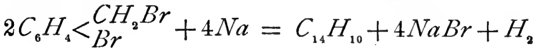
1. By passing toluene vapor through a red-hot tube containing pumice stone to expose a large heated surface:

$$2C_7H_8 = C_{14}H_{10} + 3H_2$$

2. By heating benzyl phenol with phosphorus pentoxide:

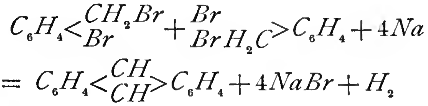
$$2C_6H_5\cdot CH_2\cdot C_6H_4(OH) = C_{14}H_{10} + C_6H_6 + C_6H_5(OH) + H_2O$$

3. By heating ortho-bromo-benzyl bromide with sodium.



$$2C_6H_4<^{CH_2Br}_{Br} + 4Na = C_{14}H_{10} + 4NaBr + H_2$$

or



$$C_6H_4<^{CH_2Br}_{Br} + {}^{Br}_{BrH_2C}>C_6H_4 + 4Na$$
$$= C_6H_4<^{CH}_{CH}>C_6H_4 + 4NaBr + H_2$$

The formation of anthracene from ortho-bromo-benzyl bromide furnishes strong proof in favor of the view that anthracene consists of two groups of $C_6H_4$, united by the group $C_2H_2$, thus: $C_6H_4\cdot C_2H_2\cdot C_6H_4$. The $C_6H_4$ groups constitute two benzene rings, while the central carbon atoms may be regarded as the residue of a third ring that has two carbon atoms in common with each of the other rings. This conception may be expressed as shown in Fig. 34.

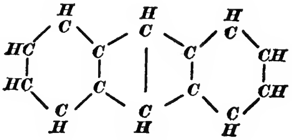


FIG. 34

The orientation of anthracene-substitution products is expressed similarly to that of naphthalene derivatives. Three mono-substitution products are possible; viz., the $\alpha$ and $\beta$ naphthalene derivatives, and the $\gamma$[*] or meso-derivatives, which contain a substituent in place of the $H$ of one of the central carbon atoms.

Anthracene crystallizes in colorless tablets exhibiting a fine blue fluorescence. It dissolves sparingly in alcohol and ether and easily in hot benzene. It melts at 213° and distils at about 360°. Its solution in benzene yields with picric acid the compound $C_{14}H_{10}2C_6H_3(NO_2)_3O$, which crystallizes in red needles.

A cold, saturated solution of anthracene in benzene exposed to sunshine deposits tabular crystals of an isomeric modification, $C_{14}H_{10}$, called *paranthracene*. It does not fuse until

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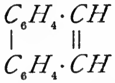
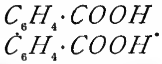
[*] $\gamma$ (gamma), the third letter in the Greek alphabet and corresponds with our letter *c*.

heated to 244°, when it is converted into anthracene. It is nearly insoluble in benzene, and is not attacked by either nitric acid or bromine.

**115. Phenanthrene** $C_{14}H_{10}$ is isomeric with anthracene, which it accompanies in coal tar. It is more soluble in petroleum spirit and in alcohol than in anthracene; the former solvent serves to separate it from the bulk of the crude anthracene, the separation being finished by fractional distillation. It is used for making black dyes. It melts at 100° and boils at 340°.

Phenanthrene is formed when stilbene or orthoditolyl is passed through a red-hot tube; since stilbene is known to contain ethylenic-linked carbon and ditolyl to be a diphenyl derivative, it is assumed that phenanthrene has the constitution  $\begin{array}{l} C_6H_4\cdot CH \\ |\qquad\;\; \| \\ C_6H_4\cdot CH \end{array}$ which is confirmed by the fact that its oxidation yields diphenic acid  $\begin{array}{l} C_6H_4\cdot COOH \\ C_6H_4\cdot COOH \end{array}$.

*Retene* $C_{18}H_{18}$ is a *methylisopropylphenanthrene* found in wood tar. *Pyrene* $C_{16}H_{10}$ and chrysene $C_{18}H_{12}$ are final products from coal-tar distillation.

### TERPENE HYDROCARBONS

**116. Oil of Turpentine.**—Oil of turpentine $C_{10}H_{16}$ is obtained by distilling the turpentine of commerce with water. Turpentine is a mixture of resin and essential oil, and flows from incisions made in the trunks of trees of the coniferous family *Pinus*, *Abies*, *Picea*, *Larix*. When this resinous substance is distilled with water, the oil passes over and the resin remains; the latter is then known as *colophony*, or *rosin*.

Oil of turpentine is a colorless, mobile liquid, having a peculiar odor and a boiling point of 158°. It is insoluble in water, but soluble in all proportions in alcohol as well as in ether. It burns with a smoky, luminous flame. Its property of dissolving resins and fats renders it useful in preparing paints and varnishes. It is also a good solvent for caoutchouc. According to their origin, the turpentines exhibit certain peculiarities, especially in their action upon polarized light. The following are the most important varieties:

1. *American oil of turpentine* is obtained from the turpentine of *Pinus palustris*. It rotates the plane of polarization to the right.
2. *English oil of turpentine* is derived from the *Pinus australis*, and is also dextrorotary.
3. *French oil of turpentine* is obtained from the *Pinus maritima;* it yields an oil that turns the plane of polarization to the left.
4. *German and Russian oil of turpentine* is distilled from the turpentine of *Pinus sylvestris*. It is lèvorotary.
5. *Venetian oil of turpentine* comes from the exudation of *Larix Europœa* and is also levorotary.

Oil of turpentine is the representative of a large class of hydrocarbons called *terpenes*, derived, like itself, from the vegetable kingdom. All the members of this group contain the same proportions of carbon and hydrogen, and the greater number have the same molecular formula as turpentine; i. e., $C_{10}H_{16}$. The terpenes resemble each other in their liability to suffer conversion into their isomerides, in their solidification by absorption of oxygen when exposed to air, and in their tendency to combine with hydrochloric acid to form crystalline compounds.

**117.** The essential oils of *bergamot*, *birch*, *camomile*, *caraway*, *hops*, *juniper*, *lemon*, *myrtle*, *nutmeg*, *orange*, *parsley*, *pepper*, *savin*, *thyme*, *tolu*, and *valerian* are all *terpenes* or mixtures of terpenes of the formula $C_{10}H_{16}$, and are generally accompanied in the natural oil by the product of its oxidation, bearing a relation to the hydrocarbon similar to that which colophony bears to turpentine. Essential *oil of poplar* is a *diterpene* $C_{20}H_{32}$. The oils of *calamus*, *cascarilla*, *cloves*, *cubebs*, *patchouli*, *cedar*, and *rosewood* are *sesquiterpenes*, having the formula $C_{15}H_{24}$.

The essential oils are generally extracted from the flowers, fruit, leaves, or seed, by distillation with water, the portion of the plant selected for extraction being suspended in the still by means of a bag, to prevent it from being scorched by contact with the hot sides of the still, and thus contaminating the distillate. The water which distils over always holds a little of the essential oil in solution, and it is in this way that the fragrant distilled waters of the druggists are obtained. When the essential oil is present in large proportion, it is collected as a separate layer on the surface of the water, from which it is easily decanted. The oil that is dissolved in the water may be separated from it by saturating the liquid with ordinary salt $NaCl$, when the oil rises to the surface, or by shaking it with ether, which dissolves the oil and separates from the water, the ethereal solution floating on the surface, and leaving the oil after the ether is distilled off.

In certain cases, like that of jasmine, for instance, where the extremely delicate perfume of the flower would naturally be injured by anything like a high temperature, the flowers are pressed between layers of suet, which thus acquires a powerful odor of the flower. Carbon disulphide is also sometimes employed as a solvent for extracting the essential oils.

**118.** All the terpenes may be considered as polymerides of the formula $C_5H_8$. A hydrocarbon having this formula and belonging to the diolefines (see Art. **85**) is called *isoprene*, and appears to have the constitution $CH_2:C(CH_3)\cdot CH:CH_2$; many terpenes yield isoprene when heated, and isoprene polymerises to terpenes.

Many of the terpenes yield 1:4 benzene dicarboxylic acid (terephthalic acid) when oxidized, thus indicating that they contain a benzene nucleus, which probably contains two alkyl groups in the 1:4 positions. Moreover, when dehydrogenized, they yield *cymene*, as, for instance, when oil of turpentine is heated with iodine; cymene is 1:4 methylisopropylbenzene (see Art. **103**), and therefore contains two $H$ atoms fewer than the true terpenes contain. The conclusion is drawn from these facts that the terpenes are isomeric modifications of cymene dihydride $H_2 : C_6H_4(CH_3) \cdot CH(CH_3)_2$; it is further supported by the discovery that a cymene dihydride, which has been synthetically prepared, has all the properties of a terpene. Much discussion concerning the occurrence of ethylenic linking in the benzene nucleus of the terpenes has taken place; some of the terpenes are capable of combining directly with two atoms of $Br$, indicating the presence of one ethylenic linking in the benzene nucleus, the remaining affinities of the carbon being probably disposed of as para linkings; while others combine directly with four atoms of $Br$ and thus appear to possess two ethylenic linkings. Most of them combine with $NOCl$ to form compounds $C_{10}H_{16} \cdot NOCl$.

The majority of the terpenes are optically active—that is, they rotate the plane of polarization of light; and most of them exist in two modifications, one of which is dextro-, while the other is levorotary. They boil at about the same temperature, so that their separation by fractional distillation is hardly possible.

**119.** The terpenes are divisible into three main groups; namely:

1. Those that are capable of combining with one molecule of halogen hydride only, provided they do not change in the meantime into isomerides: *pinene*, *camphene*, *fenchene*.
2. Those that can combine with two molecules of halogen hydride, but not with nitrous acid: *limonene*, *dipentene*, *sylvestrene*, *terpinolene*.
3. Those that combine with nitrous acid: *terpinene*, *phellandrene*.

*Pinene* $C_{10}H_{16}$ is the chief constituent of oil of turpentine, oil of juniper, of eucalyptus, of sage, etc. It exists in dextro- and levorotary form. *Dextropinene* or *australene* is the chief constituent of American and English oil of turpentine, while *levopinene* or terebenthene constitutes the French oil of turpentine. These two pinenes must be classed as *stereoisomerides*, since, as a whole, except in their optical properties, they are identical. An inactive pinene (that is, one that has no optical properties) has also been prepared. When pinene (that is, oil of turpentine) is heated at 250° in a sealed tube, it is converted into *dipentene* and a *diterpene*, known as *metaterabenthene* $C_{20}H_{32}$, which boils at 260°.

When $HCl$ is passed into oil of turpentine, well cooled, the pinene is converted into *pinene hydrochloride* $C_{10}H_{16}HCl$, which resembles camphor not only in its odor, but also in its crystalline form, and is known as *artificial camphor;* it melts at 125° and boils at 208°. When heated with a feeble alkali it loses $HCl$ and becomes *camphene*, which melts at 50° and occurs in dextro- as well as in levorotary modification.

When oil of turpentine containing water is left in contact with alcohol and nitric acid, it yields crystals of *terpin hydrate* $C_{10}H_{18}(OH)_2, H_2O$, which dissolve in boiling water, and melt at 116°, becoming anhydrous terpin $C_{10}H_{18}(OH)_2$, which sublimes. When boiled with $H_2SO_4$, this yields *terpineol* $C_{10}H_{17}\cdot OH$, which smells like the hyacinth, and boils at 215°.

By exposure to air, turpentine is slowly solidified, absorbing oxygen, and forming resinous bodies. Among these is a small quantity of *camphoric peroxide* $C_{10}H_{14}O_4$, which is decomposed by water, yielding *camphoric acid* and hydrogen peroxide, according to the equation:

$$C_{10}H_{14}O_4 + 2H_2O = C_{10}H_{16}O_4 + H_2O_2$$

This fact readily explains the frequent observations made that oil of turpentine that has been stored for some length of time frequently exhibits properties and reactions similar to those of hydrogen peroxide. By passing air and steam through oil of turpentine, a powerful oxidizing solution containing hydrogen peroxide is obtained, this solution is frequently employed for disinfecting purposes under the name of "sanitas."

*Fenchene* is obtained from oil of fennel; it is optically inactive, boils at 158°, and resists the action of nitric acid.

*Limonene* is present in many essential oils, especially in the oils of orange, lemon, and bergamot. Two active varieties—dextro- and levo-limonene—as well as inactive limonene have been obtained. It boils at 175° and its specific gravity at 20° is .846.

*Sylvestrene* occurs in Swedish and Russian oil of turpentine; it is dextrorotary, it has a boiling point of 175°, and is a comparatively stable terpene. It is characterized by giving a blue color with acetic anhydride and sulphuric acid.

*Terpinene* and *terpinolene* are optically inactive; the former and *phellandrene* form nitrites that are solids, melting at 155° and 102°, respectively.

**120. Caoutchouc,** also known as *india rubber*, may be classed among the terpene hydrocarbons, its chief constituent (a so called *polyrene*) having the empirical formula $C_5H_8$, but a molecular formula $(C_5H_8)_n$. It is the hardened, milky juice of such tropical trees as *euphorbiaceae*, *apocyneae*, and especially *Siphonia* (*ficus*) *elastica*, which grows in Brazil, etc. Incisions are made in these trees, and the milky juice thus obtained is spread upon a clay bottle-shaped mold, which is then suspended over a fire; a layer of caoutchouc is thus deposited, the thickness of which is increased by repeated applications of the milky liquid, the mold being eventually broken out of the caoutchouc bottle thus formed. The dark color of the ordinary commercial caoutchouc is believed to be due to the smoke from the fire over which it is dried, for pure caoutchouc ought to be and actually is white, and may thus be obtained by dissolving the commercial india rubber in chloroform, and precipitating it with alcohol; the precipitate forms a gummy, elastic mass when dried. Commercial caoutchouc contains, as a rule, some albumin, derived from the original milky liquid, this being really a solution of albumin holding in suspension about 30 per cent. of caoutchouc, which, when the juice is mixed with water and allowed to stand, rises to the surface like cream, becoming coherent and elastic when exposed to air.

The chief uses of caoutchouc depend rather upon its physical than its chemical properties, its lightness (having only a specific gravity of .93), its impermeability to water, and its elasticity adapting it for a multitude of purposes.

For the manufacture of *waterproof cloth* caoutchouc is dissolved in strong turpentine and the solution spread, in a viscid state, over the surfaces of two pieces of cloth of the same size, which are then laid face to face and passed between rollers, the pressure of which causes perfect adhesion between the surfaces.

Caoutchouc is slowly dissolved by carbon disulphide, benzene, chloroform, petroleum, turpentine, etc., but neither the alkalies nor diluted acid have any action upon it. When very gently heated the pliancy and extensibility of the caoutchouc greatly increases; it fuses at 121° to an oily liquid, which does not become solid but only viscid on cooling. Heated in a retort, caoutchouc is decomposed into several hydrocarbons, one of which is *isoprene* $C_5H_8$, having a boiling point of 37°, and another, *caoutchene* $C_{10}H_{16}$, which boils at 171°. Caoutchene forms a crystalline compound with water, $C_{10}H_{16}, H_2O$, which may also be obtained by boiling terpin with very dilute sulphuric acid, and distilling with water.

Caoutchouc combines with variable proportions of sulphur. The mixtures thus obtained are called *vulcanized rubber;* they are more permanently elastic than pure caoutchouc.

*Vulcanite*, or *ebonite*, is caoutchouc mixed with half its weight of sulphur, and hardened by pressure and heating. It is very hard, takes a high polish, and is used for making surgical instruments, combs, knife handles, etc. It is also especially distinguished by the large quantity of electricity which it evolves when rubbed; hence, it makes a very desirable material for the plates of electrical machines.

**121. Gutta percha** (empirical formula $C_5H_8$), like caoutchouc, is originally a milky exudation from incisions made in the wood of the Isonandra tree (*Isonandra percha*). This juice readily solidifies, when exposed to air, to a brown mass, which differs from ordinary caoutchouc by being not alone heavier, but also by being tough and inelastic when cooled. It becomes, however, quite soft and plastic when heated to about 100°. Being impervious to water, it is used as a waterproof material and for water pipes. It is a nonconductor of electricity, and is consequently used for insulating purposes.

Gutta percha is dissolved by those substances which dissolve caoutchouc and is not affected by either acids or alkalies. Gutta-percha bottles are employed for keeping hydrofluoric acid. Gutta percha readily melts and at an increased temperature decomposes, yielding products similar to those from caoutchouc.

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## CAMPHORS

**122.** Closely allied to the essential oils are the different varieties of camphor, which appear to be formed by the oxidation of hydrocarbons contained in the essential oils.

**123.** *Common*, or *Japan*, *camphor* $C_{10}H_{16}O$ is the most important variety, and is found in the camphor tree (*Laurus camphora*) growing in Japan and China, and especially abundant on the island of Formosa. When the wood is chipped and distilled with water, the camphor volatilizes and condenses in rice straw, with which the heads of the stills in which the operation is conducted are filled. The product thus obtained in the form of small crystals is refined by sublimation in glass vessels heated on a sand bath.

Camphor passes into vapor easily at ordinary temperatures, and is deposited in brilliant, octahedral crystals upon the sides of the bottle containing it. It fuses at 175° and boils at about 204°. It is rather inflammable, burning with a bright though smoky flame. It is lighter than water, its specific gravity being .985; it is only very sparingly soluble in water, but quite readily in ether as well as in alcohol.

When distilled with $P_2O_5$ common camphor loses a molecule of water and yields *cymene* (see Art. **103**):

$$C_{10}H_{16}O = C_{10}H_{14} + H_2O$$

When camphor is boiled with nitric acid it is oxidized and converted into *camphoric acid:*

$$C_{10}H_{16}O + 3O = C_{10}H_{16}O_4$$

**124.** *Borneo camphor*, or *borneol* $C_{10}H_{18}O$, is extracted from the *Dryobalanops aromatica*, a tree that grows in the Sunda Islands. It may be obtained artificially by the action of an alcoholic solution of $KOH$ on common camphor. It occurs in small, colorless, and transparent prismatic crystals. Its odor recalls at the same time that of camphor and pepper. Its taste is burning. It melts at 206° and boils at 212°. It turns the plane of polarization to the right, and is, like common camphor, nearly insoluble in water, but readily soluble in ether or alcohol. When treated with cold, fuming nitric acid, it loses two atoms of $H$ and is converted into common camphor.

**125.** *Cineol* $C_{10}H_{18}O$ is isomeric with borneol. It is the chief constituent of the oils of cajuput and wormseed. It is a colorless liquid which boils at 176°. It is one of the products of the action of sulphuric acid upon oil of turpentine.

**126.** *Menthol*, or *mint camphor* $C_{10}H_{20}O$, is the solid part of the essential oil of peppermint (*mentha piperita*), in which it exists mixed with liquid terpenes. It is deposited in crystals when oil of mint is cooled. It forms colorless crystals which fuse at 42° and boil at 213°. Dehydrating agents, such as phosphoric anhydride and zinc chloride, convert it into *menthene* $C_{10}H_{18}$.

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## BALSAMS AND RESINS

**127. Balsams.**—The vegetable exudations known as *balsams* are mixtures of essential oils with resins and acids, probably produced by the oxidation of the oils.

*Balsam of Peru* contains an oily substance termed *cinnaméin* $C_{27}H_{26}O_4$; a crystalline body *styracin* $C_9H_8O$; a crystalline volatile acid *cinnamic acid* $C_9H_8O_2$; and a peculiar resin.

*Balsam of tolu* also contains cinnamic acid and styracin, together with certain resins, which appear to have been formed by the oxidation of styracin.

*Stora*, also a balsamic exudation, contains the same substances, accompanied by *cinnamene*.

**128. Resins.**—*Colophony* is the best known member of this class of resins, which are generally distinguished by their resinous appearance, fusibility, inflammability (burning with a smoky flame), insolubility in water, and solubility in alcohol.

As to their chemical composition, they are all rich in carbon as well as in hydrogen, containing generally a small proportion of oxygen, and appear to have been formed, like colophony, by oxidation of a hydrocarbon analogous to turpentine. Most of their resins also resemble colophony in their acid characters, their alcoholic solutions reddening blue litmus paper, and the resins themselves being soluble in the alkalies. This is the case with *standarach* and *guaiacum resin*, the former of which contains three, and the latter two, resinous acids.

**129. Copal** appears to contain several resins, some of which appear to be neutral while others are acid, and is distinguished by its difficult solubility in alcohol, in which it can be dissolved only after a long exposure to the vapor of the solvent; but if it is exposed to the air for some time at a moderately high temperature, it absorbs oxygen and becomes much more easily soluble. Copal is readily dissolved by acetone. *Animi* and *elemi resins* are somewhat similar in properties to copal. All these resins are used in the manufacture of varnishes.

*Guaiacum resin* is distinguished by its tendency to become blue under the influence of certain oxidizing agents, such as chlorine and ozone, for instance.

*Amber*, a fossil resinous substance, more nearly resembles this class of bodies than any other, and contains several resinous bodies. It is distinguished by its insolubility, for alcohol dissolves only about one-eighth and ether about one-tenth of it. After fusion, however, it becomes soluble in alcohol, and is used in this state for the preparation of varnishes.

# ORGANIC CHEMISTRY

(PART 3)

## DERIVATIVES OF HYDROCARBONS

### ALCOHOLS

**1.** All carbon compounds may be regarded as derivatives of the hydrocarbons, containing one or more atoms or compound radicals in place of hydrogen, and in every one of these derivative compounds there will be found a characteristic hydrocarbon radical, which will be either monovalent, divalent, or trivalent, according as it represents the removal of one, or two, or three hydrogen atoms from a saturated hydrocarbon. Of the typical hydrocarbon radicals, $(CH_3)'$, $(C_2H_4)''$, and $(C_3H_5)'''$ may here be mentioned.

**2.** The term *alcohol*, originally limited to the one substance, namely, *spirit of wine*, is now applied to a large number of organic compounds, many of which, in their external characters, exhibit very little resemblance to common alcohol. They all have, however, an analogous constitution, having the composition of hydrocarbons in which one or more of the hydrogen atoms are replaced by a corresponding number of hydroxyl groups. Alcohols may be compared with the metallic hydroxides, not only because they contain, like these, one or more hydroxyl groups, but also because they form salts with acids, eliminating water. This similarity may be readily observed by comparing the two typical equations here shown:

(1) $C_2H_5\cdot OH + H_2SO_4 = C_2H_5\cdot HSO_4 + H_2O$

(2) $NaOH + H_2SO_4 = NaHSO_4 + H_2O$

As a divalent or a trivalent metal will form a hydroxide containing two or three hydroxyl groups, respectively, so a divalent or trivalent hydrocarbon radical will form an alcohol containing two or three hydroxyl groups; as examples, $C_2H_4(OH)_2$ and $C_3H_5(OH)_3$ may be cited.

According to the number of hydroxyl groups present in an alcohol, these compounds are known as *monohydric*, *dihydric*, *trihydric*, etc. *alcohols;* or, according to some authors, as *monatomic*, *diatomic*, *triatomic*, etc. *alcohols*.

Alcohols, as a class, have a slightly basic tendency; they readily undergo oxidation, which results in the removal of hydrogen, either with or without the substitution of an equivalent quantity of oxygen. The products of such oxidation are either *aldehydes* (or *ketones*) or *acids*, as the case may be.

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### MONOHYDRIC ALCOHOLS OF THE PARAFFIN SERIES

**3.** The alcohols of this series are the best known and most important of all this class of bodies. They are produced by the replacement of 1 hydrogen atom of a paraffin hydrocarbon by the group $OH$, and there is consequently a homologous series of alcohols, which corresponds with the homologous series of the hydrocarbons. For instance, $CH_4$ yields $CH_3\cdot OH$, $C_2H_6$ yields $C_2H_5\cdot OH$, $C_3H_8$ yields $C_3H_7\cdot OH$, and so on. The composition of these alcohols may be represented by the general formula, $C_nH_{2n+1}\cdot OH$.

The principal members of this class of alcohols, their formulas, boiling points, and common sources are enumerated in Table I.

The usual gradation of properties attending the gradation in composition among the members of homologous series of compounds, is strikingly illustrated in the series of the monohydric alcohols. The first seven members of this series

## TABLE I

### MONOHYDRIC ALCOHOLS OF THE PARAFFIN SERIES

| Name | Formula | Boiling Point | Common Source |
|---|---|---|---|
| Methyl alcohol | $CH_3 \cdot OH$ | 66° | Distillation of wood. |
| Ethyl alcohol | $C_2H_5 \cdot OH$ | 78° | Fermentation of sugar. |
| Propyl alcohol | $C_3H_7 \cdot OH$ | 97° | Fermentation of grapes. |
| Butyl alcohol | $C_4H_9 \cdot OH$ | 117° | Fermentation of beet. |
| Pentyl, or amyl, alcohol | $C_5H_{11} \cdot OH$ | 137° | Fermentation of potatoes. |
| Hexyl, or caproyl, alcohol | $C_6H_{13} \cdot OH$ | 157° | Fermentation of grapes. |
| Heptyl, or œnanthyl, alcohol | $C_7H_{15} \cdot OH$ | 175° | Distillation of castor oil with potash. |
| Octyl, or capryl, alcohol | $C_8H_{17} \cdot OH$ | 191° | Essential oil of hogweed. |
| Nonyl alcohol | $C_9H_{19} \cdot OH$ | 213° | Nonane of petroleum. |
| Cetyl alcohol | $C_{16}H_{33} \cdot OH$ | | Spermaceti. |
| Ceryl alcohol | $C_{27}H_{55} \cdot OH$ | | Chinese wax. |
| Myricyl, or melissyl, alcohol | $C_{30}H_{61} \cdot OH$ | | Beeswax. |

are liquids at ordinary temperatures, they possess characteristic and strong odors, and can be easily distilled without decomposition. Methyl, as well as ethyl, alcohol mixes freely and in all proportions with water; propyl alcohol is only sparingly soluble in water, and, beginning with this member, the solubility of these alcohols decreases rapidly, until we come to hexyl alcohol, which is entirely insoluble in water, and to octyl alcohol, which is not alone insoluble, but also possesses an oily character, leaving, for instance, a greasy spot on paper. Cetyl alcohol, ceryl alcohol, and myricyl alcohol are solid, wax-like bodies. Those members of the series of alcohols that may undergo distillation without change, show a fairly regular increase in the boiling point for each addition of $CH_2$ in the formula. The student will notice, by referring to Table I, that, excluding the difference between methyl and ethyl alcohol, the average difference in the boiling points is 19.5° for each $CH_2$ added. The compound commonly known as alcohol will be considered first.

**4. Ethyl Alcohol.**—Ethyl alcohol $C_2H_5 \cdot OH$, popularly known as *spirits of wine* or plainly *alcohol*, has been known for a very long time, its use dating back as far as the sixteenth century. Lavoisier determined it qualitatively, and we are indebted to Saussure for the first quantitative determination of it. This alcohol, though only occurring in small quantities, is widely distributed in nature. It is found in coal tar, bone oil, wood spirit, bread, etc., and also occurs in diabetic urine.

Ethyl alcohol may be prepared synthetically (1) by combining $C$ and $H$ to form acetylene $C_2H_2$, which, by means of nascent hydrogen, may be converted into ethene $C_2H_4$; ethene is then treated with concentrated $H_2SO_4$ whereby ethyl hydrogen sulphate $C_2H_5 \cdot HSO_4$ is obtained, from which $C_2H_5 \cdot OH$ may be produced by distillation. This method was discovered by Faraday, and corroborated in 1855 by Berthelot. (2) By heating ethylene gas with hydriodic acid and decomposing the ethyl iodide so formed with potassium hydrate:

$$\begin{aligned} &(1) & C_2H_4 + HI &= C_2H_5I \\ &(2) & C_2H_5I + KOH &= C_2H_5 \cdot OH + KI \end{aligned}$$

The fact that ethyl iodide $CH_3 \cdot CH_2I$ will give alcohol in this reaction justifies the formula $CH_3 \cdot CH_2 \cdot OH$ for ethyl alcohol. (3) By bringing aldehyde in contact with sodium amalgam in presence of water. The nascent hydrogen formed in this case fixes upon the aldehyde, converting it into alcohol, thus:

$$\underset{\text{aldehyde}}{C_2H_4O} + H_2 = \underset{\text{alcohol}}{C_2H_6O}$$

**5.** The most important method by which alcohol may be prepared—and, in fact, the one on which we are dependent—is by the fermentation of sugar. Whenever a plant juice containing sugar is left exposed to air, it slowly undergoes a certain change and loses its natural sweet taste. This change may be considered to consist in a breaking up of the sugar into carbon dioxide and alcohol, and may be expressed by the equation:

$$\underset{\text{sugar}}{C_6H_{12}O_6} = \underset{\text{alcohol}}{2C_2H_6O} + \underset{\text{carbon dioxide}}{2CO_2}$$

This process is known as *alcoholic fermentation.* Careful investigations have revealed the fact that such fermentation is caused by the presence of micro-organisms of either animal or vegetable origin. These micro-organisms, known as *ferments*, are of different kinds, and cause different kinds of fermentation with different products. Among the kinds of fermentation, the following may be specially mentioned:

1. *Alcoholic*, or *vinous*, *fermentation* is caused by a vegetable ferment present in ordinary yeast. The ferment consists of small round cells arranged in chains. The products of its action are, as previously mentioned, alcohol and carbon dioxide.

2. *Lactic-acid fermentation* is due to a vegetable ferment present in milk. It has the property of converting the sugar into lactic acid.

3. *Acetic-acid fermentation* is due to a vegetable ferment converting alcohol into acetic acid.

The germs of the various ferments exist in the air; and, whenever they find favorable conditions, they develop and produce their characteristic effects. They will not develop in a solution of pure sugar. The variety of sugar that is fermentable, and the one from which alcohol is obtained, is not ordinary cane sugar, but a variety known as *grape sugar* or *glucose.* In order that the ferment may grow, there must be present in the solution, besides the sugar, substances that contain nitrogen. These, as well as the sugar, are contained in the juices pressed out from various fruits, and, consequently, those juices readily undergo fermentation.

In the manufacture of alcohol, a solution containing either starch or sugar is first prepared from the residue of wine presses or from some kind of grain or potatoes. In case the solution contains grape sugar, this undergoes fermentation directly when the ferment is added. If the substance in solution is cane sugar, this is first changed by the ferment into grape sugar, and the fermentation then takes place as in the first case.

To obtain alcohol from fermented liquids, they must be distilled. The apparatus now used for this operation has reached such a degree of excellence that alcohol of 95 per cent. may be obtained immediately by one distillation.

Absolutely pure alcohol is obtained by rectifying the alcohol of commerce over hygroscopic substances, such as anhydrous potassium carbonate, quicklime, or barium oxide. The last portions of water are removed, and absolute alcohol is obtained by redistilling the rectified alcohol with barium oxide; or some sodium may be dissolved in the alcohol, which is then rectified on the water bath.

On a large scale, alcohol is usually made from the starch contained in potatoes and such grains as rice, rye, etc. The starch $C_6H_{10}O_5$ is first converted into either glucose $C_6H_{12}O_6$, by heating it with very dilute sulphuric acid (afterwards neutralized with chalk), or into maltose $C_{12}H_{22}O_{11}$, by mixing it with an infusion of malt; the glucose or maltose is fermented by yeast. The wash, as it is termed, is then distilled, the stills being constructed with great ingenuity to effect the concentration of the alcohol at the least possible expense.

Even wooden fiber, paper, linen, etc., which have the same empirical formula, may be converted into glucose by the action of $H_2SO_4$, and may thus be made a source of alcohol.

**6.** Alcohol is a colorless mobile liquid, with a burning taste and a characteristic and pleasant odor, though it is claimed that perfectly anhydrous alcohol really does not exhibit any traces of this odor at all. It remains a liquid at very low temperatures, solidifying only at $-130.5°$. It boils at 78.3°. It takes fire when a flame is brought near its surface, and burns with a pale smokeless flame. Alcohol evaporates easily when exposed to the air, without combining with oxygen, and it readily absorbs water or moisture from the air. It dissolves many gases, liquids, and solids. *Tinctures* are solutions of various medicinal substances in alcohol.

Among the simpler substances that are soluble in alcohol may be mentioned iodine. Potassium and sodium hydrates dissolve in it readily, and the same is true of most of the mineral acids. Many of the chlorides are soluble in alcohol; such as those of calcium, strontium, zinc, and cadmium, besides ferric, cupric, mercuric, and auric chlorides. It dissolves the natural alkaloids, the essential oils, resins, etc.

Alcohol may be mixed with water in all proportions, evolving a little heat and giving a mixture rather smaller in bulk than the sum of its constituents. This may be shown by filling a vessel, shaped as shown in Fig. 1, with water up to the neck joining the two globes, carefully filling the upper globe to the brim with alcohol, inserting the stopper, and inverting the vessel. The contraction of the mixture will then leave a vacuum in the tube and the dissolved air from the water will discharge itself into this in numerous large bubbles. The greatest contraction occurs when the volumes of alcohol and water are nearly equal; for instance, at 0°, 53.9 measures of alcohol added to 49.8 measures of water, gives not 103.7, but 100, measures of the mixture. The attraction of alcohol for water affords one reason for its power of preserving animal and vegetable substances from putrefaction by removing the water necessary for that change.

FIG. 1

The following is an accurate method for diluting any given alcohol solution of definite percentage: Designate the volume percentage of the stronger alcohol by $V$ and that of the weaker alcohol by $v$. Mix $v$ volumes of the stronger alcohol with water to make $V$ volumes of the product. Allow the mixture to stand till full contraction has taken place, and till it has reached the temperature of the original alcohol and water, and make up any deficiency in the $V$ volumes with water.

EXAMPLE.—It is desired to dilute a distillate containing 50 per cent. of alcohol by volume until it contains 30 per cent. To 30 volumes of the 50-per-cent. alcohol add enough water to make 50 volumes, or place 150 c. c. of the distillate in a 250 c. c. flask, fill to the mark with water, mix, cool, and fill to the mark again.

By oxidation. alcohol is converted first into aldehyde $CH_3 \cdot CHO$, and then into acetic acid $CH_3 \cdot COOH$.

*Ethoxides* or *ethylates* are compounds formed by the replacement of hydrogen in alcohols by metals; they correspond with the hydroxides, $C_2H_5$ standing in place of $H$; for instance, *sodium ethoxide* $C_2H_5\cdot ONa$, *aluminum ethoxide* $(C_2H_5O)_6Al_2$. Sodium ethoxide is used in surgery as a caustic. Water decomposes the ethoxides, yielding alcohol and hydroxides, as is seen from the following equation:

$$C_2H_5ONa + HOH = C_2H_5OH + NaOH$$

*Barium ethoxide* $(C_2H_5O)_2Ba$ is obtained by the action of anhydrous baryta on absolute alcohol. A trace of water precipitates barium hydroxide from the solution. On heating the alcoholic solution, the barium ethoxide precipitates, being less soluble in hot alcohol.

*Aluminum ethoxide* $(C_2H_5O)_6Al_2$ is produced by heating aluminum in alcohol with a little iodine. It is very probable that $Al_2I_6$ is first produced; this, however, is quickly decomposed by the alcohol, forming aluminum ethoxide and hydrogen iodide. The latter, with the excess of $Al$, evolves $H$ and forms more $Al_2I_0$, which, in its turn, decomposes a fresh portion of alcohol, and thus a small quantity of iodine carries on a continuous action.

*Thallium ethoxide* $C_2H_5OTl$ is a liquid remarkable for its high specific gravity (3.68), and its great refractive and dispersive action on light.

**7.** The simplest chemical test for alcohol is to add to the suspected liquid hydrochloric acid and enough potassium bichromate to give it an orange color, to divide it between two test tubes for comparison, and to heat one of them till the liquid boils. If alcohol should be present, the liquid will change its color to green and evolve the peculiar fragrant smell of aldehyde. The reaction that takes place may be expressed by the following equation:

$$K_2Cr_2O_7 + 8HCl + 3C_2H_6O$$
$$= 2KCl + Cr_2Cl_6 + 3C_2H_4O + 7H_2O$$

A test that is frequently used, and is even more accurate, consists in warming the liquid to be tested, adding first a little solid iodine, and then, very carefully, weak potash until the liquid is just bleached. On stirring with a glass rod, a pale-yellow crystalline precipitate of iodoform is deposited, and its odor, resembling that of saffron, is perceived:

$$C_2H_6O + 6KOH + I_8 = \underset{\text{iodoform}}{CHI_3} + \underset{\substack{\text{potassium}\\\text{formate}}}{KCO_2H} + 5KI + 5H_2O$$

Alcohol may also be recognized by the production of acetic acid when its vapor is mixed with air and exposed to the action of platinum black, which acts by favoring oxidation:

$$C_2H_6O + O_2 = \underset{\text{acetic acid}}{C_2H_4O_2} + H_2O$$

**8. Uses of Alcohol.**—Alcohol is used as a combustible in spirit lamps. In the arts, it is employed in the manufacture of ether, chloroform, perfumeries, extracts, and many other products.

As a solvent, it is largely used in the laboratory and the pharmacy. In Germany, England, and France, alcohol employed for certain industrial uses is exempted from the greater part of the internal revenue tax, when it has previously been mixed with about one-tenth of wood spirit and a small percentage of mineral oils and resin. Such a mixture is of course unfit for the manufacture of liquors, without losing its utility as a solvent.

Alcohol exists in fermented liquors, such as wine, cider, and beer. It is contained in much larger quantities in whiskies, brandies, and other spirits. These are the products of the distillation of various alcoholic liquids. They are more or less rich in alcohol. Brandy is prepared by the distillation of wine, cider, or from the products of fermentation of cherry juice (cherry brandy), sugar cane (rum), beetroot molasses (beet brandy). Whisky is distilled from fermented starchy material, such as corn, rye, potatoes, etc., the starch being first saccharified.

**9.** The usual method of determining the strength of alcohol is to take its specific gravity by measuring a few cubic centimeters of it into a light stoppered bottle, the weight of which has been ascertained. The weight of 1 cubic centimeter of the alcohol in grams will be its specific gravity very nearly. The alcohol of the United States pharmacopœia contains 91 per cent. alcohol by weight and 94 per cent. by volume. Dilute alcohol of the pharmacopœia contains 50 per cent. alcohol by volume. *Proof spirit* formerly meant the weakest alcohol that would answer the old rough test of firing gunpowder that had been moistened with it and kindled. At present the proof spirit of the United States custom house is a spirit that contains 50 per cent. alcohol by volume. In England, proof spirit is a spirit that contains 57.1 per cent. alcohol by volume.

**10. Methyl Alcohol.**—Methyl alcohol $CH_3 \cdot OH$ is also known as *wood spirits.* It was discovered in 1812 by Taylor. It is found in nature in combination with oil of wintergreen. This alcohol is formed, together with many other substances, in the dry distillation of wood and is therefore contained in crude pyroligneous, or acetic, acid $CH_3CO_2H$. Wood is distilled in large quantities for various purposes; chiefly, however, for making charcoal, and in some charcoal factories the distillate is collected and utilized. Wood is distilled also for the purpose of making wood vinegar or chemically pure acetic acid.

It is not an easy matter to get pure methyl alcohol from wood spirits, as it cannot be purified by fractional distillation, on account of containing a considerable quantity of acetone $CH_3 \cdot CO \cdot CH_3$, the boiling point of which lies very closely to methyl alcohol. The best way to obtain a fairly pure methyl alcohol is by treating the impure alcohol with calcium chloride, with which it forms a crystalline compound $CaCl_2(CH_4O)_4$. The crystals are drained, dried, and distilled with water, yielding dilute methyl alcohol, which may be rectified by repeated distillation and finally dehydrated over quicklime.

Much methyl alcohol is now obtained by distilling the refuse of the beet-sugar manufactory, and this refuse has become important as the source of many methyl compounds employed in making dyes.

Methyl alcohol resembles ethyl alcohol, but possesses a somewhat different odor. It has a specific gravity of .8142 and a boiling point of 66.5°. It is very inflammable and burns with an almost invisible flame. It is miscible with water, alcohol, and ether in all proportions, and acts as an intoxicant like ethyl alcohol. In its concentrated form, it is poisonous. It is an excellent solvent for fats, oils, and resins, and is extensively used for this purpose.

Methyl alcohol is distinguished from ethyl alcohol by the iodoform test; but in the presence of air and platinum black, yields formic aldehyde $HCHO$ and formic acid $HCO_2H$. The formic acid may be distinguished from acetic acid by its property of reducing silver ammonio-nitrate to the metallic state when gently heated with it.

**11. Isomerism Among Monohydric Alcohols.** Methyl and ethyl alcohol being mono-substitution derivatives of methane and ethane, respectively, no position isomerides of these compounds are known. It has already been noticed that two mono-substitution derivatives of propane are possible; namely, those that have the substituent attached to the end of the three-carbon chain, and those in which the substituent is attached to the center-carbon atom; the former kind is known as the *normal propyl derivative*, the latter as the *isopropyl derivative*. Thus, the general formula for a normal propyl derivative is $CH_3 \cdot CH_2 \cdot CH_2X'$, while that for an isopropyl derivative is $CH_3 \cdot CHX' \cdot CH_3$, or $(CH_3)_2 : CHX'$. Hence, there is a *normal propyl alcohol* and an *isopropyl alcohol*.

Since butane may be regarded as methyl propane (a mono-substitution product of propane), it may be expected to exist in two modifications. The first of these, normal butane, can yield two mono-substitution derivatives; namely,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2X'$$

and $$CH_3 \cdot CH_2 \cdot CHX' \cdot CH_3$$

while the second, secondary butane, can also yield two mono-substitution derivatives; namely,

$$(CH_3)_2 : CH \cdot CH_2X'$$

and $$(CH_3)_2 : CX' \cdot CH_3$$

Hence, there should be four butyl alcohols.

Pentane is methyl butane, but it exists in only three—instead of four—modifications, because the methyl butanes corresponding with the second and third formulas given above would have the same structure, By writing the formulas for a mono-substitution product of pentane, it will be found that eight different compounds are possible, and in many cases eight are known.

All these isomeric alcohols are divided into three classes, as follows:

1. Those in which the $OH$ group is attached to a carbon atom, which is itself attached to only one other carbon atom. These alcohols are known as *primary alcohols*, and contain the group $\cdot C \begin{smallmatrix} \lessdot H_2 \\ \lessdot OH \end{smallmatrix}$.

2. Those in which the $OH$ group is attached to a carbon atom, which is itself attached to two other carbon atoms. The members of this class are known as *secondary alcohols*, and contain the group $: C < \begin{smallmatrix} H \\ OH \end{smallmatrix}$.

3. Those in which the $OH$ group is attached to a carbon atom, which by itself is attached to three other carbon atoms. The members of this class are known as *tertiary alcohols*, and contain the group $\vdots C \cdot OH$.

A number of examples of these three alcohols are given below:

| | | |
|---|---|---|
| Methyl alcohol | $H \cdot CH_2OH$ | Primary. |
| Ethyl alcohol | $CH_3 \cdot CH_2OH$ | Primary. |
| Normal propyl alcohol | $CH_3 \cdot CH_2 \cdot CH_2OH$ | Primary. |
| Isopropyl alcohol | $(CH_3)_2 : CHOH$ | Secondary. |
| Normal butyl alcohol | $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2OH$ | Primary. |
| Primary isobutyl alcohol | $(CH_3)_2 : CH \cdot CH_2OH$ | Primary. |
| Secondary butyl alcohol | $\begin{smallmatrix} CH_3 \cdot CH_2 \\ CH_3 \end{smallmatrix} > CHOH$ | Secondary. |
| Tertiary butyl alcohol | $(CH_3)_3 \vdots COH$ | Tertiary. |

Of the eight pentyl alcohols four are primary, three are secondary, and one is tertiary.

**12.** Greater facility in naming these numerous compounds is obtained by making methyl alcohol, also called *carbinol*, the starting point, and assuming the alcohols to be derived from it by the substitution of alcohol radicals for the hydrogen in the methyl group. Then, the primary alcohols will be mono-substitution derivatives of carbinol, as shown in the following formulas:

| | |
|---|---|
| Carbinol | $CH_3\cdot OH$. |
| Primary propyl alcohol, or ethyl carbinol | $CH_2(C_2H_5)\cdot OH$. |
| Primary butyl alcohol, or propyl carbinol | $CH_2(C_3H_7)\cdot OH$. |

The secondary alcohols may be regarded as di-substitution products of carbinol; secondary propyl alcohol, or *dimethyl carbinol* $CH(CH_3)_2\cdot OH$, is evidently identical with isopropyl alcohol. Secondary butyl alcohol is *ethyl methyl carbinol* $CH(C_2H_5)(CH_3)\cdot OH$. Secondary amyl alcohol is *methyl propyl carbinol* $CH(CH_3)(C_3H_7)\cdot OH$. Another secondary amyl alcohol is *diethyl carbinol* $CH(C_2H_5)_2\cdot OH$. The tertiary alcohols would be tri-substitution products of carbinol. Tertiary butyl alcohol is *trimethyl carbinol* $C(CH_3)_3\cdot OH$. Tertiary pentyl alcohol is *ethyl dimethyl carbinol* $C(C_2H_5)(CH_3)_2\cdot OH$.

**13.** The three classes of alcohol are distinguished by their behavior under the action of oxidizing agents, which also serves to settle their constitution.

A primary alcohol, when oxidized, yields first an aldehyde, and ultimately an acid, containing the same number of carbon atoms as the alcohol did; thus, for instance, ethyl alcohol $CH_3\cdot C\begin{smallmatrix}\lessgtr H_2\\ < OH\end{smallmatrix}$ yields ethyl aldehyde $CH_3\cdot C\begin{smallmatrix}\lessgtr O\\ < H\end{smallmatrix}$ and acetic acid $CH_3\cdot C\begin{smallmatrix}\lessgtr O\\ < OH\end{smallmatrix}$.

A secondary alcohol, under the same condition, yields a ketone containing the same number of carbon atoms as the alcohol. For instance, secondary propyl alcohol $(CH_3)_2 : C<\begin{smallmatrix}OH\\ H\end{smallmatrix}$ yields dimethyl ketone $(CH_3)_2 : C : O$.

A tertiary alcohol is either broken up into two or more acids containing less carbon, or it may give rise to a ketone containing one atom less carbon than itself, the atom of carbon being oxidized to either carbonic or formic acid. For instance, tertiary butyl alcohol $C(CH_3)_3 \cdot OH$ yields acetone $(CH_3)_2 : CO$ and formic acid $H \cdot COOH$.

**14.** Another method for distinguishing between a primary, secondary, and tertiary alcohol consists in converting the alcohol into the corresponding iodide by distilling with iodine and phosphorus. The iodide is distilled with a mixture of silver nitrite and fine sand, when the corresponding nitroparaffin is obtained; thus, ethyl alcohol is converted into ethyl iodide, which, in its turn, yields nitroethane $C_2H_5NO_2$, according to the equation:

$$\underset{\text{ethyl iodide}}{CH_3 \cdot CH_2 \cdot I} + AgNO_2 = \underset{\text{nitroethane}}{CH_3CH_2 \cdot NO_2} + AgI$$

The distillate is mixed with potassium nitrite and weak potash, and dilute sulphuric acid is gradually added; if the alcohol is primary, a red solution of the corresponding *potassium nitrolate* will be obtained, the nitroparaffin having been converted into the corresponding *nitrolic acid* by the nitrous acid; thus, nitroethane yields nitrolic acid:

$$CH_3CH_2 \cdot NO_2 + HNO_2 = CH_3 \cdot C(NO_2) : NOH + H_2O$$

Nitrolic acids are colorless, but their salts are distinguished by their red color. They are very unstable, being decomposed into nitrous oxide and a fatty acid; thus, nitrolic acid yields nitrous oxide and acetic acid. If the alcohol is secondary, a blue solution of a *pseudonitrol* will be obtained; thus, secondary amyl alcohol $CH(CH_3)(C_3H_7) \cdot OH$ would yield the secondary nitroparaffin $CH(CH_3)(C_3H_7) \cdot NO_2$, which would be converted by $HNO_2$ into pseudonitrol $C(NO)(CH_3)(C_3H_7) \cdot NO_2$, giving a blue solution. If the alcohol is tertiary, no color is produced, the tertiary nitroparaffin not being attacked by nitrous acid.

**15. General Method for Preparing the Alcohols.** The easiest and most convenient method for preparing the alcohols consists in treating the corresponding halogen substitution products of the hydrocarbons with moist silver oxide. If, for instance, normal butyl bromide is treated with moist silver oxide, normal butyl alcohol is obtained, as is seen from the subjoined equation:

$$2CH_3\cdot CH_2\cdot CH_2\cdot CH_2Br + Ag_2O + H_2O$$
$$= 2CH_3\cdot CH_2\cdot CH_2\cdot CH_2OH + 2AgBr$$

The secondary and the tertiary butyl bromides will, under similar treatment, yield the secondary and the tertiary alcohol, respectively.

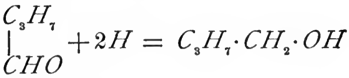
As the alcohols form the basis for the production of a large number of compounds on the small scale, their general reactions will be best understood when these other compounds are considered.

**16. Normal Propyl Alcohol.**—Normal propyl alcohol $C_3H_7\cdot OH$ or $C_2H_5\cdot CH_2\cdot OH$ was discovered by Chancel in 1857. It is found in the latter portions of the distillate obtained in rectifying crude spirits of wine. It is a colorless liquid with a pleasant odor. It boils at 97° and has a specific gravity of .82. It is miscible with water in all proportions, from which it can be again separated on adding calcium chloride. By oxidation, it is converted into propionic aldehyde $C_2H_5\cdot CHO$ and propionic acid $C_2H_5\cdot CO_2H$.

*Isapropyl alcohol* is a colorless liquid, which boils at 85° and which can be "salted out" from aqueous solutions like the normal alcohol. It may be obtained by reducing acetone with nascent hydrogen.

**17. Butyl Alcohol.**—Butyl alcohol $C_4H_9\cdot OH$, which is mentioned in Table 1 as being obtained from the fusel oil from the rectification of beet-root alcohol, is now frequently called *fermentation butyl alcohol* or *primary isobutyl alcohol*, to distinguish it from the normal butyl alcohol, which is the real member of this homologous series. Fermentation butyl alcohol was discovered by Würtz in 1852. It dissolves in 10.5 times its own volume of water, and boils at 106°, and so cannot be the normal member of this series, which requires an average increase of 19.5° in the boiling point for each additional carbon atom (see Art. **3**). It is a colorless liquid, having a strange odor resembling fusel oil, and has a specific gravity of .805. It may be salted out of its aqueous solution by nearly all salts which are soluble in water.

*Normal butyl alcohol* or *propyl carbinol* $C_3H_7 \cdot CH_2 \cdot OH$ is a liquid having a pleasant odor, boils at 117°, and has a specific gravity of .824. It is obtained by the action of sodium amalgam, in presence of water, to furnish nascent hydrogen, on butyl aldehyde:



$$\begin{matrix} C_3H_7 \\ | \\ CHO \end{matrix} + 2H = C_3H_7 \cdot CH_2 \cdot OH$$

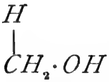
butyl aldehyde

*Secondary butyl alcohol* was obtained by De Luynes, and has the formula $CH_3 \cdot CH_2 \cdot CH : OHCH_3$. It boils at about 99° and has a specific gravity of .85.

*Tertiary butyl alcohol* is also known under the name of *trimethyl carbinol.* It is a compound, crystallizing in prisms and melting at 23°. Its boiling point is about 83°, and it is soluble in water in all proportions.

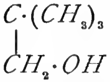
**18. Amyl Alcohols.**—Amyl alcohols have the formula $C_5H_{12}O$, and there exist, theoretically, eight isomeric amyl alcohols, all of which are known.

1. Four primary alcohols that may be regarded as formed by the substitution of various alcohol radicals for one atom of hydrogen of the methyl group in methyl alcohol:



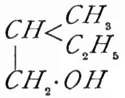
$$\begin{matrix} H \\ | \\ CH_2 \cdot OH \end{matrix}$$

methyl alcohol



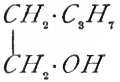
$$\begin{matrix} C \cdot (CH_3)_3 \\ | \\ CH_2 \cdot OH \end{matrix}$$

tertiary butyl carbinol



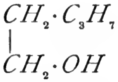
$$\begin{matrix} CH < \begin{matrix} CH_3 \\ C_2H_5 \end{matrix} \\ | \\ CH_2 \cdot OH \end{matrix}$$

active amyl alcohol



$$\begin{matrix} CH_2 \cdot C_3H_7 \\ | \\ CH_2 \cdot OH \end{matrix}$$

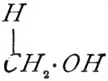
normal amyl alcohol butyl carbinol



$$\begin{matrix} CH_2 \cdot C_3H_7 \\ | \\ CH_2 \cdot OH \end{matrix}$$

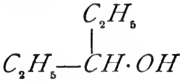
amyl alcohol of fermentation isobutyl carbinol

2. Three secondary alcohols, in which two atoms of hydrogen of the methyl group in methyl alcohol are replaced by alcoholic groups:



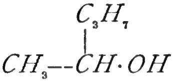
$$\begin{matrix} H \\ | \\ CH_2 \cdot OH \end{matrix}$$

methyl alcohol



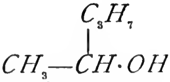
$$\begin{matrix} & & C_2H_5 \\ & & | \\ C_2H_5 & — & CH \cdot OH \end{matrix}$$

diethyl carbonyl



$$\begin{matrix} & & C_3H_7 \\ & & | \\ CH_3 & -- & CH \cdot OH \end{matrix}$$

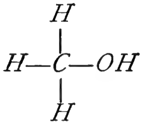
propylmethyl carbinol



$$\begin{matrix} & & C_3H_7 \\ & & | \\ CH_3 & — & CH \cdot OH \end{matrix}$$

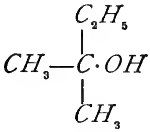
isopropylmethyl carbinol

3. One tertiary alcohol, in which one ethyl group and two methyl groups replace the three hydrogen atoms of the $CH_3$ in methyl alcohol:



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -OH \\ & | & \\ & H & \end{array}$$

methyl alcohol



$$\begin{array}{ccc} & C_2H_5 & \\ & | & \\ CH_3- & C & \cdot OH \\ & | & \\ & CH_3 & \end{array}$$

dimethyl ethyl carbinol

*Normal amyl alcohol* $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$ is a liquid of specific gravity .829, which boils at 137°, and which is almost insoluble in water.

*Amyl alcohol of fermentation* $\begin{matrix} CH_3 \\ CH_3 \end{matrix}{>}CH \cdot CH_2 \cdot CH_2 \cdot OH$ is obtained by fractional distillation of the fusel oil from potatoes and beet root, as well as of that from grapes, whisky, etc. Pure isobutyl carbinol is a colorless, somewhat oily liquid, soluble in 50 parts of water. It has a specific gravity of .823 and boils at 131.4°.

The crude isobutyl carbinol is an oily liquid with an offensive odor. It boils at 129° to 132° and turns the plane of polarized light to the left. Tertiary amyl alcohol or dimethyl ethyl carbinol is a mobile, colorless liquid, having an odor resembling that of camphor. At −12° it forms a crystalline mass, it boils at 102.5°, and at 200° is decomposed.

**19. Higher Alcohols.**—Of the rapidly increasing number of higher alcohols, only a few of the most important can be considered in this treatise.

*Normal hexyl alcohol* $C_5H_{11} \cdot CH_2 \cdot OH$ has been obtained from the volatile oil of the seeds of an umbelliferous plant, *Heracleum giganteum*, which contains butyrate of hexyl $C_6H_{13} \cdot C_4H_7O_2$, and which yields the alcohol, when distilled with potash:

$$C_6H_{13} \cdot C_4H_7O_2 + KOH = C_6H_{13}OH + C_3H_7 \cdot COOK$$

The normal alcohol boils at 157°. The *fermentation hexyl alcohol*, or *caproyl alcohol*, which boils at 150°, is that obtained by distilling fermented grape husks; it has a more unpleasant smell than the normal alcohol.

*Normal capryl*, or *octyl*, *alcohol* $C_8H_{17}\cdot OH$ is obtained from the essential oil of the cow parsnip or hogweed (*Heracleum spondylium*) by distilling it with potash, which decomposes the *octyl acetate* of which the oil chiefly consists:

$$CH_3COOC_8H_{17} + KOH = C_8H_{17}\cdot OH + CH_3COOK$$

It boils at 191° and has a specific gravity of .83. Bouis discovered *secondary octyl alcohol.* By boiling one of the acids produced by the saponification of castor oil, *ricinoleic acid*, with potassium hydrate, he succeeded in obtaining *sebacic acid* and a new secondary alcohol. This secondary octyl alcohol is a colorless liquid with a pleasant aromatic odor, and it boils at 170°. The subjoined equation explains its formation sufficiently:

$$\underset{\substack{\text{ricinoleic}\\ \text{acid}}}{C_{18}H_{34}O_3} + 2KOH = \underset{\substack{\text{potassium}\\ \text{sebacate}}}{K_2C_{10}H_{16}O_4} + \underset{\substack{\text{octyl}\\ \text{alcohol}}}{C_8H_{18}O} + H_2$$

*Cetyl alcohol*, or *ethal* $C_{16}H_{33}OH$, is obtained from spermaceti found in the cranial sinuses of the sperm whale. This substance is *cetin*, or *cetyl palmitate*, and, when boiled for some time with potash dissolved in alcohol, it yields cetyl alcohol and potassium palmitate:

$$C_{15}H_{31}\cdot COOC_{16}H_{33} + KOH = C_{16}H_{33}\cdot OH + C_{15}H_{31}\cdot COOK$$

On mixing the alcoholic solution with water, the cetyl alcohol is precipitated in the solid state, being itself insoluble in water. Cetyl alcohol is a crystalline body, fusing at 49.5° and boiling at 344°.

*Ceryl alcohol* $C_{27}H_{55}\cdot OH$ is prepared from Chinese wax, the product of an insect of the cochineal tribe. Its chief constituent is *cerotin*, or *ceryl cerotate*, and, when fused with potash, gives ceryl alcohol and potassium cerotate, according to the subjoined equation:

$$C_{26}H_{53}\cdot COOC_{27}H_{55} + KOH = C_{27}H_{55}\cdot OH + C_{26}H_{53}\cdot COOK$$

By treating the fused mass with water, the cerotate is dissolved, and the ceryl alcohol, which remains undissolved, may be obtained in crystalline form by dissolving it in ether.

*Melissyl*, or *myricyl*, *alcohol* $C_{30}H_{61}\cdot OH$ is derived from beeswax. When this is boiled with alcohol, about one-third of its weight is left undissolved; this is *myricin*, or *melissyl palmitate* $C_{15}H_{31}\cdot COOC_{30}H_{61}$. By fusing this with potash, it is made to yield potassium palmitate and melissyl alcohol, which latter is a crystalline substance, fusing at 85°.

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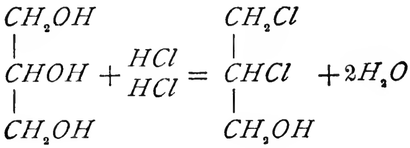
## MONOHYDRIC ALCOHOLS OF THE OLEFINE AND ACETYLENE SERIES

**20.** The alcohols of this class are formed from the olefine and the acetylene series in exactly the same manner as the ordinary alcohols, just studied, are formed from the paraffin series. Their general formulas, therefore, are $C_nH_{2n-1}OH$ and $C_nH_{2n-3}OH$, respectively. They are unsaturated compounds and readily combine with hydrogen to form the alcohols of the preceding class. Those that are known are primary alcohols; as, for instance, allyl alcohol $CH_2:CH\cdot CH_2\cdot OH$, formed from propylene. Vinyl alcohol $CH_2:CH\cdot OH$, the basis of which is ethylene, is a secondary alcohol, which probably exists in crude ether. It cannot, however, be isolated because it is immediately transposed into aldehyde $CH_3\cdot CHO$.

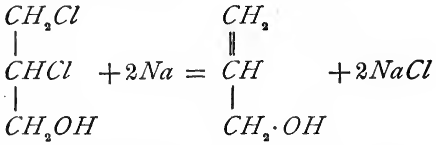
**21. Allyl Alcohol.**—Allyl alcohol $C_3H_5\cdot OH$ or $CH_2:CH\cdot CH_2\cdot OH$ is formed in several ways from glycerine:

1. By introducing two chlorine atoms into glycerine $C_3H_5(OH)_3$ in the place of two hydroxyl radicals, we obtain *dichlorhydrin* $C_3H_5Cl_2\cdot OH$, according to the subjoined equation:



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{c} HCl \\ HCl \end{array} = \begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2OH \end{array} + 2H_2O$$

The dichlorhydrin thus obtained is treated with sodium, which extracts the chlorine:



$$\begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2OH \end{array} + 2Na = \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2\cdot OH \end{array} + 2NaCl$$

2. By treating glycerine with iodide of phosphorus, allyl iodide $C_3H_5I$ is formed, and by heating this to 100° with 20 parts of water allyl alcohol is formed.

3. By heating 4 parts of glycerine with 1 part of crystallized oxalic acid in a retort at about 195°, as long as water distils over, and afterwards raising the temperature, when the allyl alcohol distils over, the glycerine is first converted into *monoformin*:

$$\underset{\text{glycerine}}{CH_2OH\cdot CHOH\cdot CH_2OH} + \underset{\substack{\text{oxalic}\\\text{acid}}}{(COOH)_2}$$

$$= \underset{\text{monoformin}}{CH_2OH\cdot CHOH\cdot CH_2(OCHO)} + CO_2 + H_2O$$

The monoformin is then decomposed into allyl alcohol, water, and $CO_2$; thus,

$$\underset{\text{monoformin}}{CH_2OH\cdot CHOH\cdot CH_2(OCHO)}$$

$$= \underset{\text{allyl alcohol}}{CH_2:CH\cdot CH_2OH} + H_2O + CO_2$$

Allyl alcohol is a mobile liquid with a suffocating odor; its boiling point is at 97°, and it has a specific gravity of .87. It dissolves in all proportions in water. Nascent hydrogen does not act on it, or, at least, the action, if any, takes place with difficulty. If cautiously oxidized with $Ag_2O$, it yields glycerine, but stronger oxidation converts it into *acrylic aldehyde* or *acrolein* $CH_2:CH\cdot CHO$ and *acrylic acid* $CH_2:CH\cdot COOH$. This shows it to be a primary alcohol. Crude wood spirit contains, as a rule, a little allyl alcohol.

**22. Propargyl Alcohol.**—Propargyl, or *propinyl*, alcohol $C_3H_3\cdot OH$ or $CH\vdots C\cdot CH_2OH$ is the alcohol corresponding with allylene. It is prepared by treating brom-allyl alcohol $CH_2:CBr\cdot CH_2OH$ with potash, the reaction that occurs may be represented as follows:

$$CH_2:CBr\cdot CH_2OH+KOH$$
$$=CH\vdots C\cdot CH_2OH+KBr+H_2O$$

It is a mobile liquid with an agreeable fragrant odor, it has a specific gravity of .96, boils at 115°, and burns with a luminous flame. Since it contains the $CH\vdots C$ group, it is capable of yielding metallic derivatives; for instance, cuprous propargyl alcohol $CCu:C:CH_2OH$, which is obtained as a green precipitate.

### MONOHYDRIC ALCOHOLS OF THE BENZENE SERIES

**23.** It would appear at first sight, as though the hydroxyl compound produced by introducing $OH$ in the place of one of the hydrogen atoms of benzene should be an alcohol. If the structure of benzene were correctly represented by the benzene ring, however, this alcohol would partake of the nature of a tertiary alcohol, since $OH$ would be combined to a carbon atom, itself attached by three atom-fixing powers to two other carbon atoms. As a fact, however, the hydroxyl-substitution products of the benzene hydrocarbons cannot be classed with the alcohols *when the substitution occurs* in the benzene nucleus. Such substitution products as $C_6H_5(OH)$, $C_6H_4(OH)_2$, $C_6H_4(OH)(CH_3)$ differ to such an extent from the alcohols that they are classed apart under the name *phenols.*

Only such hydroxyl derivatives of benzene hydrocarbons are considered alcohols (and are termed *aromatic alcohols*) as have the group $OH$ substituted for $H$ in the side chain; thus, while $C_6H_4(OH)CH_3$ is a phenol, its isomeride $C_6H_5\cdot CH_2\cdot OH$ is a primary alcohol, known as *benzyl alcohol* or *phenyl carbinol.* Fig. 2 represents the structure of the $C_6H_4(OH)CH_3$ molecule, while Fig. 3 represents that of the $C_6H_5CH_2\cdot OH$ molecule; the illustrations show clearly the difference. It will be clearly seen that it is possible to have secondary alcohols—e.g., $C_6H_5\cdot CHOH\cdot CH_3$ (from ethyl benzene) — and tertiary alcohols—e. g., $C_6H_5\cdot COH{<}\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}$ (from isopropyl benzene).

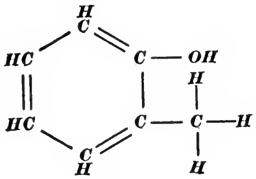


FIG. 2

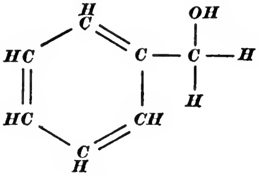


FIG. 3

For every alcohol there is an isomeric phenol, and it is possible to have a phenyl alcohol; as, for instance,

$$C_6H_4\cdot OH\cdot CH_2OH$$

Like the paraffin alcohols, the aromatic alcohols may be prepared from the halogen substituted hydrocarbons by the action of moist silver oxide or an alkali, but the substituted halogen must, of course, be in the side chain, e. g.,

$$C_6H_5\cdot CH_2Cl \text{ (benzyl chloride)}$$

**24. Benzyl Alcohol.**—Benzyl alcohol, or *benzoic alcohol* $C_6H_5\cdot CH_2OH$, is found in nature in the balsams of Peru and Tolu, and in storax. In these substances it is, for the most part, in combination with benzoic and cinnamic acids. It is prepared by treating the oil of bitter almonds, which is the corresponding aldehyde, with nascent hydrogen:

$$\underset{\substack{\text{oil of bitter}\\ \text{almonds}}}{C_6H_5\cdot CHO}+2H = C_6H_5\cdot CH_2OH$$

It is also prepared by replacing the chlorine in benzyl chloride $C_6H_5\cdot CH_2Cl$ by hydroxyl, which can be accomplished by boiling the chloride for some time with water. The replacement may be expressed by the equation:

$$C_6H_5\cdot CH_2Cl+H_2O = C_6H_5\cdot CH_2OH+HCl$$

Benzyl alcohol is a colorless oily liquid with a faint but disagreeable odor. Its specific gravity is 1.06, and its boiling point is at 206°.

Only a limited number of alcohols analogous to benzyl alcohol have been prepared, and they are not of sufficient importance to be considered here.

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### THIO-ALCOHOLS, OR SULPHUR ALCOHOLS

**25.** Thio-alcohols, or sulphur alcohols, also known as *mercaptans*, are derived from the alcohols by the substitution of sulphur for oxygen.

**26. Mercaptan.**—Mercaptan $C_2H_5 \cdot SH$ obtained its name from its remarkable action on mercury compounds (*mercurio aptum*). It is prepared by distilling calcium sulphethylate with potassium hydrosulphide:

$$\underset{\text{calcium sulphethylate}}{Ca(C_2H_5SO_4)_2} + 2KSH = CaSO_4 + K_2SO_4 + \underset{\text{mercaptan}}{2(C_2H_5 \cdot SH)}$$

A solution of potassium hydrosulphide is made by passing $H_2S$ to saturation into a solution of potash (Sp. Gr. 1.3), and this is distilled with an equal volume of calcium sulphethylate of the same specific gravity. The mercaptan, which is characterized by its powerful odor, resembling garlic, forms the upper layer of the distillate. Mercaptan is a volatile liquid of specific gravity .835, and a boiling point at 36°. It burns with a blue flame, and is only sparingly soluble in water, but dissolves readily in alcohol and ether. It is unaffected by caustic alkalies, but potassium and sodium act on it, displacing hydrogen and forming *potassium mercaptide* $C_2H_5 \cdot SK$ and *sodium mercaptide* $C_2H_5 \cdot SNa$, both of which have crystalline structures and are soluble in water.

Mercuric oxide reacts with mercaptan, forming, with evolution of heat, a white, crystalline, and inodorous compound, which is known as *mercuric mercaptide* $(C_2H_5S)_2Hg$. The reaction that takes place may be expressed by the following equation:

$$HgO + 2(C_2H_6 \cdot SH) = (C_2H_5S)_2Hg + H_2O$$

Mercuric mercaptide is insoluble in water, but soluble in alcohol and strong hydrochloric acid. Mercaptides of other metals may be precipitated by metallic salts from an alcoholic solution of mercaptan. They are also called thioethoxides.

**27. Diethyl Sulphide.**—By distilling mercuric mercaptide, *diethyl sulphide*, or thio-ether $C_2H_5 \cdot S \cdot C_2H_5$, may be obtained:

$$(C_2H_5S)_2Hg = (C_2H_5)_2S + HgS$$

This compound may also be prepared by distilling potassium sulphethylate with potassium sulphide:

$$2KC_2H_5SO_4 + K_2S = 2K_2SO_4 + (C_2H_5)_2S$$

It closely resembles mercaptan, but has a much higher boiling point, namely, 92°. Its alcoholic solution gives, with mercuric chloride, a white crystalline precipitate $(C_2H_5)_2S, HgCl_2$.

**28. Ethyl Disulphide.**—Ethyl disulphide, or *diethyl disulphide* $(C_2H_5)_2S_2$, is obtained when potassium disulphide and sulphethylate are distilled, or by heating mercaptan and sulphur to 150°:

$$2(C_2H_5SH) + S = (C_2H_5)_2S_2 + H_2S$$

or by decomposing sodium mercaptide with iodine:

$$2(C_2H_5SNa) + I_2 = 2NaI + (C_2H_5)_2S_2$$

It is an unpleasant smelling liquid of relatively high boiling point (151°).

**29. Ethyl Oxysulphide.**—This compound $(C_2H_5)_2OS$ is a thick liquid, which is miscible in water. *Diethyl trisulphide* $(C_2H_5)_2S_3$ is obtained by heating the disulphide with sulphur. *Diethyl tetrasulphide* $(C_2H_5)_2S_4$ is the product of the action of disulphur dichloride on mercaptan:

$$S_2Cl_2 + 2(C_2H_5 \cdot SH) = (C_2H_5)_2S_4 + 2HCl$$

It is a colorless oily liquid which is converted into diethyl pentasulphide $(C_2H_5)_2S_5$ by heating with sulphur at 150°. Diethyl pentasulphide is a soft, elastic mass.

**30. Diethyl dioxysulphide,** or **ethyl sulphone** $(C_2H_5)_2SO_2$, is obtained when ethyl sulphide is oxidized by strong nitric acid. It is a very stable crystalline solid, which fuses at 70°, sublimes at 100°, and boils at 248°. It is soluble in water as well as in alcohol.

When ethyl sulphide and ethyl iodide are heated together with a little water for a number of hours in a flask with an inverted condenser, the mixture, on cooling, deposits colorless prisms of *triethyl-sulphine iodide* $(C_2H_5)_3S\cdot I$, which are insoluble in ether, but soluble in water as well as in alcohol. This compound is distinguished for producing a series of compounds in which the iodine is replaced by other halogen radicals, giving rise to *triethyl-sulphine salts*, in which $S$ is quadrivalent; thus, in the iodide, it is attached to four monad radicals, viz., $(C_2H_5)_3$ and $I$. By decomposing the iodide with moist silver oxide, the *triethyl-sulphine hydroxide* $(C_2H_5)_3S\cdot OH$ is obtained. It is a deliquescent crystalline compound, possessing the property of a powerful caustic alkali.

**31. Diethyl-sulpho-dimethyl methane** $(CH_3)_2C(SO_2C_2H_5)_2$ is used under the name of *sulphonal* as one of the most favored modern hypnotics. It is a colorless solid, crystallizing in prisms, melting at 125°, and boiling at 300°. It is only slightly soluble in water.

**32. Xanthic Acid.**—Xanthic acid $C_2H_5\cdot O\cdot CS\cdot SH$ is obtained as a potassium salt by saturating alcohol with potassium hydroxide and stirring with excess of carbon disulphide:

$$C_2H_5\cdot OH + CS_2 + KOH = \underset{\text{potassium xanthate}}{C_2H_5\cdot O\cdot CS_2K} + H_2O$$

Potassium xanthate forms brilliant, slender, colorless prisms. It is freely soluble in water and alcohol, but insoluble in ether, and is gradually destroyed, on exposure to air, by the oxidation of part of the sulphur. Xanthic acid may be prepared by decomposing this salt with dilute sulphuric or hydrochloric acid. Xanthic acid is a colorless, oily liquid, heavier than water, of powerful characteristic odor, and very combustible; it reddens litmus paper. Exposed to a gentle heat (about 24°), it is decomposed into alcohol and carbon disulphide. Exposed to air, or even kept beneath the surface of water open to air, it becomes covered with a whitish crust and is gradually destroyed.

Xanthic acid may be represented as the sulphur analogue of hydroxypropionic, or lactic, acid $C_2H_4(OH)\cdot CO\cdot OH$. Potassium propionate is formed when $CO_2$ acts on potassium ethoxide (see Art. **6**), while the xanthate is formed when $CS_2$ acts on $C_2H_5\cdot OH$ and $KOH$, which are equivalent to potassium ethoxide and water.

**33.** **Ethyl sulphinic acid** $C_2H_5\cdot SO\cdot OH$ is obtained as a zinc salt by the action of sulphur dioxide on a cooled ethereal solution of zinc ethide:

$$Zn(C_2H_5)_2+2SO_2 = (C_2H_5\cdot SO_2)_2Zn$$

The acid itself is a syrupy liquid. It can evidently be regarded as propionic acid $C_2H_5\cdot COOH$, in which the carbon of the carboxyl is replaced by quadrivalent sulphur.

**Ethyl sulphonic acid** $C_2H_5\cdot SO_2\cdot OH$ is produced when ethyl sulphinic acid $C_2H_5\cdot SO\cdot OH$ is oxidized by nitric acid. It is an oily liquid (Sp. Gr. 1.3), which may be crystallized by cooling. It forms very soluble salts, which are not readily decomposed by heat. This acid may be regarded as derived from alcohol $C_2H_5\cdot OH$, by the substitution, for the $OH$, of the sulphuric-acid residue $SO_2\cdot OH$ (or, what is the same thing, $H_2SO_4 - OH$), while ethyl sulphinic acid contains the sulphurous-acid residue $SO\cdot OH$ (or $SO_3H_2 - OH$). By treatment with $PCl_5$, the $OH$ in ethyl sulphonic acid may be replaced by $Cl$, producing ethyl sulphonic chloride $C_2H_5\cdot SO_2Cl$.

## DIHYDRIC ALCOHOLS, OR GLYCOLS

**34.** Dihydric alcohols may be regarded as being derived from saturated hydrocarbons by the substitution of two equivalents of hydroxyl for two atoms of hydrogen; or, equally well, as olefine compounds that have combined with two hydroxyl groups. The latter assumption is expressed by their nomenclature; viz., ethylene glycol, propylene glycol, butylene glycol, etc.

They are formed, as a whole, by the following processes:

1. By combining an olefine with bromine, treating the resulting dibromide with an alcoholic solution of potassium acetate, or with silver acetate, whereby it is converted into a diacetate of the olefine, and decomposing this compound with potassium hydroxide, whereby potassium acetate and a dihydric acid are formed, the latter of which may be distilled off:

$$\underset{\text{ethene bromide}}{C_2H_4Br_2} + \underset{\text{silver acetate}}{2AgOC_2H_3O} = 2AgBr + \underset{\text{ethene diacetate}}{C_2H_4(OC_2H_3O)_2}$$

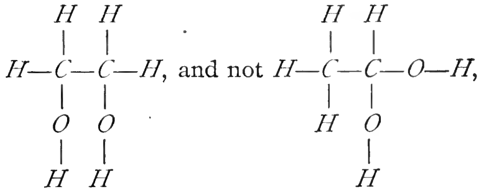
$$\underset{\text{ethene diacetate}}{C_2H_4(OC_2H_3O)_2} + 2KOH = \underset{\substack{\text{potassium}\\\text{acetate}}}{2KOC_2H_3O} + \underset{\substack{\text{ethene}\\\text{alcohol}}}{C_2H_4(OH)_2}$$

2. By combining an olefine with hypochlorous acid, and treating the resulting compound (a chlorhydrin) with moist silver oxide:

$$\underset{\text{ethene}}{C_2H_4 + ClOH} = \underset{\text{ethene chlorhydrin}}{C_2H_4ClOH}$$

$$2C_2H_4ClOH + Ag_2O + H_2O = 2AgCl + 2C_2H_4(OH)_2$$

The simplest glycol would be $CH_2(OH)_2$ from methane; this compound, however, has never been isolated, and it appears to be a fact that no compound whatever seems to exist that has two hydroxyl groups linked to one carbon atom. There is evidence to show that in all the glycols the $OH$ groups are attached to different carbon atoms. For instance, *ethylene glycol* is $CH_2OH \cdot CH_2OH$, not $CH_3 \cdot CH(OH)_2$, or, graphically,



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & O & & O & \\ & | & & | & \\ & H & & H & \end{array}, \text{ and not } \begin{array}{ccccccc} & H & & H & & & \\ & | & & | & & & \\ H- & C & - & C & - & O & -H \\ & | & & | & & & \\ & H & & O & & & \\ & & & | & & & \\ & & & H & & & \end{array},$$

and this one cannot exist in isomeric forms. *Propylene glycol* may be either $CH_2OH \cdot CH_2 \cdot CH_2OH$ or $CH_3 \cdot CHOH \cdot CH_2OH$, the former of which contains two primary alcohol groups, and may be termed *diprimary glycol*, while the latter is *secondary primary glycol.* Since *disecondary*, *ditertiary*, *secondary tertiary*, and *primary tertiary* glycols are possible, the cases of isomerism are very frequent.

**35.** The $OH$ groups in the glycols are capable of the same transformations as is the $OH$ group in a monohydric alcohol; the $H$ in them can be replaced by alkali metals, the groups can be exchanged for acid radicals, etc. There are two series of so substituted glycols known; namely, one in which only one hydroxyl group is altered, and the other in which both $OH$ groups are altered; for instance, $CH_2 \cdot ONa \cdot CH_2OH$ and $CH_2ONaCH_2ONa$, or $CH_2Cl \cdot CH_2OH$ and $CH_2Cl \cdot CH_2Cl$.

The oxidation of glycol results in the same kind of products as result from the oxidation of the alcohols, but since there are two alcohol groups to be oxidized, an extremely large number of products is obtained; for example, the two primary alcohol groups in $CH_2OH \cdot CH_2OH$ can both be oxidized to aldehyde groups $CHO \cdot CHO$, or to acid groups $COOH \cdot COOH$, or only one of them may be so oxidized, yielding *alcohol aldehydes* $CHO \cdot CH_2OH$ or *alcohol acids* $COOH \cdot CH_2OH$; aldehyde acids $CHO \cdot COOH$ will also be possible. If the glycol contains a secondary alcohol group $(:CHOH)$, *ketone alcohols*, *ketone aldehydes*, *ketone acids*, and *diketones* may also be prepared. Hence, the glycols give rise to a very large number of derivatives, many of which are very important, although the same cannot be really said of the glycols themselves.

**36. Glycol.**—Glycol, also known as *ethene alcohol* $C_2H_4(OH)_2$, was discovered in 1856. It is prepared by causing either iodide or bromide of ethylene to react with silver acetate:

$$(1) \quad C_2H_4I_2 + \underset{\text{silver acetate}}{\left\{\begin{matrix} AgC_2H_3O_2 \\ AgC_2H_3O_2 \end{matrix}\right.} = \underset{\text{ethylene diacetate}}{(C_2H_4)'' \left\{\begin{matrix} C_2H_3O_2 \\ C_2H_3O_2 \end{matrix}\right.} + 2AgI$$

and saponifying the resulting ethylene diacetate by potassium hydrate:

(2)

$$\underset{\text{ethylene diacetate}}{\left.\begin{matrix} C_2H_3OO \\ C_2H_3OO \end{matrix}\right\} (C_2H_4)} + 2KOH = \underset{\text{potassium acetate}}{2(C_2H_3OOK)} + \underset{\text{glycol}}{C_2H_4(OH)_2}$$

It is best prepared by *Hüfner* and *Zöller's process*, which consists in decomposing ethene bromide with potassium carbonate. Ethene, prepared from alcohol and sulphuric acid, is first converted into ethene bromide by passing it slowly into 50 grams of bromine under water, well cooled, until the bromine is either entirely or at least nearly bleached. The heavy layer of ethene bromide is shaken with a little weak potash, the upper watery layer drawn off, and 50 grams of the bromide heated with 40 grams of potassium carbonate and 100 cubic centimeters of water for about 16 to 18 hours in a flask connected with an upright condenser as shown in Fig. 4, when ethene bromide no longer condenses and runs back; the condenser is then placed in its proper position so that the distillate can be collected, and the contents of the flask distilled. After all the water has passed over, the flask is strongly heated by a large Bunsen burner, when the glycol distils over.

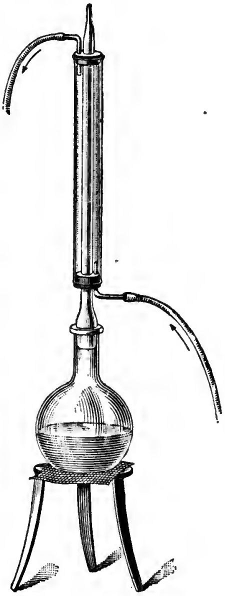


FIG. 4

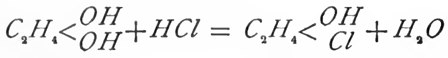
The action of potassium carbonate on ethene bromide may be represented by the subjoined equation:

$$C_2H_4Br_2 + K_2CO_3 + H_2O = C_2H_4(OH)_2 + 2KBr + CO_2$$

Glycol is a somewhat syrupy, colorless, and odorless liquid with a specific gravity of 1.125 at 0°; it has a decidedly sweetish taste, hence its name, which is derived from the Greek γλυκύς, *glykys*, meaning "sweet." Glycol mixes with water and alcohol in all proportions, but it is scarcely soluble in ether. It boils at 197.5° and distils without alteration.

**37.** Glycol readily dissolves sodium, forming *monosodium glycol* $C_2H_4 \cdot OH \cdot ONa$ and *disodium glycol* $C_2H_4 \cdot (ONa)_2$. Water converts both these compounds into glycol and sodium hydroxide.

**Glycol chlorhydrin** $C_2H_4 \cdot OH \cdot Cl$ is prepared by passing hydrochloric-acid gas into glycol·



$$C_2H_4{<}\substack{OH\\OH}+HCl = C_2H_4{<}\substack{OH\\Cl}+H_2O$$

glycol glycol chlorhydrin

It may also be obtained by the combination of ethylene $C_2H_4$ with hypochlorous acid $ClOH$. It permits the conversion of a dihydric to a monohydric alcohol, for it yields ethyl alcohol when acted on by the nascent hydrogen from water and sodium amalgam:

$$C_2H_4 \cdot OHCl + 2H = C_2H_5 \cdot OH + HCl$$

When oxidized, it yields *monochloracetic acid* $CH_2Cl \cdot COOH$, in which it is obvious that $Cl$ cannot be attached to the same carbon atom as that to which the $O$ and the $OH$ are attached (or the substance would not be an acid). This proves that glycol chlorhydrin must contain $Cl$ and $OH$ attached to different carbon atoms, and settles the constitution of glycol.

The first stage in the oxidation of glycol is the formation of glycol *dialdehyde*, or *glyoxal;* the relation of this compound to glycol is shown thus:

$CH_2OH \cdot CH_2OH$ (glycol)
$CHO \cdot CHO$ (glyoxal)

The products of a further oxidation are the two acids:

$COOH \cdot CH_2OH$ (glycolic acid)
$COOH \cdot COOH$ (oxalic acid)

**Hydrobenzoin** $(C_6H_5)CHOH{:}CHOH(C_6H_5)$ is a glycol derived from stilbene (diphenylethylene $C_6H_5 \cdot CH{:}CH \cdot C_6H_5$). It may also be produced by the action of nascent hydrogen on benzoic aldehyde $C_6H_5 \cdot CHO$. It crystallizes in plates and melts at about 134°.

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### TRIHYDRIC ALCOHOLS OR GLYCEROLS

**38.** Trihydric alcohols are regarded as being derived from saturated hydrocarbons by substitution of three hydroxyl groups for 3 atoms of hydrogen. Since, as has been stated previously, two hydroxyl groups cannot remain combined with 1 carbon atom, there can be no glycerol that contains less than 3 carbon atoms, and $C_3H_5(OH)_3$ must be the lowest member of this group. The radicals of the glycerols may obviously be regarded as trivalent radicals, that is $(C_3H_5)'''$; they are known as *glyceryl*, or *propenyl*. The number of known glycerols is rather limited, and what has been said with regard to isomerism, substitution derivatives, and oxidation products of the glycols, applies with even greater force to the glycerols, where there are three hydroxyl groups to be substituted and three alcohol groups to be oxidized.

**39. Glycerine.**—Glycerine $C_3H_5(OH)_3$, or $CH_2OH \cdot CHOH \cdot CH_2 \cdot OH$, is also known as *glycerol*, or *propenyl alcohol.* It was discovered by Scheele in 1779, and thoroughly investigated by Berthelot, who demonstrated its character as a trihydric alcohol.

Glycerine occurs very widely distributed as the alcoholic, or basic, constituent of the fats. The acids with which it is in combination are members of the fatty-acid series, with the exception of *oleic acid*, which belongs to a different series. Besides oleic acid, the two acids most frequently met with in fats are *palmitic* and *stearic acids.* When a fat is saponified with caustic potash, it yields free glycerine and the potassium salts of the acid. The reactions in the case of the glycerine compounds of palmitic and stearic acids may be expressed by the subjoined equations:

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{palmitic acid}}{3C_{15}H_{31}\cdot COOH} = \underset{\substack{\text{glycerine tripalmitate}\\ \text{or palmitin}}}{(C_{15}H_{31}\cdot COO)_3C_3H_5} + 3H_2O$$

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{stearic acid}}{3C_{17}H_{35}COOH} = \underset{\substack{\text{glycerine tristearate}\\ \text{or stearin}}}{(C_{17}H_{35}COO)_3C_3H_5} + 3H_2O$$

*Saponification.*

$$\underset{\text{palmitin}}{(C_{15}H_{31}\cdot COO)_3C_3H_5} + 3KOH = \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\substack{\text{potassium}\\ \text{palmitate}}}{3C_{15}H_{31}CO_2K}$$

$$\underset{\text{stearin}}{(C_{17}H_{35}\cdot COO)_3C_3H_5} + 3KOH = \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\substack{\text{potassium}\\ \text{stearate}}}{3C_{17}H_{35}CO_2K}$$

The fats are also decomposed by superheated steam, yielding free glycerine and the free acids, and this method is used on a large scale, a little lime being added to facilitate the process. Lead oxide decomposes fats, yielding a mixture of glycerine and the lead salts of the acids. The mixture is known in medicine as *lead plaster*. Glycerine is formed in small quantities by the alcoholic fermentation of sugar. It is obtained in large quantities in the arts as an accessory product in the manufacture of stearin candles.

Glycerine may be produced from propenyl bromide $(C_3H_5)Br_3$. The process consists in converting the propenyl bromide into propenyl triacetate $(C_3H_5)(OC_2H_3O)_3$ by the action of silver acetate, and decomposing this acetate with potash. Or it may also be prepared from propylene by combining it with chlorine to form propylene chloride $C_3H_6Cl_2$, which is heated with iodine chloride to convert it into propenyl tri-iodide $C_3H_5I_3$; by heating this in a sealed tube, with approximately twenty times its own volume of water at about 160°, it is converted into glycerine:

$$C_3H_5I_3 + 3HOH = C_3H_5(OH)_3 + 3HI$$

**40. Properties of Glycerine.**—Glycerine is a colorless liquid of syrupy consistency and taste. It has a specific gravity of 1.269, and its boiling point is 290°, at which temperature it commences to decompose in part, giving off, among other products, a substance called *acrolein* $C_3H_4O$, having an intensely pungent odor. It is slightly volatile at 100°, but is entirely stable at ordinary temperatures. When perfectly pure and anhydrous, it crystallizes on long exposure at −40°, the crystals melting again at 17°. A strong aqueous solution of glycerine, however, crystallizes at 0°, especially if a ready-made crystal is introduced in the mass thus cooled. It attracts moisture from the air, and mixes with water and alcohol in all proportions. When heated to 150°, it becomes inflammable and burns with a flame resembling that of alcohol.

Confectioners and brewers use glycerine to sweeten their products, and it is useful in keeping substances moist and pliant. Equal volumes of water and glycerine are used for filling gas meters, being much less easily frozen and less liable to dry up.

Two compounds corresponding with the ethoxide may be obtained by the action of metallic sodium on glycerine dissolved in alcohol; namely, *sodium propenoxide* $C_3H_5(OH)_2ONa$, and *disodium propenoxide* $C_3H_5\cdot OH(ONa)_2$. Glycerine does not yield an aldehyde when oxidized, but it yields *glyceric acid* $C_2H_3(OH)_2\cdot COOH$, which is also called *dihydroxypropionic acid*, since it is propionic acid $C_2H_5\cdot COOH$, in which 2 atoms of $H$ have been replaced by $(OH)_2$. The best test for identifying glycerine is to mix it with powdered $KHSO_4$ and heat it strongly, when the pungent odor of acrolein, previously mentioned, is perceived. It is the acrolein that causes the offensive smell of smoldering candles made of tallow. Another important property by which glycerine is distinguished is that of conversion into *nitroglycerin* $C_3H_5(NO_3)_3$, or **glyceryl trinitrate,** when cautiously added to a mixture of equal volumes of nitric and sulphuric acids cooled in water. The nitroglycerin separates as a heavy oil when the mixture is poured into much water, and a drop of the oil placed on an anvil and struck with a hammer detonates with a deafening report. Nitroglycerin is much used for blasting in mines and quarries. It is extremely dangerous to handle and has caused many fatal accidents.

By the action of dehydrating agents on glycerine, 1 molecule of water can be abstracted and *glycide alcohol* $CH_2\overset{O}{\diagup\;\diagdown}CH\cdot CH_2OH$ produced. Glycide alcohol is a colorless liquid, boiling at 162°, and is miscible with water, alcohol, and ether. It recombines with $H_2O$ to form glycerine again and combines with $HCl$ to form chlorhydrin.

The trihydric alcohols yield halogen compounds, having either one, two, or three of the hydroxyl groups replaced by one of those elements; thus, glycerine $C_3H_5(OH)_3$ yields a *monochlorhydrin* $C_3H_5(OH)_2Cl$, a *dichlorhydrin* $C_3H_5(OH)Cl_2$, and a *trichlorhydrin* $C_3H_5Cl_3$; the latter is identical with trichloropropane.

Monochlorhydrin and dichlorhydrin are prepared by saturating glycerine with hydrochloric acid, and heating for several hours at 100°; this is then neutralized with $Na_2CO_3$, and shaken with ether. On distilling the ethereal solution, the chlorhydrin comes over at about 140°, which is its boiling point, while the dichlorhydrin boils at 174°. They are liquids heavier than water, in which monochlorhydrin is more soluble than dichlorhydrin, and are both soluble in alcohol and ether. Potash converts dichlorhydrin into epichlorhydrin $C_3H_5\cdot OCl$ by removing $HCl$.

### TETRA-, PENTA-, AND HEXA-HYDRIC ALCOHOLS

**41.** Alcohols containing four, five, and six, and even as many as seven, eight, or nine, hydroxyl groups are known to exist. The number of hydroxyl groups present in an alcohol is ascertained by heating the alcohol with acetic anhydride $(CH_3CO)_2O$ and sodium acetate, when as many acetic radicals (*acetyl* $CH_3CO$) will enter into the composition of the alcohol as there are hydroxyl groups in the alcohol; for example, a compound known as *erythrite* has been classed as a tetrahydric alcohol, because it is known to form an acetate containing four acetic radicals:

$$C_4H_6(OH)_4+4(CH_3CO)_2O=C_4H_6(OCH_3CO)_4+4CH_3COOH$$

The lowest member of each series of polyhydric alcohols must have at least as many carbon atoms as it has $OH$ groups, otherwise one carbon atom would be linked to two hydroxyl groups, and the compound would break up. The derivatives and oxidation products of these alcohols are similar in constitution to those of glycol.

Most of the known higher alcohols are obtained from natural sources. Many of them are distinguished by a sweet taste, and some, indeed, were, for a considerable time, classed with the sugars, with which they are closely connected.

**42. Erythrite, erythrol,** or **phycite** $C_4H_6(OH)_4$, or $CH_2OH\cdot(CHOH)_2\cdot CH_2OH$, was discovered in 1849 by Stenhouse. It is prepared from certain lichens, such as the *Roccella tinctoria*, the *Roccella montagnei*, etc., by boiling them with milk of lime, filtering, precipitating the excess of lime by $CO_2$, evaporating the filtrate to a small bulk, and treating with alcohol, when erythrite crystallizes out in prisms, which fuse at 126° and boil at 330°. Erythrite has a feeble, sweet taste; it is soluble in water and boiling absolute alcohol, but insoluble in ether.

Erythrite shows, in some cases, reactions that are similar to glycerine. When erythrite is dissolved in nitric acid, and sulphuric acid is added to the solution, *nitro erythrite* $C_4H_6(NO_3)_4$ is obtained as a crystalline precipitate, which possesses the same explosive properties as nitroglycerin.

When heated with formic acid $H\cdot COOH$, it yields *erythro-glycol* $C_4H_6(OH)_2$, as is seen by the subjoined equation:

$$C_4H_6(OH)_4 + H\cdot COOH = C_4H_6(OH)_2 + 2H_2O + CO_2$$

When heated with $KOH$, erythrite is converted into potassium oxalate and acetate:

$$C_4H_6(OH)_4 + 3KOH = \underset{\substack{\text{potassium}\\\text{oxalate}}}{K_2C_2O_4} + \underset{\substack{\text{potassium}\\\text{acetate}}}{KC_2H_3O_2} + H_2O + 4H_2$$

**43. Mannite,** or **mannitol** $CH_2\cdot OH\cdot(CHOH)_4\cdot CH_2OH$, will be readily recognized by its formula as a hexahydric alcohol. Mannite is found widely distributed in the vegetable kingdom. It is the most abundant constituent of *manna*,* which is the partly dried-up sap that flows from several species of ash, and which is obtained from incisions in the bark of the tree. It is prepared by dissolving manna in distilled water, in which the white of an egg has previously been beaten up. After the solution is boiled for a few minutes, it is filtered and allowed to cool, when the liquid solidifies to a mass of crystals, which are purified by filtration and recrystallization. Mannite also occurs in the juice of trees, plants, mushrooms, seaweed, etc. Mannite is soluble in water and alcohol, but insoluble in ether. It has a slightly sweet taste and melts at 166°.

By oxidation in contact with platinum black, mannite is converted into the sugar *mannose* $C_6H_{12}O_6$, and when the oxidation is continued, it is converted into *mannonic acid* $CH_2OH \cdot (CHOH)_4 \cdot CO_2H$. By fuming nitric acid, or, more easily, by a mixture of nitric and sulphuric acids, mannite is converted into *nitromannite*, or *mannyl hexanitrate* $C_6H_8(NO_3)_6$, a crystalline body that explodes violently by percussion or when suddenly heated, and is reconverted into mannite by ammonium sulphide. With sulphuric acid, mannite forms *sulphomannitic acid* $C_6H_{14}O_6 \cdot 3SO_3$.

Three different and distinct varieties of mannite are in existence. They vary in optical activity—a difference that will be treated later.

Mannite treated with hydriodic acid is converted into secondary hexyl iodide, or hexene hydriodide:

$$\begin{aligned} &C_6H_{14}O_6 + 11HI \\ = {} &\underset{\substack{\text{secondary hexyl iodide} \\ (C_6H_{13}I)}}{CH_3 \cdot CH_2 \cdot CH_2CH_2 \cdot CHI \cdot CH_3} + 6H_2O + 5I_2 \end{aligned}$$

**44. Dulcite,** or **dulcitol** $C_6H_8(OH)_6$, is isomeric with mannite. It is a crystalline body obtained from manna,

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* The manna of the Scripture was obtained from the branches of Tamarix Gallica. It contained no mannite, but a substance of similar properties.

exported from Madagascar, from which it is extracted with boiling water. It is found in the sap of the so called *yellow cow-wheat* (*Melampyrum nemorosum*), the *common spindle tree* (*Euonymus Europæus*), and the *knotted figwort* (*Serophularia nodosa*). It is a viscous, sweet substance, resembling mannite in most of its properties, but differing in crystalline form and in melting point (dulcite melts at 188°, while mannite melts at 166°); it is much less soluble in water than mannite, almost insoluble in alcohol. Heated with hydriodic acid, it forms secondary hexyl iodide, identical with that obtained from mannite.

**Sorbitol,** or **sorbite** $C_6H_8(OH)_6$, is another isomeride of mannite, which occurs in the berries of the *mountain ash* (*Sorbus aucuparia*) in minute crystals, easily soluble in water. It is more easily fusible (110°) than the others.

**45. Mannitane** $C_6H_8(OH)_4O$ is produced when mannite is heated to 200°.

$$C_6H_8(OH)_6 = C_6H_8(OH)_4O + H_2O$$

It is a viscous substance, very similar to glycerine, which on long exposure to the action of aqueous vapor, is converted into mannite. It forms compounds, when heated with fatty acids, that are similar to the glycerides.

**46. Perseitol,** or **mannoheptitol** $C_7H_{16}O_7$, is a heptahydric alcohol, which occurs in the leaves and berries of *Laurus persca*, and has been synthetically prepared from mannose (a sugar, having the formula $C_6H_{12}O_6$). It crystallizes in microscopic needles and melts at 188°.

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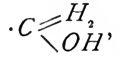
## ALDEHYDES

**47.** The name aldehyde is derived from *alcohol dehydrogenatum*, which indicates that the members of this group are oxidized alcohols. To be more exact, they are the first products of the oxidation of all alcohols containing the primary alcohol group  $\cdot C\begin{array}{l}\diagup H_2\\ \diagdown OH\end{array}$, which is converted into

$\cdot C\Big<^{O}_{H} + H_2O$. They hold, consequently, a position intermediate between alcohols and acids and differ from the parent alcohols by 2 atoms of $H$, and correspond with the general formula $C_nH_{2n+1}CHO$. For instance:

$$CH_3\cdot C\Big<^{H_2}_{OH} \quad \text{yields} \quad CH_3\cdot C\Big<^{O}_{H},$$

ethyl alcohol acetic aldehyde

There are one or more aldehydes corresponding with each of the alcohols so far described. They are readily converted by oxidation into the corresponding acid, the group $C\Big<^{O}_{H}$ being changed to $C\Big<^{O}_{OH}$. The aldehydes are named after the acids into which they are converted. Since the oxidation of primary alcohols to aldehydes consists merely in the removal of $H_2$, and since the aldehyde in all its reactions appears to still contain the alkyl radical that was originally contained in the alcohol, the above view of the constitution of these compounds may be presumed to be the correct one.

**48.** Table II enumerates the aldehydes known so far. They may all be prepared by heating the calcium salt of the corresponding acid with calcium formate.

**49.** A general idea of the characteristics and various methods of preparation of the aldehydes will be obtained from the description of the most prominent members of this class of compounds, the reactions of which may be considered identical with those of the majority of the other aldehydes.

**50. Acetic Aldehyde.**—Acetic aldehyde $CH_3\cdot CHO$, also known as *ethyl aldehyde*, was discovered by Döbereiner in 1821. It is prepared by distilling alcohol with manganese dioxide and dilute sulphuric acid, or, better, by distilling alcohol with potassium dichromate and sulphuric acid. The process requires a good deal of care, on account of the violence of the action and the volatility of the aldehyde.

## TABLE II

### ALDEHYDES

| Chemical Name | Formula | Source | Boiling Point | Melting Point |
|---|---|---|---|---|
| Formic aldehyde | $H \cdot CHO$ | Oxidation of methyl alcohol | 21° | |
| Acetic aldehyde | $CH_3 \cdot CHO$ | Oxidation of ethyl alcohol | 21° | |
| Propionic aldehyde | $C_2H_5 \cdot CHO$ | Oxidation of propyl alcohol | 49° | |
| Butyric aldehyde | $C_3H_7 \cdot CHO$ | Oxidation of butyl alcohol | 74° | |
| Valeric aldehyde | $C_4H_9 \cdot CHO$ | Oxidation of amyl alcohol | 102° | |
| Caproic aldehyde | $C_5H_{11} \cdot CHO$ | Distillation of calcium formate with calcium caproate | 128° | |
| Œnanthic aldehyde | $C_6H_{13} \cdot CHO$ | Distillation of castor oil | 155° | |
| Caprylic aldehyde | $C_7H_{15} \cdot CHO$ | Distillation of castor oil | 160° | |
| Rutic aldehyde | $C_9H_{19} \cdot CHO$ | Oil of rue | | |
| Lauric aldehyde | $C_{11}H_{23} \cdot CHO$ | Oil of rue | | 44.5° |
| Myristic aldehyde | $C_{13}H_{27} \cdot CHO$ | | | 52.5° |
| Palmitic aldehyde | $C_{15}H_{31} \cdot CHO$ | | | 58.5° |
| Stearic aldehyde | $C_{17}H_{35} \cdot CHO$ | | | 63.5° |
| Glyoxal aldehyde | $CHO \cdot CHO$ | Oxidation of glycol | | |
| Glyceric aldehyde | $C_2H_5O \cdot CHO$ | Oxidation of glycerol | | |
| Acrylic aldehyde | $C_2H_3 \cdot CHO$ | Oxidation of allyl alcohol | 52.5° | |
| Crotonic aldehyde | $C_3H_5 \cdot CHO$ | | 104° | |
| Benzoic aldehyde | $C_6H_5 \cdot CHO$ | Bitter-almond oil | 179° | |
| Cinnamic aldehyde | $C_8H_7 \cdot CHO$ | Oil of cinnamon | 246° | |
| Salicylic aldehyde | $C_6H_5O \cdot CHO$ | Oil of meadowsweet | 196° | |
| Cuminic aldehyde | $C_9H_{11} \cdot CHO$ | Oil of cumin | 235° | |
| Anisic aldehyde | $C_7H_7O \cdot CHO$ | Oil of anise | 248° | |
| Vanillic aldehyde | $C_7H_7O_2 \cdot CHO$ | Vanilla pods | | 80° |
| Pyromucic aldehyde | $C_4H_3O \cdot CHO$ | Distillation of bran with dilute sulphuric acid | | 162° |

A suitable laboratory apparatus is shown in Fig. 5, and a good way of preparing acetic aldehyde is as follows: 120 grams granulated potassium dichromate are placed in the Florence flask *A*, the capacity of which should be about 2 liters; a mixture of 160 grams concentrated sulphuric acid, 480 grams of water, and 120 grams of alcohol is then carefully prepared, cooled, and, after it has obtained the ordinary temperature, poured very slowly through the funnel tube *B* into the flask. The two wide-mouthed bottles *C* and *D*, which are about half filled with ether, having been previously connected with the flask by means of the condenser *F*, are placed in a basin filled with ice water. The condenser should also be supplied with ice water, or, if this be impossible, with as cool water as can be obtained.

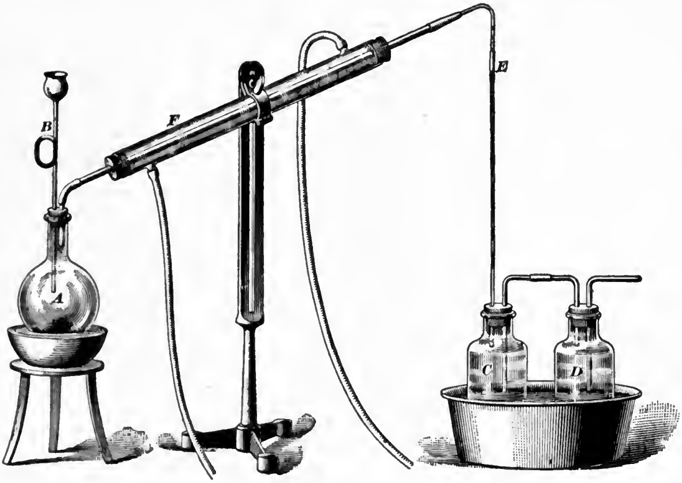


FIG. 5

As soon as the acid mixture is added, the action starts, as a rule, rather violently, and care should therefore be taken, as has been previously mentioned, to add the mixture very slowly. The aldehyde thus formed, together with some alcohol and water vapor, passes into the condenser tube, where the greater part of the alcohol and water is condensed and returned to the flask, while the aldehyde, being much more volatile, passes into the ether in bottles *C* and *D*, where it is absorbed. After the action is over, the apparatus is disconnected at $E$, and the ether bottles are connected by means of the small piece of rubber tubing at $E$, with an apparatus generating ammonia gas and provided with a tube containing calcium chloride to dry the gas. The dried ammonia gas is passed into the ethereal solution of aldehyde. A beautiful crystallized compound of aldehyde, known as *aldehyde ammonia*, is thus obtained and deposited in the ether bottles. The ether is poured off and the crystals placed on filter paper. They gradually undergo a change in the air, becoming yellow, and acquiring a peculiar odor. The aldehyde thus obtained may be freed from water by standing over fused calcium chloride and redistilling.

The preparation of aldehyde as described above illustrates the use of $K_2Cr_2O_7$ and $H_2SO_4$ as an oxidizing agent on organic compounds. The production of aldehyde, without regarding minor secondary reactions, may be represented by the subjoined equation:

$$\begin{aligned} &3C_2H_5OH + K_2Cr_2O_7 + 4H_2SO_4 \\ &= \underset{\text{acetic aldehyde}}{3CH_3 \cdot CHO} + 7H_2O + \underset{\text{chrome alum}}{2KCr(SO_4)_2} \end{aligned}$$

Considerable quantities of aldehyde occur in the "first runnings" obtained in the manufacture of alcohol from potatoes and sugar beet, being probably formed by oxidation of the spirit during the filtration through charcoal, to which it is subjected for the removal of fusel oil and other impurities.

Aldehyde is also produced by distilling a mixture of an acetate and a formate; as, for instance:

$$\underset{\substack{\text{potassium}\\\text{acetate}}}{CH_3 \cdot COOK} + \underset{\substack{\text{potassium}\\\text{formate}}}{H \cdot COOK} = \underset{\substack{\text{acetic}\\\text{aldehyde}}}{CH_3 \cdot CHO} + \underset{\substack{\text{potassium}\\\text{carbonate}}}{KO \cdot COOK}$$

This illustrates a *general reaction for producing aldehydes*, namely, distilling a salt of the corresponding acid together with a formate. The calcium salts are, as a rule, the best adapted for this purpose.

**51. Properties of Acetic Aldehyde.**—Acetic aldehyde is a colorless liquid with a suffocating odor. It boils at 21°, has a specific gravity of .801 at 0°, and mixes in all proportions with water, alcohol, and ether. From a chemical point of view, its most characteristic property is its power to unite directly with other substances. This aldehyde is considered a strong reducing agent, as it combines eagerly with oxygen to form acetic acid; thus,

$$CH_3{\cdot}CHO + O = \underset{\text{acetic acid}}{C_2H_4O_2}$$

It reduces silver nitrate solutions, depositing the silver as a bright mirror, and this reaction can be used to detect the presence of the substance. It combines with ammonia, forming aldehyde ammonia $C_2H_4OHNH_2$. It unites with the alkaline bisulphites, forming crystallizable compounds represented by the formulas

$$C_2H_4O{\cdot}HKSO_3 \text{ and } C_2H_4O{\cdot}HNaSO_3$$

By the action of sodium amalgam and water, aldehyde is converted (by the nascent hydrogen present) into alcohol:

$$C_2H_4O + 2H = C_2H_6O$$

An important derivation of aldehyde, known as *acetaldoxime*, results from the action of hydroxylamine on aldehyde:

$$CH_3CHO + \underset{\text{hydroxylamine}}{H_2NOH} = \underset{\text{acetaldoxime}}{CH_3CH{:}N{\cdot}OH} + H_2O$$

This body represents a numerous class, the *oximes*, which are formed by the reaction of hydroxylamine with bodies containing the carbonyl group. Acetic aldehyde unites with hydrocyanic acid, forming the compound $CH_3{\cdot}CH(OH)(CN)$, belonging to the *ethylidene cyanohydrins*. This compound is a liquid, soluble in water and alcohol, and boiling at 183°, which is converted by acids and alkalies into lactic acid, with the disengagement of ammonia.

If sulphur dioxide is added to a dilute magenta solution until the latter is decolorized, the addition of a trace of aldehyde will immediately restore the pink color. Nearly all the aldehydes respond to this test.

**52. Polymerides of Acetic Aldehyde.**—Aldehyde has a great tendency to become converted into polymeric modifications by uniting with itself.

*Paraldehyde* $C_6H_{12}O_3$ is formed by adding a few drops of concentrated sulphuric acid to aldehyde, which causes the liquid to become hot. On cooling to 0°, the paraldehyde solidifies in crystalline form. It melts at 10.5°, dissolves in eight times its own volume of water, and boils at 124°. When distilled with diluted sulphuric acid, hydrochloric acid, etc., it is converted into aldehyde. The specific gravity of its vapor has been found to be 4.583, which leads to the molecular weight 132.4, and, consequently, to the formula $C_6H_{12}O_3$. It is called a polymeric modification of aldehyde. Neither the cause of the peculiar action nor the structure of the product is known.

*Metaldehyde* $C_6H_{12}O_3$ is isomeric with paraldehyde and is formed in much the same way, only a temperature below 0° is most favorable to its formation. It crystallizes in needles, which are insoluble in water, and but slightly soluble in alcohol, ether, or chloroform. It sublimes when heated to 112° without melting, and when heated in a sealed tube at 116°, it is reconverted into aldehyde. Determinations by Raoult's method show that the molecular weight of *freshly prepared* metaldehyde is identical with that of paraldehyde. On standing, it is converted into paraldehyde and, probably, a substance having the formula $(C_2H_4O)_4$. Distilled with dilute sulphuric acid, metaldehyde is readily reconverted into aldehyde.

**53.** *Formic*, or *methyl*, *aldehyde* $H{\cdot}CHO$ was discovered by Hofmann. It is produced by the slow combustion of methyl alcohol, brought about by a red-hot spiral of platinum:

$$CH_3{\cdot}OH + O = H_2O + H{\cdot}CHO$$

It is also formed in the distillation of barium and calcium formates. Formic aldehyde is known only as a vapor at high temperatures, and in aqueous solution. The latter has a suffocating odor and powerful antiseptic properties; *formalin* is a 40-per-cent. solution of it, and is used as an antiputrescent and caustic. It reduces ammoniacal silver nitrate. The easiest way to produce formic aldehyde consists in cautiously oxidizing methyl alcohol with $MnO_2$ and $H_2SO_4$, when one part of the alcohol is oxidized to formic aldehyde, which then combines with the rest of the alcohol, yielding *methylal* $CH_2(OCH_3)_2$; when this is distilled with dilute acids, it yields formic aldehyde and methyl alcohol. If an aqueous solution of formic aldehyde is evaporated over sulphuric acid, the polymeride *trioxymethylene*, or *paraformaldehyde* $C_3H_6O_3$, is obtained. When heated, this begins to volatilize at 100°, it fuses at 171° and is converted into the gaseous formic aldehyde; if the latter is collected over mercury, it becomes gradually reconverted into the polymeride. When formic aldehyde is allowed to remain in contact with lime water, it undergoes a polymerization that produces *formose*, a mixture of sugars $C_6H_{12}O_6$. This change is of remarkable importance, owing to the fact that it is the beginning of synthesizing sugars.

**54.** *Propionic aldehyde* $C_2H_5{\cdot}CHO$ is prepared by oxidizing normal propyl alcohol, or by distilling a mixture of calcium propionate and formate. It has a specific gravity of .804 at 20°, it boils at 49°, and dissolves in five volumes of water.

*Valeral*, or *isovaleric*, *aldehyde* has a characteristic and oppressive smell of apples. Its specific gravity is .82 and it boils at 95.5°.

*Œnanthic aldehyde*, or *œnanthol* $C_6H_{13}{\cdot}CHO$, is extracted by hydrogen sodium sulphite from the liquid obtained by the destructive distillation of castor oil. It has a specific gravity of .827, boils at 155°, and has a nauseating odor.

**55. Acrylic and Crotonic Aldehydes.**—Of the aldehydes obtained from alcohols belonging to the olefines and the acetylene series, acrylic aldehyde and crotonic aldehyde are the only important compounds that can be treated upon here.

*Acrolein*, or *acrylic aldehyde* $CH_2:CH\cdot CHO$, is prepared by the dehydration of glycerine, when that substance is heated with phosphoric oxide, strong sulphuric acid, or acid potassium sulphate. It is always produced in the destructive distillation of neutral fats containing glycerine, and is the cause of that intolerably pungent odor attending this process. Acrolein is a volatile liquid, which boils at 52.4, and which has a specific gravity of .84. It is readily soluble in alcohol and ether, but only sparingly in water. Its vapor is intensely irritating (the smell of burning fat is caused by it) and has a violent action on the mucous membrane of the eyes. Unlike most aldehydes, it does not combine with $NaHSO_3$, but it forms a resinous body with potash and soda, and reduces ammoniacal $AgNO_3$, which converts it into *acrylic acid* $C_2H_3\cdot CO_2H$. Nascent hydrogen converts it into allyl alcohol. Acrolein, by keeping, becomes a white, solid body, known as *disacryl*, which appears to be polymeric with it, though it cannot be reconverted into acrolein. With hydrochloric acid, acrolein forms a crystalline body, $C_3H_4O\cdot HCl$, which, when distilled with potash, yields *metacrolein* $C_9H_{12}O_3$, corresponding with paraldehyde. Metacrolein is a crystalline compound, which boils at 50°, and which is reconverted into acrolein when heated to 160°. It is, like acrolein, readily soluble in alcohol and ether, but only sparingly soluble in water.

*Crotonic aldehyde* $CH_3\cdot CH:CH\cdot CHO$ is produced by heating acetic aldehyde to 100° with dilute hydrochloric acid or with zinc chloride and a little water. Neither the hydrochloric acid nor the zinc chloride apparently takes any active part in the reaction, but they act simply as dehydrating agents, and the reaction that takes place may be assumed to be represented correctly by the following equation:

$$CH_3CHO + CH_3CHO = H_2O + CH_3\cdot CH:CH\cdot CHO$$

Crotonic aldehyde is a colorless liquid with an irritating odor resembling that of acrolein; it boils at 104° and is sparingly soluble in water. In contact with air, or with moist silver oxide, it is readily oxidized to *crotonic acid* $C_3H_5 \cdot CO_2H$.

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### ALDEHYDES FROM POLYHYDRIC ALCOHOLS

**56.** The aldehydes from polyatomic alcohols may be *di-* or *poly-aldehydes* and *aldehyde alcohols;* the latter are of much more importance since it has been proved that several of the sugars can be regarded as belonging to this class of substances. The sugars will, however, receive our attention later.

*Glyoxal*, or *oxalic aldehyde* $CHO \cdot CHO$, or $C_2H_2O_2$, is prepared by the cautious oxidation of alcohol or, better, acetic aldehyde with nitric acid. Glyoxal is a deliquescent amorphous solid, slightly colored, and very soluble in water, as well as in alcohol. Its aqueous solution reduces ammonio-nitrate of silver. Like other aldehydes, glyoxal forms a crystalline compound with $NaHSO_3$. Potash and soda convert it into a yellow resinous body. With ammonia it yields glycosine:

$$3C_2H_2O_2 + 4NH_3 = 6H_2O + N_4(C_2H_2)_3$$

Glyoxal is the aldehyde corresponding to oxalic acid $CO_2H \cdot CO_2H$.

*Glyceric aldehyde* $CH_2OH \cdot CHOH \cdot CHO$ is an aldehyde alcohol, which is obtained by the cautious oxidation of glycerine. By condensation, it is converted into *acrose*, one of the sugars.

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### ALDEHYDES OF THE AROMATIC ALCOHOLS

**57.** *Benzoic aldehyde*, or *benzaldehyde*, or *oil of bitter almonds* $C_6H_5 \cdot CHO$, was discovered in 1803 and thoroughly investigated by Liebig and Wöhler. It occurs in combination with *amygdalin*, a bitter substance found in bitter almonds, laurel leaves, cherry kernels, etc. Amygdalin belongs to the class of bodies known as *glucosides*, which will be treated later on. Amygdalin itself, under the influence of *emulsin*, a peculiar albuminoid ferment, which occurs with it in the plants, breaks up into benzoic aldehyde, hydrocyanic acid, and dextrose:

$$\underset{\text{amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{dextrose}}{2C_6H_{12}O_6} + \underset{\substack{\text{benzoic}\\ \text{aldehyde}}}{C_7H_6O} + \underset{\substack{\text{hydrocyanic}\\ \text{acid}}}{HCN}$$

The presence of hydrocyanic acid renders crude oil of bitter almonds very poisonous.

Benzoic aldehyde can be prepared in various ways; namely:

1. By oxidizing benzyl alcohol:

$$C_6H_5CH_2OH + O = C_6H_5 \cdot CHO + H_2O$$

2. By treating benzoyl chloride, the chloride of benzoic acid, with nascent hydrogen:

$$C_6H_5 \cdot COCl + 2H = C_6H_5 \cdot CHO + HCl$$

3. By treating benzal chloride with water or milk of lime.

$$C_6H_5 \cdot CHCl_2 + H_2O = C_6H_5 \cdot CHO + 2HCl$$

4. From the reduction of the corresponding acid (distillation of a mixture of benzoate and formate of calcium).

Benzoic aldehyde is prepared either from bitter almonds, which yield from 1.5 to 2 per cent., or from benzal chloride, according to the reaction given.

Pure benzoic aldehyde is a thin, colorless liquid, of great refractive power, and possesses a characteristic pleasant odor. It boils at 179° and has a specific gravity of 1.05. It is only very sparingly soluble in water, but miscible in all proportions with alcohol and ether, and is precipitated therefrom on addition of water. Exposed to the air, it rapidly oxidizes and is converted into crystalline benzoic acid. It has less reducing action on metallic salts than is exerted by the aldehydes of the acetic series. Benzoic aldehyde is dissolved by a strong solution of sodium sulphite, and, if dilute sulphuric acid is added, drop by drop, to this solution, it soon deposits large crystals of the compound of benzoic aldehyde with the acid sulphite, $C_7H_6O \cdot NaHSO_3$; the crystals dissolve when heated, but are redeposited as soon as the heated mass begins to cool.

Ammonia converts it into *hydrobenzamide* $(C_6H_5\cdot CH)_3N_2$, a white crystalline body:

$$3(C_6H_5\cdot CHO)+2NH_3=(C_6H_5\cdot CH)_3N_2+3H_2O$$

All the aromatic aldehydes act with ammonia in a similar manner, and are thereby distinguished from the fatty aldehydes.

A good method of identifying bitter-almond oil is to heat it in a test tube with some caustic potash, dissolve the cooled mass in water, and add $HCl$, which precipitates feathery crystals of benzoic acid.

*Benzaldoxime* $C_6H_5\cdot CH:N\cdot OH$ exists in a liquid, or $\alpha$-form, and a solid, or $\beta$-form.

**58.** *Cinnamic aldehyde* $C_6H_5\cdot CH:CH\cdot CHO$ constitutes the essential part of the volatile oils of cinnamon and cassia. It may be prepared synthetically by passing hydrochloric-acid gas, which acts as a dehydrating agent, into a mixture of acetic and benzoic aldehydes:

$$\underset{\substack{\text{acetic}\\\text{aldehyde}}}{CH_3\cdot CHO}+\underset{\substack{\text{benzoic}\\\text{aldehyde}}}{C_6H_5\cdot CHO}=\underset{\substack{\text{cinnamic}\\\text{aldehyde}}}{C_6H_5\cdot CH:CH\cdot CHO}+H_2O$$

Cinnamic aldehyde is a colorless liquid, with aromatic odor, which boils at 246°. When exposed to air, it becomes oxidized and is thus converted into *cinnamic acid* $C_6H_5\cdot CH\cdot CH\cdot CO_2H$.

**59.** *Salicylic aldehyde* $C_6H_4OH\cdot CHO$, or *oil of meadow-sweet* (*Spiræal Umaria*) is obtained by oxidizing salicin with potassium dichromate and sulphuric acid. It is a colorless, thin, and highly refractive liquid, which boils at 196° and has a specific gravity of 1.17. It has a pleasant odor and a burning taste. It is quite soluble in water and dissolves in alcohol and ether in all proportions. It stains the skin yellow, and its solution gives an intense violet color with ferric chloride. It resembles benzoic aldehyde in its behavior with ammonia, which converts it into *hydrosalicyl amide* $(C_6H_5O\cdot CH)_3N_2$; but it differs from benzoic and cinnamic aldehydes by easily combining with alkalies to form compounds in which an atom of hydrogen is displaced by the metal; thus, for instance:

$$C_6H_5O\cdot CHO + KOH = C_6H_4OK\cdot CHO + H_2O$$

This reaction indicates that salicylic aldehyde is *hydroxybenzaldehyde* $C_6H_4(OH)\cdot CHO$, and, since the $OH$ group is attached to the benzene nucleus, the compound is a *phenol aldehyde.*

A general reaction of obtaining hydroxybenzaldehydes consists in heating the corresponding phenol with chloroform and an alkali; thus, salicylic aldehyde is produced when phenol is heated with chloroform and $KOH$, as expressed by the following equation:

$$C_6H_5\cdot OH + CHCl_3 + 4KOH$$
$$= C_6H_4(OK)\cdot CHO + 3KCl + 3H_2O$$

The potassium derivative may be distilled with dilute acid to obtain the aldehyde. A mixture of $CHCl_3$ and $KOH$ is potential potassium formate:

$$CHCl_3 + 4KOH = H\cdot COOK + 3KCl + 2H_2O$$

so that probably the reaction may be regarded as one between phenol and potassium formate:

$$C_6H_5OH + H\cdot COOK = C_6H_4(OK)\cdot CHO + H_2O$$

**60. Vanillin.**—When 1:2-monomethyl pyrocatechol (guiacol) $C_6H_4(OCH_3)(OH)$, a derivative of 1:2-dihydroxybenzene, is similarly treated, it yields *vanillin*, or *methyl protocatechuic aldehyde.*

Vanillin is extracted from the pods of *vanilla planifolia*, a Mexican plant, by boiling them with alcohol. It forms needles, melts at 80°, and sublimes. It is sparingly soluble in water, and is characterized by its well known agreeable odor and taste. Vanillin, which is much used as a flavoring agent, is made artificially by the oxidation of *coniferin* $C_{16}H_{22}O_8$ with chromic acid. Coniferin, as the name indicates, is a crystalline glucoside, extracted from pine wood or other coniferous plants and trees. When oxidized, it yields *glycovanillin*, the glucoside of vanillin

$C_6H_3(OCH_3)(O \cdot C_6H_{11}O_5) \cdot CHO$, which in turn yields glucose and vanillin on hydrolysis. Artificial vanillin for flavoring purposes is now also prepared from *benzaldehyde*.

**61.** *Cuminic*, or *cumic*, *aldehyde*, or *cuminol*, is 1:4-isopropyl benzaldehyde $C_6H_4 \cdot C_3H_7 \cdot CHO$. It exists together with cymene $C_{10}H_{14}$, in the essentials of cumin, caraway, and water hemlock, and is obtained by agitating either of these oils with acid sodium sulphite $NaHSO_3$, which takes up the cumic aldehyde but not the cymene, and forms a crystalline compound, which, when distilled with potash, yields the cumic aldehyde. Cumic aldehyde is a slightly yellow or colorless liquid of fragrant odor, which boils at 235°.

**62.** *Anisic aldehyde* $C_6H_4(OCH_3) \cdot CHO$ is prepared by heating the essential oils of anise and fennel with dilute nitric acid. These oils contain a fragrant camphor-like substance termed *anethol* $C_{10}H_{12}O$, which there is some ground for representing as derived from phenol $C_6H_5 \cdot OH$, by the replacement of $H$ in $C_6H_5$ by allyl, and of the $H$ in $OH$ by methyl, leading to the rational formula $C_6H_4(C_3H_5)OCH_3$. Anisic aldehyde is a colorless oil, having an aromatic odor and a burning taste. It has a specific gravity of 1.123 and boils at 248°. It is nearly insoluble in water, but soluble in alcohol and ether in all proportions.

**63.** *Pyromucic aldehyde*, or *furfurol* $C_4H_3O \cdot COH$, is formed by the dry distillation of sugar, and by distilling bran with dilute sulphuric acid or zinc chloride. To prepare it, 1 part of bran is mixed with 1 part of sulphuric acid diluted with 3 parts of water, and the distillate is saturated with sodium carbonate mixed with common salt, and again distilled. On adding common salt to the second distillate, the furfurol separates from the watery liquid in the form of a heavy oil. Pyromucic aldehyde is a colorless liquid with a pleasant odor resembling that of bitter almonds; its specific gravity is 1.17 and its boiling point at 162°. It dissolves in twelve times its weight of water and is very soluble in alcohol. This aldehyde unites with acid sodium sulphite, forming a crystalline compound $C_5H_4O_2SO_3NaH$, which is only sparingly soluble in alcohol and which is converted by sodium amalgam into furfuryl alcohol $C_6H_5O_2$. By oxidation with silver oxide, pyromucic aldehyde is converted into the corresponding acid, namely, *pyromucic acid* $C_5H_4O_3$, and by nitric acid, into oxalic acid. With ammonia, it behaves as an aromatic aldehyde, forming furfuramide, in which 3 molecules of furfurol have exchanged $O_3''$ for $N_2'''$:

$$3C_5H_4O_2 + 2NH_3 = (C_5H_4O)_3N_2 + 3H_2O$$

# ORGANIC CHEMISTRY

(PART 4)

## DERIVATIVES OF HYDROCARBONS

### ACIDS

**64. Organic Acids.**—Organic acids, also known as *carbon acids*, may be defined as compounds that contain the univalent group $COOH$ linked to a hydrocarbon radical, and they may be considered as being derived from hydrocarbons, by the substitution of one or more $COOH$ groups for an equal number of hydrogen atoms.

Many of these acids are the second oxidation products of the primary alcohols, the group $\cdot C\begin{matrix}\diagup H_2\\ \diagdown OH\end{matrix}$ in the alcohol being converted into the group $\cdot C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown OH\end{matrix}$, or, in other words, these acids are derived from the primary alcohols by the substitution of 1 atom of $O$ for 2 atoms of $H$. The general formula of an acid, then, is $R\cdot COOH$, where $R$ represents a hydrocarbon residue, or radical. Isomerism among the acids is solely confined to the hydrocarbon radicals.

The basicity of an acid is limited to the number of $COOH$ groups it contains, thus showing that it is the $H$ in this group that is replaced by metals in the formation of salts.

As it is not possible to treat on all the organic acids in detail, the most important acids are enumerated in the following tables, showing their formula, the source from which they are derived, and the group to which they belong.

## TABLE III

### MONOBASIC ACIDS OF THE ACETIC SERIES $C_nH_{2n+1}COOH$

| Name of Acid | Formula | Source |
|---|---|---|
| Formic | $H\cdot CO_2H$ | Red ants and nettles. |
| Acetic | $CH_3\cdot CO_2H$ | Vinegar. |
| Propionic | $C_2H_5\cdot CO_2H$ | Oxidation of oils. |
| Butyric | $C_3H_7\cdot CO_2H$ | Rancid butter. |
| Valeric | $C_4H_9\cdot CO_2H$ | Valerian root. |
| Caproic | $C_5H_{11}\cdot CO_2H$ | Rancid butter. |
| Œnanthic | $C_6H_{13}\cdot CO_2H$ | Oxidation of castor oil. |
| Caprylic | $C_7H_{15}\cdot CO_2H$ | Rancid butter. |
| Pelargonic | $C_8H_{17}\cdot CO_2H$ | Geranium leaves. |
| Rutic, or capric | $C_9H_{19}\cdot CO_2H$ | Rancid butter. |
| Undecylic | $C_{10}H_{21}\cdot CO_2H$ | Oil of rue. |
| Lauric | $C_{11}H_{23}\cdot CO_2H$ | Bayberries. |
| Tridecylic | $C_{12}H_{25}\cdot CO_2H$ | Coconut oil. |
| Myristic | $C_{13}H_{27}\cdot CO_2H$ | Nutmeg butter. |
| Pentadecylic | $C_{14}H_{29}\cdot CO_2H$ | Agaricus integer (a fungus). |
| Palmitic | $C_{15}H_{31}\cdot CO_2H$ | Palm oil. |
| Margaric | $C_{16}H_{33}\cdot CO_2H$ | |
| Stearic | $C_{17}H_{35}\cdot CO_2H$ | Tallow. |
| Nondecylic | $C_{18}H_{37}\cdot CO_2H$ | |
| Arachidic, or butic | $C_{19}H_{39}\cdot CO_2H$ | Butter; earthnut. |
| Nardic | $C_{20}H_{41}\cdot CO_2H$ | Beef fat. |
| Behenic | $C_{21}H_{43}CO_2H$ | Oil of ben. |
| Lignoceric | $C_{23}H_{47}CO_2H$ | Beech-wood tar. |
| Hyænic | $C_{24}H_{49}CO_2H$ | Hyæna fat. |
| Cerotic | $C_{26}H_{53}CO_2H$ | Beeswax. |
| Melissic | $C_{29}H_{59}CO_2H$ | Beeswax. |

## TABLE IV

### MONOBASIC ACIDS OF THE ACRYLIC SERIES $C_nH_{2n-1}CO_2H$

| Name of Acid | Formula | Source |
|---|---|---|
| Erucic, or brassic | $C_{21}H_{41}\cdot CO_2H$ | Colza oil (Brassica oleifera). |
| Crotonic . . . . . . . . | $C_3H_5\cdot CO_2H$ | |
| Angelic. . . . . . . . . | $C_4H_7\cdot CO_2H$ | Angelica root. |
| Pyroterebic . . . . . | $C_5H_9\cdot CO_2H$ | Turpentine. |
| Damaluric . . . . . . | $C_6H_{11}\cdot CO_2H$ | Cow's urine. |
| Campholic . . . . . . | $C_9H_{17}\cdot CO_2H$ | Camphor. |
| Cimicic . . . . . . . . . | $C_{14}H_{27}\cdot CO_2H$ | Tree bug. |
| Hypogæic. . . . . . . | $C_{15}H_{29}\cdot CO_2H$ | Oil of groundnut. |
| Oleic . . . . . . . . . . . | $C_{17}H_{33}\cdot CO_2H$ | Many oils. |
| Doeglic. . . . . . . . . | $C_{18}H_{35}\cdot CO_2H$ | Doegling train oil. |
| Acrylic . . . . . . . . . | $C_2H_3\cdot CO_2H$ | Oxidation of acrolein. |

## TABLE V

### MONOBASIC ACIDS OF THE SORBIC SERIES $C_nH_{2n-3}CO_2H$

| Name of Acid | Formula | Source |
|---|---|---|
| Tetrolic. . . . . . . . . | $C_3H_3\cdot CO_2H$ | Chlorocrotonic acid. |
| Sorbic . . . . . . . . . . | $C_5H_7\cdot CO_2H$ | Mountain-ash berries. |
| Linoleic . . . . . . . . | $C_{15}H_{27}\cdot CO_2H$ | Poppy and linseed oils. |
| Homolinoleic. . . . | $C_{17}H_{31}\cdot CO_2H$ | Cottonseed oil. |
| Behenolic. . . . . . . | $C_{21}H_{39}\cdot CO_2H$ | Brassic acid. |

## TABLE VI

### MONOBASIC ACIDS OF THE BENZOIC SERIES

| Name of Acid | Formula | Source |
|---|---|---|
| Benzoic......... | $C_6H_5 \cdot CO_2H$ | Gum benzoin. |
| Toluic.......... | $C_7H_7 \cdot CO_2H$ | Toluene. |
| Mesitylenic ..... | $C_8H_9 \cdot CO_2H$ | Mesitylene. |
| Cuminic ........ | $C_9H_{11} \cdot CO_2H$ | Cumin oil. |
| Homocuminic ... | $C_{10}H_{13} \cdot CO_2H$ | |

## TABLE VII

### MONOBASIC ACIDS OF THE CINNAMIC SERIES

| Name of Acid | Formula | Source |
|---|---|---|
| Cinnamic ....... | $C_8H_7 \cdot CO_2H$ | Storax. |
| Atropic......... | $C_8H_7 \cdot CO_2H$ | Atropine. |
| Phenyl-crotonic. | $C_9H_9 \cdot CO_2H$ | |
| Phenyl-angelic.. | $C_{10}H_{11} \cdot CO_2H$ | |
| Cumenyl-acrylic. | $C_{11}H_{13} \cdot CO_2H$ | |
| Cumenyl-crotonic | $C_{12}H_{15} \cdot CO_2H$ | |
| Cumenyl-angelic. | $C_{13}H_{17} \cdot CO_2H$ | |

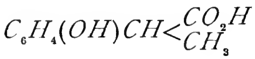
## TABLE VIII

### MONOBASIC ACIDS OF THE LACTIC SERIES

| Name of Acid | Formula | Source |
|---|---|---|
| Glycolic......... | $CH_2(OH) \cdot CO_2H$ | Oxidation of glycol and of alcohol. |
| Lactic .......... | $C_2H_4(OH) \cdot CO_2H$ | Fermentation of milk sugar. |
| Butylactic....... | $C_3H_6(OH) \cdot CO_2H$ | Oxidation of butyl glycol. |
| Valerolactic ..... | $C_4H_8(OH) \cdot CO_2H$ | |
| Leucic .......... | $C_5H_{10}(OH) \cdot CO_2H$ | Oxidation of leucine. |

## TABLE IX

### MONOBASIC HYDROXYACIDS FROM BENZENE HYDROCARBONS

| Name of Acid | Formula | Source |
|---|---|---|
| Salicylic | $C_6H_4(OH)\cdot CO_2H$ | Oil of wintergreen. |
| Anisic | $C_6H_4(OCH_3)\cdot CO_2H$ | Oil of anise. |
| Protocatechuic | $C_6H_3(OH)_2\cdot CO_2H$ | Decomposition of resins by *KOH*. |
| Phloretic |  $C_6H_4(OH)CH{<}\genfrac{}{}{0pt}{}{CO_2H}{CH_3}$ | Decomposition of phloretin by *KOH*. |
| Vanillic | $C_6H_3(OH)(OCH_3)\cdot CO_2H$ | Oxidation of vanillin. |
| Tannic | $C_{13}H_9O_7\cdot CO_2H$ | Gallnuts. |
| Gallic | $C_6H_2(OH)_3\cdot CO_2H$ | Gallnuts. |
| Caffeic | $C_8H_7O_2\cdot CO_2H$ | Coffee. |
| Quinic | $C_6H_{11}O_4\cdot CO_2H$ | Cinchona bark. |
| Ellagic | $C_{13}H_7O_8\cdot CO_2H$ | Bezoar stones. |

## TABLE X

### ACIDS PRODUCED BY OXIDATION OF CARBOHYDRATES

| Name of Acid | Formula | Source |
|---|---|---|
| Saccharic | $C_4H_8O_4(CO_2H)_2$ | Oxidation of sugar. |
| Mucic | | Oxidation of gum. |

## TABLE XI

### ACIDS FROM CLOSED-CHAIN COMPOUNDS

| Name of Acid | Formula | Source |
|---|---|---|
| Pyromucic....... | $C_4H_3O\cdot CO_2H$ | Distillation of mucic acid. |
| Meconic ........ | $C_5H(OH)O_2(CO_2H)_2$ | Opium. |

## TABLE XII

### DIBASIC ACIDS OF THE OXALIC SERIES

| Name of Acid | Formula | Source. |
|---|---|---|
| Oxalic.......... | $CO_2H\cdot CO_2H$ | Wood sorrel. |
| Malonic......... | $CH_2(CO_2H)_2$ | Oxidation of malic acid. |
| Succinic ........ | $C_2H_4(CO_2H)_2$ | Amber. |
| Pyrotartaric..... | $C_3H_6(CO_2H)_2$ | Distillation of tartaric acid. |
| Adipic.......... | $C_4H_8(CO_2H)_2$ | Oxidation of oleic acid. |
| Pimelic......... | $C_5H_{10}(CO_2H)_2$ | Oxidation of oleic acid. |
| Suberic......... | $C_6H_{12}(CO_2H)_2$ | Oxidation of cork. |
| Azelaic......... | $C_7H_{14}(CO_2H)_2$ | Oxidation of castor oil. |
| Sebacic......... | $C_8H_{16}(CO_2H)_2$ | Distillation of oleic acid. |
| Brassylic........ | $C_9H_{18}(CO_2H)_2$ | Oxidation of behenolic acid. |
| Roccellic........ | $C_{15}H_{30}(CO_2H)_2$ | Roccella tinctoria. |

## TABLE XIII

### DIBASIC ACIDS OF THE FUMARIC SERIES

| Name of Acid | Formula | Source |
|---|---|---|
| Fumaric | $C_2H_2(CO_2H)_2$ | Fumitory. |
| Maleic | | Distillation of malic acid. |
| Itaconic | $C_3H_4(CO_2H)_2$ | Distillation of citric acid. |
| Citraconic | | Distillation of citric acid. |
| Mesaconic | | Distillation of citric acid. |
| Hydromuconic | $C_4H_6(CO_2H)_2$ | Distillation of mucic acid. |

## TABLE XIV

### DIBASIC ACIDS OF THE TARTARIC SERIES

| Name of Acid | Formula | Source |
|---|---|---|
| Tartronic | $CH(OH)(CO_2H)_2$ | Oxidation of glycerine. |
| Mesoxalic | $C(OH)_2(CO_2H)_2$ | Oxidation of amidomatonic acid. |
| Malic | $C_2H_3(OH)(CO_2H)_2$ | Unripe apples. |
| Tartaric | $C_2H_2(OH)_2(CO_2H)_2$ | Grape juice. |
| Racemic | | |

## TABLE XV

### DIBASIC ACIDS FROM OXIDATION OF HYDROCARBONS

| Name of Acid | Formula | Source |
|---|---|---|
| Phthalic ........ | $C_6H_4(CO_2H)_2$ | Oxidation of naphthalene. |
| Isouvitic........ | $C_7H_6(CO_2H)_2$ | Gamboge refuse with $KOH$. |
| Cumidic ........ | $C_6H_2(CH_3)_2(CO_2H)_2$ | Oxidation of durene. |

## TABLE XVI

### TRIBASIC VEGETABLE ACIDS

| Name of Acid | Formula | Source |
|---|---|---|
| Tricarballylic.... | $C_3H_5(CO_2H)_3$ | Beet root. |
| Citric........... | $C_3H_4(OH)(CO_2H)_3$ | Lemon juice. |
| Aconitic ........ | $C_3H_3(CO_2H)_3$ | Monkshood. |

## TABLE XVII

### ACIDS CONTAINING NITROGEN

| Name of Acid | Formula | Source |
|---|---|---|
| Hydrocyanic .... | $CNH$ | Fermentation of bitter almonds. |
| Picric........... | $C_6H_2(NO_2)_3OH$ | Nitration of phenol. |
| Hippuric........ | $C_8H_8NO\cdot CO_2H$ | Horse urine. |
| Uric............ | $C_5H_4N_4O_3$ | Human urine. |

## ACIDS FROM MONOHYDRIC ALCOHOLS OF THE PARAFFIN HYDROCARBONS

**65.** These acids belong to the *fatty*, or *acetic*, *series*, and are therefore also known as *fatty acids*. The lower members of this series are of an oily consistency, while the higher members are fatty solids.

**66. Formic Acid.**—Formic acid $H\cdot CO_2H$ was discovered by S. Fischer, in 1670. It occurs in nature in red ants, in stinging nettles, in the young shoots of certain varieties of coniferous trees, etc. Formic acid is formed in a great number of reactions, particularly in the oxidation of methyl alcohol, in the decomposition of hydrocyanic acid by acids or alkalies, in the distillation of oxalic acid, and in the oxidation of many organic matters, such as starch, sugar, etc. Berthelot achieved its direct synthesis by heating carbon monoxide for a long time at 100° in a sealed tube containing a concentrated solution of potassium hydrate:

$$CO + KOH = \underset{\text{potassium formate}}{HCO\cdot OK}$$

It is best prepared by distilling oxalic acid with glycerine. Thirty grams of crystallized oxalic acid and 200 cubic centimeters of glycerine are heated in a flask of about 500 cubic centimeters capacity, which is provided with a thermometer and connected with a Liebig condenser (an apparatus similar to that usually used for distilling operations), to about 80° to 90°, when formic acid distils over, together with the water of crystallization of the oxalic acid, and carbonic-acid gas is evolved:

$$CO_2H\cdot CO_2H = H\cdot CO_2H + CO_2$$

When the evolution of $CO_2$ ceases, a fresh quantity of oxalic acid may be added and the operation continued, the same glycerine serving for the conversion of a large quantity of oxalic acid. The formic acid first produced converts the glycerine into *monoformin*; thus,

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{formic acid}}{H\cdot CO_2H} = \underset{\text{monoformin}}{C_3H_5(OH)_2(CO_2H)} + H_2O$$

The monoformin is then decomposed by the water of crystallization of the oxalic acid, the equation being reversed, and glycerine being reproduced. By continuing this process, formic acid of 56-per-cent. strength may be obtained.

To obtain the acid in its most concentrated state, the dilute acid is saturated with lead oxide, the liquid is evaporated to complete dryness, and the dried lead formate thus obtained, reduced to a fine powder, is very gently heated in a glass tube connected with a condensing apparatus, through which a current of dry hydrogen sulphide passes. The formic acid is then redistilled with a little lead formate to remove all traces of $H_2S$.

Pure anhydrous formic acid is a clear, colorless liquid, which slightly fumes in the air. It has a specific gravity of 1.22, boils at 99°, and crystallizes in large brilliant plates when cooled to 0°. It has a pungent smell, and is extremely corrosive, attacking the skin and producing rather painful blisters, or ulcers, which heal very slowly. It mixes in all proportions with water, alcohol, and ether; the aqueous solution of formic acid closely resembles acetic acid in taste and odor. It is inflammable and burns with a blue flame. If formic acid is added to a solution of silver nitrate and the liquid is heated, it soon becomes clouded, and silver is precipitated and carbon dioxide disengaged, the formic acid being oxidized in reducing the silver nitrate:

$$H \cdot CO_2H + O = CO_2 + H_2O$$

**67. Formates.**—Formic acid is a very energetic acid, which strongly reddens blue litmus paper and perfectly neutralizes the bases. As formic acid is a monobasic acid, one of its hydrogen atoms can be replaced by an equivalent atom of a metal and thus a salt is formed; these salts are known as *formates*, and their general formulas may be expressed as $M'CHO_2$, $M''(CHO_2)_2$, $M'''(CHO_2)_3$, etc., according to the valence of the metal, which is indicated in the general formula by $M'$, $M''$, $M'''$, etc. All the formates are soluble in water, and their solutions form dark-red mixtures with ferric salts. When distilled with strong sulphuric acid, they give off carbon monoxide and leave a residue of sulphate.

The most characteristic formates are *cupric formate* $Cu(CHO_2)_2,4H_2O$, which crystallizes in magnificent prisms, and *lead formate* $Pb(CHO_2)_2$, which forms long colorless needles.

Formic acid is used in making some of the coal-tar dyes.

**68. Acetic Acid.**—Acetic acid, or *methyl-formic acid* $CH_3 \cdot CO_2H$, is the acid of vinegar. It is the product of the oxidation of alcohol. It is formed in various other reactions, among which are the oxidation of aldehyde, the action of carbon dioxide on sodium methyl, the decomposition of methyl cyanide by potassium hydrate, and last, but not least, the dry distillation of a great number of common organic substances, such as *wood*, *starch*, *sugar*, *gum*, etc.

Large quantities of acetic acid are annually used in the arts, and they are mostly obtained by the destructive distillation of wood or sawdust. The distillation is conducted in large iron cylinders, heated directly by a fire, to which a worm, or condenser, continually cooled by a circulation of cold water through pipes surrounding it, is attached. A sour, watery liquid, a quantity of tar, and a large quantity of inflammable gas pass over, while charcoal remains in the retort. The acid liquid is subjected to distillation, the first portion being collected apart for the preparation of wood spirit. The remainder is saturated with lime, concentrated by evaporation, and mixed with a solution of sodium sulphate, whereby calcium sulphate is precipitated, while the acetic acid combines with the soda. The filtered solution is evaporated to its crystallizing point; and the crystals are drained as much as possible from the dark, tarry mother-liquor, and deprived by heat of their combined water. The dried salt is then cautiously fused, by means of which the last portions of the accompanying tar are either decomposed or expelled; the fused salt is then redissolved in water and recrystallized. Pure sodium acetate, thus obtained, readily yields acetic acid by distillation with sulphuric acid.

**69. Vinegar.**—Vinegar is the product of the acid fermentation of wine and other alcoholic liquids. The following process, known as the *Orleans process*, is largely employed for the conversion of wine into vinegar. A small quantity of warm vinegar is first introduced into large vats, which have already been used for the operation and are therefore impregnated with the peculiar ferment formed; quantities of wine are then added at intervals of several days, the vats being maintained at a temperature between 24° and 27°. In about two weeks, the acetification is complete, and a portion of the vinegar is withdrawn and replaced by a new quantity of wine, which also becomes converted into vinegar—thus making the process continuous. Under these circumstances, the alcohol is converted into acetic acid by the influence of a microscopic organism known as *Mycoderma aceti*, which appears on the surface of the liquid, where it absorbs oxygen from the air and subsequently cedes it to the alcohol. Its action may be compared with that of platinum black.

*Quick Vinegar Process.*—A weak spirit mixed with a little yeast or beet-root juice, heated to about 27°, is caused to trickle slowly from pieces of cord fixed in a perforated shelf over a quantity of wooden shavings previously soaked in vinegar to impregnate them with the mycoderm, or acetic ferment. The shavings are packed in a tall barrel (see Fig. 6) in which holes have been bored in order to allow the passage of air. The oxidation of the alcohol soon raises the temperature to about 38°, which occasions a free circulation of air among the shavings. The mixture is passed three or four times through the barrel, and in about 36 hours the conversion into vinegar is

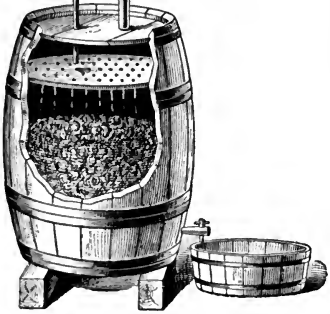


FIG. 6

completed. If the supply of air is insufficient, alcohol is lost in the form of aldehyde vapor, the irritating odor of which pervades the air.

White vinegar is prepared from light wines by a similar process. Malt vinegar is made from infusion of malt fermented by yeast with free contact of air.

Vinegar contains, on an average, from 4 to 8 per cent. of acetic acid. Its aroma is due to the presence of a little acetic ether. Apple, or cider, vinegar is most esteemed for domestic use in this country; but in most of the European countries, wine vinegar is preferred.

By distilling vinegar, a weak acetic acid is obtained, which may be concentrated by redistilling and receiving separately the portion distilling between 110° and 120°.

**70. Properties of Acetic Acid.**—Acetic acid is a strongly acid liquid of pungent odor; it feels slippery to the touch, blisters the skin, and solidifies in the cold to large crystalline plates, which melt at 17° (glacial acetic acid). It boils at 118° and burns with a flame similar to that of alcohol. The specific gravity of the pure acid is 1.063 at 18°; the strength of this acid cannot, however, be inferred from its specific gravity, as with other liquids, owing to the fact that it is increased by addition of water until it reaches 1.079 (70 per cent. of acid), when it is diminished by the addition of more water, so that a 50-per-cent. acid has the same specific gravity as the pure acid.

Acetic acid is one of the most stable of the organic acids, and it is unattacked by most oxidizing agents. When its vapor is passed through a red-hot tube, it yields several products, among which marsh gas and acetone are conspicuous. Most of its salts, known as *acetates*, are soluble in water, so that they are not easily precipitated; but if acetic acid is exactly neutralized by ammonia and stirred with silver nitrate, a precipitate of *silver acetate* $CH_3 \cdot CO_2Ag$ is obtained, and *mercurous acetate* $CH_3 \cdot CO_2Hg$ may be obtained in a similar way. Ferric chloride added to the neutral solution gives a fine red color.

**71.** A large number of acetates find employment of various kinds in the arts. Those formed by the weaker bases, such as $Fe_2O_3$ and $Al_2O_3$, are easily decomposed by boiling with water, basic acetates being precipitated; hence, the aluminum and ferric acetates are much used by dyers and calico printers as *mordants*, the basic acetates being deposited in the fabric, and forming insoluble compounds with coloring matters.

*Potassium acetate* $KC_2H_3O_2$ is prepared by saturating acetic acid with potassium carbonate, and evaporating to dryness; it is thus obtained as a crystalline, deliquescent mass, which is very soluble in water, and which melts at 292°.

*Sodium acetate* $NaC_2H_3O_2,3H_2O$ is prepared by neutralizing acetic acid with sodium carbonate. It crystallizes in prisms, which are very soluble in water and become efflorescent in dry air.

*Neutral lead acetate* $Pb(C_2H_3O_2)_2,3H_2O$, which is commonly known as *sugar of lead*, is made on the large scale by dissolving lead oxide in acetic acid. It crystallizes well, and is soluble in 1.5 parts of water at ordinary temperatures. It has a nauseous, sweet taste, and is poisonous. It melts in its water of crystallization at 75°.

The neutral solution of lead acetate dissolves oxide of lead, forming basic salts, according to the amount of lead oxide dissolved. The more important of these are a *dibasic lead acetate* $Pb(C_2H_3O_2)_2,PbO,4H_2O$ and a *tribasic lead acetate* $Pb(C_2H_3O_2)_2,2PbO,nH_2O$. These two salts are, as a rule, simultaneously formed when a solution of lead acetate and litharge are boiled together. It is used in the laboratory and is known to the pharmacist as *Goulard's extract.* If a few drops of it are added to ordinary water, a cloud is produced, owing to the formation of lead carbonate. If carbonic-acid gas is passed into a solution of the sub-acetate of lead, a deposit of lead carbonate is obtained.

*Neutral copper acetate* $Cu(C_2H_3O_2)_2,H_2O$ is prepared through double decomposition by mixing hot solutions of sodium acetate and cupric sulphate. The cupric acetate is deposited on cooling in beautiful prisms of a deep bluish-green color. They dissolve in five times their weight of boiling water. The dilute aqueous solution is decomposed by boiling, a tribasic acetate being formed, while acetic acid is liberated. When cupric acetate is heated, it first loses its water of crystallization, and decomposes when the temperature reaches about 240°, disengaging acetic acid, acetone, and carbon dioxide. The residue is finely divided copper. The product of the distillation is a blue liquid, which, when rectified, yields colorless acetic acid mixed with a small quantity of acetone.

The name *verdigris* is applied to a basic acetate of copper consisting mostly of a dibasic acetate $Cu(C_2H_3O_2), CuO, 6H_2O$. Verdigris is prepared by exposing to the air copper sheets piled up in layers with the pulp of grapes. In a few weeks the metal becomes covered with bluish crusts of verdigris, which are scraped off and brought on the market in the form of light-blue balls. The alcohol formed by the fermentation of the sugar contained in the grape pulp, becomes oxidized by the air and is converted into acetic acid, and under the influence of the latter, the copper itself absorbs oxygen. Water and basic copper acetate are thus formed.

*Emerald Green.—Emerald green*, or *cupric aceto-arsenite* $(CH_3 \cdot CO_2)_2Cu, Cu_3(AsO_3)_2, As_4O_6$ is made by boiling verdigris with white arsenic water. It is used for coloring wall papers, etc., notwithstanding its poisonous character.

*Ferric acetate* $Fe(C_2H_3O_2)_3$ and ferrous acetate $Fe(C_2H_3O_2)_2$ are much used in the arts. The aqueous solution of ferric acetate has a blood-red color. It is decomposed when boiled, precipitating ferric hydroxide and acetic acid. Under the name of *iron liquor*, ferrous acetate is largely used as a mordant in dyeing.

*Silver acetate* $AgC_2H_3O_2$ is only slightly soluble in water, and is precipitated when concentrated solutions of sodium acetate and silver nitrate are mixed. It is deposited from boiling water in brilliant, pearly, flexible plates, which darken on exposure to light, as all silver salts do.

*Ammonium acetate* $NH_4C_2H_3O_2$ is obtained as a deliquescent, crystalline mass, when acetic acid is saturated by a current of ammonia gas. It is very soluble in water, as well as in alcohol, and when subjected to heat, it first loses ammonia, then acetic acid, and finally distils as *acetamide:*

$$NH_4C_2H_3O_2 = H_2O + \underset{\text{acetamide}}{C_2H_3O \cdot NH_2}$$

When distilled in the presence of phosphoric anhydride, ammonium acetate yields *methyl cyanide*, or *acetonitrile:*

$$NH_4C_2H_3O_2 = C_2H_3N + 2H_2O$$

**72. Synthesis of Acetic Acid.**—Acetic acid has been obtained synthetically by the following reactions:

1. $C$ heated in vapor of $S$ yields $CS_2$.

2. $CS_2$ vapor mixed with $Cl$ and passed through a red-hot tube yields:

$$CS_2 + 3Cl_2 = S_2Cl_2 + CCl_4$$

3. Vapor of $CCl_4$ passed through a red-hot tube yields chlorine and *tetrachlorethene* $C_2Cl_4$.

4. $C_2Cl_4$ acted on by $Cl$ and water, in sunlight, yields *trichloracetic acid:*

$$C_2Cl_4 + Cl_2 + 2H_2O = 3HCl + CCl_3 \cdot CO_2H$$

5. When trichloracetic acid is acted on by nascent hydrogen, it yields acetic acid:

$$CCl_3 \cdot CO_2H + 6H = CH_3 \cdot CO_2H + 3HCl$$

The acid may also be prepared from methane by the action of carbon oxychloride, which converts it into acetyl chloride, a compound that furnishes acetic acid when decomposed by water:

$$(1) \qquad CH_4 + COCl_2 = CH_3 \cdot COCl + HCl$$

$$(2) \qquad CH_3 \cdot COCl + HOH = CH_3 \cdot COOH + HCl$$

The group $CH_3 \cdot CO$, which remains unchanged during the last reaction, is known as *acetyl* $C_2H_3O$, and may be considered as ethyl $C_2H_5$, in which $H_2$ has been replaced by $O''$.

There is a similar *acid radical* corresponding with each *alcohol radical;* a few examples are given below:

| *Alcohol Radicals* | *Acid Radicals* |
|---|---|
| Methyl $CH_3$ | Formyl $CHO$ |
| Ethyl $CH_3 \cdot CH_2$ | Acetyl $CH_3 \cdot CO$ |
| Propyl $C_2H_5 \cdot CH_2$ | Propionyl $C_2H_5 \cdot CO$ |
| Butyl $C_3H_7 \cdot CH_2$ | Butyryl $C_3H_7 \cdot CO$ |
| Amyl $C_4H_9 \cdot CH_2$ | Valeryl $C_4H_9 \cdot CO$ |

It will be seen later that the alcohol radicals combine in pairs with oxygen to produce ethers of the type $\begin{matrix}R\\R'\end{matrix}\!>O$. The acid radicals combine with oxygen in a similar manner to produce *acid anhydrides*, such as $\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!>O$, acetic anhydride.

**73.** *Acetic anhydride*, or *diacetyl oxide*, also known as *anhydrous acetic acid* $(CH_3 \cdot CO)_2O$, is prepared by distilling acetyl chloride with an equal weight of perfectly anhydrous sodium acetate:

$$CH_3COCl + CH_3 \cdot COONa = (CH_3CO)_2O + NaCl$$

It distils over as a colorless heavy oil, smelling of acetic acid, and irritating the eyes. Its boiling point is at 137°, and its specific gravity is 1.073. It dissolves slowly in water, being gradually converted into acetic acid:

$$(C_2H_3O)_2O + H_2O = 2C_2H_3O(OH)$$

Acetic anhydride may also be prepared by heating lead acetate with carbon disulphide:

$$2Pb(CH_3CO_2)_2 + CS_2 = 2(CH_3 \cdot CO)_2O + 2PbS + CO_2$$

By carefully acting on acetic anhydride with sodium amalgam and water, it has been converted into aldehyde and alcohol:

$$(CH_3 \cdot CO)_2O + 2H_2 = 2(CH_3 \cdot CHO) + H_2O$$

and $$CH_3 \cdot CHO + H_2 = CH_3 \cdot CH_2 \cdot OH$$

From this circumstance it is called acetyl hydride—a name sometimes given, as already mentioned, to aldehyde.

*Acetyl dioxide*, or *acetic peroxide* $(CH_3\cdot CO)_2O_2$, is a remarkable compound, obtained by the action of barium dioxide on acetic anhydride. It is a thick liquid, possessing energetic oxidizing properties, and it decomposes with explosive violence on heating.

**74. Propionic Acid.**—Propionic acid $C_2H_5\cdot CO_2H$ is formed in small quantities by the distillation of wood, and by the fermentation of various organic bodies, particularly calcium lactate and tartrate. It is prepared most readily by treating ethyl cyanide with caustic potash:

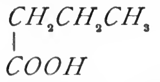
$$C_2H_5\cdot CN + KOH + H_2O = C_2H_5\cdot CO_2K + NH_3$$

or by the action of carbon dioxide on sodium ethyl:

$$CO_2 + NaC_2H_5 = C_2H_5\cdot CO_2Na$$

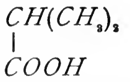
Propionic acid is a colorless liquid with penetrating odor, somewhat resembling that of acetic acid. It has a specific gravity of .99 and boils at 141°. It is miscible with water in all proportions. It is not of any importance in the arts. The *propionates* are, as a whole, easily soluble in water, *silver propionate*, however, being an exception, as it is only sparingly soluble therein. *Lead propionate* is much more difficult to crystallize than lead acetate.

**75. Butyric Acids.**—Butyric acid $C_3H_7CO_2H$ exists in two modifications; viz.:



$$\begin{array}{l}CH_2CH_2CH_3\\ |\\ COOH\end{array}$$

normal butyric acid



$$\begin{array}{l}CH(CH_3)_2\\ |\\ COOH\end{array}$$

isobutyric acid

The *normal acid* was discovered in butter, where it exists combined with glycerol in *butyrin*, by Chevreul, a French chemist. The normal acid is usually prepared from cane sugar by dissolving it in water, adding a little tartaric acid, boiling to convert the sucrose into glucose, and adding to the cooled liquid some putrid cheese rubbed up in about thirty times its weight of milk. Some chalk is stirred into the mixture, which is then allowed to ferment for a week at a temperature of from 30° to 35°. The glucose $C_6H_{12}O_6$ undergoes the *lactic fermentation*, and is converted into lactic acid $C_3H_6O_3$, which is converted by the chalk into calcium lactate, forming a pasty mass of crystals. After a time the mass becomes liquid again, evolving bubbles of hydrogen and carbon dioxide, and forming a strong solution of calcium butyrate, produced by the *butyric fermentation.* When this is mixed with strong hydrochloric acid, the butyric acid rises to the surface and forms an oily layer, which may be removed and purified by distillation.

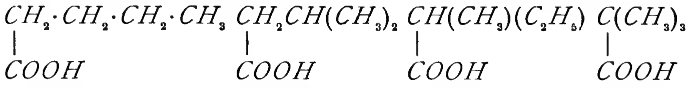
Butyric acid is a colorless liquid having a very disagreeable smell, similar to that of rancid butter; it has a specific gravity of .96 and boils at 163°. It is very strongly acid and quite soluble in water. Butyric acid perfectly neutralizes the bases, forming *butyrates.* These compounds are mostly soluble in water and have a fatty feel. *Calcium butyrate* $Ca(C_4H_7O_2)_2$ is more soluble in cold than in hot water; its cold saturated solution becomes a solid mass when heated to 70°.

*Isobutyric acid* $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH-CO\cdot OH$ occurs in the free state in the fruit of the *Ceratonia siliqua* (St. John's bread), and as ether in *parsnip oil.* It is formed by the oxidation of isobutyl alcohol, and it may be obtained by decomposing isopropyl cyanide:

$$C_3H_7CN+2H_2O = NH_3+C_3H_7\cdot CO_2H$$

This acid in general closely resembles normal butyric acid, but its odor is less pungent and offensive. It is not soluble in water, its specific gravity is .96, and it boils at 154°.

**76. Valeric Acids.**—Four varieties of valeric acid, having the formula $C_4H_9\cdot CO_2H$, are possible and known:



$$\begin{array}{cccc} CH_2\cdot CH_2\cdot CH_2\cdot CH_3 & CH_2CH(CH_3)_2 & CH(CH_3)(C_2H_5) & C(CH_3)_3 \\ | & | & | & | \\ COOH & COOH & COOH & COOH \end{array}$$

| | | | |
|---|---|---|---|
| propyl acetic,<br>or<br>normal valeric, acid | isopropyl acetic,<br>or<br>isovaleric, acid | methyl ethyl<br>acetic acid | trimethyl<br>acetic acid |

*Propyl acetic*, or *normal valeric, acid* $C_4H_9\cdot COOH$ is an oily liquid; it has a specific gravity of .957 and boils at 185°. Its odor somewhat resembles that of butyric acid, though it is not quite as intense.

*Isopropyl acetic*, or *isovaleric, acid* is the so called *ordinary valeric acid.* It was discovered by Chevreul, who obtained it from dolphin oil. It occurs in valerian root, angelica root, and many other plants. It is prepared by oxidizing amyl alcohol with a mixture of potassium dichromate and sulphuric acid; 4 parts of potassium dichromate, 6 parts of oil of vitriol, and 8 parts of water are mixed in a good sized retort, to which 1 part of amyl alcohol is cautiously added, the retort being kept in ice-cold water to moderate the violence of the reaction. When the change appears complete, the deep-green liquid is distilled nearly to dryness, the product mixed with excess of potassium hydrate, and the aqueous solution separated from the oily, colorless liquid, which floats upon it. The alkaline solution is then evaporated and decomposed by sulphuric acid. The greater part of the valeric acid then separates out as an oily liquid which is lighter than water; this liquid is a hydrate, having the composition $C_5H_{10}O_2, H_2O$. When distilled alone, it undergoes decomposition; at first water with a little of the acid appears, which is eventually followed by the pure acid $C_5H_{10}O_2$. Isovaleric acid is a thin, oily liquid with an odor characteristic to the valerian root. It has a specific gravity of .947 and boils at 175°. It dissolves in 30 parts of water, from which it is precipitated by the addition of neutral salts. It has a sharp acid taste, reddens litmus paper, and burns with bright but smoky flame.

*Trimethyl acetic acid*, sometimes called *neopentoic acid*, is formed when potassium hydrate is boiled with cyanide derived from trimethyl carbinol:

$$(CH_3)_3C\cdot CN + 2H_2O = (CH_3)_3C\cdot COOH + NH_3$$

It is a crystalline mass, fusible at 35°, and boiling at 163°. It is soluble in about 40 parts of water at 20°.

**77. Caproic, or Hexoic, Acids.**—These acids have the formula $C_5H_{11}\cdot CO_2H$; they occur in cow's and goat's milk, in certain cheeses, etc. Eight modifications are possible, though only five of them are known so far.

*Normal caproic*, or *pentyl formic, acid* $CH_3(CH_2)_4 \cdot CO_2H$ may be obtained by heating normal pentyl cyanide $CH_3(CH_2)_4CN$ with a strong solution of potash. It is also produced, together with other acids of the fatty series, by the oxidation of albuminous substances. It is a clear, oily liquid of sweet, pungent odor. It has a specific gravity of .945 and boils at 205°.

**78. Œnanthic, or Heptoic, Acid.**—Œnanthic acid $C_6H_{13} \cdot CO_2H$ is found among the products of fats distilled by superheated steam. It may also be obtained by oxidizing œnanthic aldehyde with potassium dichromate and sulphuric acid. It has a disagreeable odor, boils at 223°, and has a specific gravity of .93. Many of the *œnanthates*, i. e., salts of œnanthic acid, are nearly insoluble in water. The strong solutions of the alkali œnanthates become gelatinous on cooling, like solution of soap.

**79. Caprylic, or Octoic, Acid.**—Caprylic acid $C_7H_{15} \cdot CO_2H$ occurs as a glyceride in the butter made of cow's milk, in coconut oil, and in human fat, and is found in the fusel oil of wines and in old cheese. It is the first acid of this series that exists as a solid at ordinary temperatures. It fuses at 16° and boils at 236°; it has a faint but unpleasant odor, which becomes more distinctive on heating. It is only very sparingly soluble in water. The *caprylates*, with the exception of those of the alkalies, are hardly soluble in water, but dissolve more freely in alcohol.

**80. Pelargonic, or Nonoic, Acid.**—Pelargonic acid $C_8H_{17}CO_2H$ was originally obtained from the leaves of the geranium (*Pelargonium roseum*). It is also obtained by the action of nitric acid on the essential oil of rue. It is an oily liquid of faint and slightly unpleasant odor; it boils at 253° and crystallizes when cooled to 12°. It has a specific gravity of .91 and is not soluble in water.

**81. Rutic, or Capric, Acid.**—Rutic acid $C_9H_{19}CO_2H$ occurs as a glyceride in butter, coconut oil, and fusel oils. It is obtained pure, but only in comparatively small quantities, from the fusel oil of the Scotch whisky distilleries, after the amyl alcohol has been distilled off at 132°. This residue consists chiefly of amyl rutate, and when this is distilled with potash, amyl alcohol is given off and potassium rutate is left behind, from which rutic acid is obtained by redistillation with sulphuric acid.

Rutic acid is a slightly odorous, crystalline, solid substance, which fuses at 28.5° and boils at 269°; its odor increases when it is warmed, and resembles somewhat the odor of goats. It does not dissolve in cold water, but in hot water, alcohol, ether, or nitric acid it is slightly soluble.

**82. Lauric, or Dodecatoic, Acid.**— Lauric acid $C_{11}H_{23}\cdot CO_2H$ is obtained from a fatty substance in the fruits of the bay tree (*Laurus nobilis*), and in the solid fat and volatile oil of pichurim beans, or sassafras nuts (*Faboe Pichurim maj.*). It is prepared by saponifying these fats with a caustic alkali, and decomposing the resulting soap with either hydrochloric or tartaric acid. Lauric acid is a crystalline solid, which fuses at 44°. It is insoluble in water, but dissolves readily in alcohol, from which it separates in needle-shaped crystals.

**83. Palmitic Acid.**—Palmitic acid $C_{15}H_{31}CO_2H$ is the first of the fatty acids, which are found as glycerides in vegetable and animal fats, and which form true *soaps* with the alkalies, such soaps being the salts formed by the fatty acid with the alkali metal; they are characterized by easy lathering when dissolved in soft water, by being precipitated from their aqueous solution by $NaCl$, and by giving an oily layer of the melted fatty acid with any of the common mineral acids.

Palmitic acid is prepared on a large scale by distilling palm oil by means of superheated steam, which decomposes the oil into fatty acids and glycerol. The fatty acids solidify on cooling. The preparation of palmitic acid in the laboratory consists in boiling palm oil with potash, by which it is converted into potassium palmitate and oleate; to this is added some dilute sulphuric acid, by which a mixture of palmitic and oleic acid is precipitated. This mixed precipitate is washed and dried, and then dissolved in hot alcohol, from which the palmitic acid crystallizes out on cooling, leaving the oleic acid in solution.

Palmitic acid is a colorless, tasteless solid. It is insoluble in water, but readily soluble in hot alcohol and ether, forming acid solutions from which the acid crystallizes out in needles, or separates in a solid mass on cooling. It melts at 62°, and, at a higher temperature, takes fire and burns with a bright, but somewhat smoky flame. It forms salts having the composition $M'C_{16}H_{32}O_2$, $M''(C_{16}H_{32}O_2)_2$, etc., known as *palmitates*. The substance known as *adipocere*, a wax-like mass, which is left when animal bodies decompose in the earth, is a mixture of calcium and potassium palmitates.

**84. Margaric Acid.**—Margaric acid $C_{16}H_{33}\cdot CO_2H$ is obtained by boiling cetyl cyanide with potassium hydroxide:

$$C_{16}H_{33}CN + KOH + H_2O = NH_3 + C_{17}H_{33}O_2K$$

The solid potassium salt thus obtained is decomposed by boiling dilute hydrochloric acid, and the separated margaric acid is precipitated and purified. Margaric acid crystallizes like palmitic acid, the crystals fuse at 60°, and are soluble in alcohol as well as in ether.

**85. Stearic Acid.**—Stearic acid $C_{17}H_{35}\cdot CO_2H$ may be extracted from suet by boiling it with potash, decomposing the resulting soap with hydrochloric acid, drying the separated fatty acids, and dissolving them in the least possible quantity of hot alcohol. This retains the oleic acid in solution and deposits a mixture of stearic and palmitic acid on cooling; the mixture is carefully dried between paper, and the crystallization process from alcohol repeated a few times until the mixture fuses at 69°. The stearic acid exists in suet, and nearly all other solid fats, in the form of the glyceride *stearin*, mixed with palmitin and a little olein. When saponified by potash, these yield the stearate, palmitate, and oleate of potassium. On the large scale, impure stearic acid is prepared for the manufacture of stearin candles by saponifying some of the harder fats, generally with lime. The resulting lime soap, decomposed by sulphuric acid, yields a mixture of fatty acids, which are pressed, first in the cold, and afterwards at a higher temperature, in order to separate the oleic acid from the less fusible palmitic and stearic acids.

Stearic acid is a crystalline solid, melting at 69.2°. After cooling, the fused stearic acid becomes a laminated, white mass. Its specific gravity is 1, thus equaling that of water. It does not dissolve in water, but is soluble in alcohol and ether. The alcoholic solution deposits it in small pearly scales, which appear to have lost their greasy touch. It is inflammable, and burns with a bright luminous flame. The alkalies dissolve stearic acid on heating, forming *stearates*, which are the components of ordinary soap. White, common soap made from tallow and soda consists principally of *sodium stearate* $C_{17}H_{35} \cdot CO_2Na$, which may be crystallized from alcohol. It dissolves in a little water to a clear solution, but when this is largely diluted, it deposits scaly crystals of the *acid sodium stearate* $(C_{17}H_{35} \cdot CO_2)_2HNa$. *Potassium stearate* behaves in a similar way. The other stearates are insoluble; those of calcium and magnesium are precipitated when hard water is brought in contact with the soap.

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## MONOBASIC ACIDS FROM MONOHYDRIC ALCOHOLS OF THE OLEFINE SERIES

**86. Acrylic, or Oleic, Series of Acids.**—*Acrylic acid* $CH_2 : CH \cdot CO_2H$ is prepared by the oxidation of acrolein by oxide of silver:

$$C_2H_3 \cdot CHO + Ag_2O = C_2H_3 \cdot CO_2H + Ag_2$$

Acrylic acid is a colorless liquid with a strong and slightly aromatic odor, and is miscible in all proportions with water. It solidifies at low temperature, melts at 7°, and boils at 140°. Nascent hydrogen converts it into propionic acid $C_2H_5 \cdot CO_2H$.

The metallic *acrylates*, except the silver salt, are very soluble in water, but decompose when heated to 100°. *Silver acrylate* $C_3H_3O_2Ag$ and *lead acrylate* $(C_3H_3O_2)_2Pb$ crystallize in shining needles. *Potassium acrylate*, fused with potassium hydroxide, yields acetate and formate of potassium, as will be seen from the subjoined equation:

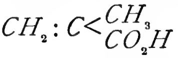
$$C_2H_3\cdot CO_2K + KOH + H_2O = CH_3\cdot CO_2K + H\cdot CO_2K + H_2$$

**87. Crotonic Acids.**—Crotonic acid has the formula $C_3H_5\cdot CO_2H$, and three modifications of this acid are known:

1. *Solid crotonic acid* $CH_3\cdot CH:CH\cdot CO_2H$ occurs in crude pyroligneous acid, and is obtained by oxidizing crotonic aldehyde with silver oxide. Solid crotonic acid crystallizes in slender needles or in large plates; it melts at 72°, and boils at 180°. It dissolves in 12 parts of water at 20°. It has an odor like that of butyric acid, into which it is converted by nascent hydrogen. Fused $KOH$ converts it into potassium acetate:

$$C_3H_5\cdot CO_2H + 2KOH = 2(CH_3\cdot CO_2K) + H_2$$

2. *Isocrotonic acid* $CH_2:CH\cdot CH_2\cdot CO_2H$ occurs in croton oil. When $PCl_5$ acts on ethylaceto-acetate, it produces β-isochloro-crotonic acid $CH_3\cdot CH:CCl\cdot CO_2H$, which, by treatment with nascent hydrogen, yields isocrotonic acid. It is a liquid, has a specific gravity of 1.018 at 25°, boils at 172°, and is converted into the solid acid at 180°. When fused with $KOH$, it is converted into acetate.



3. *Methylacrylic acid* $CH_2:C<^{CH_3}_{CO_2H}$ occurs in chamomile oil. It is a crystalline solid, with an odor resembling that of mushrooms; it melts at 16° and boils at 160°. It is converted by nascent hydrogen into isobutyric acid, and when fused with $KOH$, yields propionate and formate.

**88. Angelic Acid.**—Angelic acid $C_4H_7\cdot CO_2H$ exists in angelica root, in the flowers of chamomile, and in moschus root, a drug imported from Asia Minor. It is obtained from angelica root by boiling it with water and lime, and distilling the filtered and concentrated liquid with dilute sulphuric acid. Angelic acid crystallizes in long prisms and needles, fusing at 45° and boiling at 185°. It has an aromatic taste and odor, and is soluble in hot water and in alcohol and ether. When boiled for some time, it is converted into an isomeride, *methyl crotonic*, or *tiglic, acid* $C_3H_4(CH_3)\cdot CO_2H$, which is also obtained from croton oil, and together with angelic acid from cumin oil (*Cuminum cyminum*). Fused with $KOH$, angelic acid yields acetate and propionate of potassium.

**89. Pyroterebic Acid.**—Pyroterebic acid $C_5H_9\cdot CO_2H$ is produced by the distillation of terebic acid $C_7H_{10}O_4$, which is a product of the action of nitric acid on turpentine. It is an oily liquid with a characteristic odor, having a specific gravity of 1.01 and a boiling point at 210°. Fused $KOH$ converts it into acetate and butyrate of potassium.

**90. Hypogæic Acid.**—Hypogæic acid $C_{15}H_{29}\cdot CO_2H$ is extracted from the groundnut (*Arachis hypogæa*). It is also obtained by the oxidation of *axinic acid* $C_{18}H_{28}O_2$, an acid produced by the saponification of *age*, or *axin*, a fatty substance contained in the Mexican plant *Coccus axinus*. Hypogæic acid is a crystalline body, which fuses at 33°. It is soluble in alcohol as well as ether.

*Physetoleic acid* is isomeric with hypogæic acid and is obtained from spermaceti oil. It is, like its isomeride, a crystalline body, but differs from it by fusing at 30°.

*Goeidic acid* is another isomeride, which is obtained by the action of nitrogen trioxide $N_2O_3$ on hypogæic acid. It fuses at 38°.

**91. Oleic Acid.**—Oleic acid $C_{17}H_{33}\cdot CO_2H$, the most important acid of this series, is present as olein in the fatty oils, as, for instance, olive and almond oils. It may be prepared by boiling olive oil with potash, and decomposing the solution with hydrochloric acid; the oleic acid is separated as a fatty layer contaminated with a little stearic and palmitic acid. To purify the oleic acid thus obtained, it is heated over the water bath with litharge at about 100° for 2 to

3 hours, when a mixture of oleate, stearate, and palmitate of lead is formed. The mixture is then treated with ether, which dissolves the lead oleate. The liquid is decanted, and vigorously shaken with hydrochloric acid, whereby the lead is precipitated as chloride, while the oleic acid remains in solution in the ether. The ether is distilled off, the impure oleic acid is dissolved in ammonia, and precipitated by barium chloride; the barium oleate thus obtained is recrystallized from alcohol, and decomposed by tartaric acid to separate the oleic acid.

Large quantities of oleic acid are now obtained as a secondary product in the manufacture of stearin candles, by treating with sulphuric acid the lime soap resulting from the action of lime on tallow. The fatty acids, which result from the decomposition, washed with hot water, solidify on cooling. This solidified mass is subjected to hydraulic pressure, when it yields a liquid that is comparatively rich in oleic acid. It is sold under the name of *red oil.*

Oleic acid is a colorless oil, which solidifies at 0° and melts again at 14°. It is tasteless, odorless, and neutral to litmus; it becomes, however, quickly yellow and acid by oxidation when exposed to air, and acquires a rancid, disagreeable odor. It is insoluble in water, very soluble in alcohol, and dissolves in all proportions in ether. When distilled, it decomposes, yielding a number of products among which sebacic acid $C_8H_{16}(CO_2H)_2$ is the most prominent; it can, however, be distilled in a current of superheated steam at a temperature of 250° without decomposition. Its specific gravity is .898 at 19°. Cold sulphuric acid dissolves it without decomposition. It dissolves solid fats, stearic and palmitic acids, and is dissolved by bile, with formation of a soap. When fused with $KOH$, it is converted into potassium acetate and palmitate, according to the equation:

$$C_{17}H_{33}\cdot CO_2H + 2KOH = CH_3\cdot CO_2K + C_{15}H_{31}\cdot CO_2K + H_2$$

Nitrous acid converts oleic acid into the isomeric *elaidic acid*, which is a solid and fuses at 45°. Nitric acid attacks oleic acid eagerly, decomposing it into several acids of the acetic or oxalic acid series, and giving off red nitrous vapors.

**Oleates.**—Oleates are the salts of oleic acid. The alkali oleates are decomposed by an excess of water into free alkalies and insoluble acid oleates. *Sodium oleate* $NaC_{18}H_{33}O_2$ is always present in ordinary soap and may be crystallized from absolute alcohol. *Barium oleate* is a crystalline powder, which is insoluble in water and only sparingly soluble in boiling alcohol. *Lead oleate* fuses at 80° and solidifies on cooling to a translucent, brittle mass, which is soluble in ether.

**92. Erucic Acid.**—Erucic acid $C_{21}H_{41}\cdot CO_2H$ is obtained by extraction from the seeds of mustard, rape, and grapes. It is a crystalline substance, which fuses at 34°. When fused with $KOH$, it is converted into potassium acetate and butate, according to the equation:

$$C_{21}H_{41}\cdot CO_2H + 2KOH = CH_3\cdot CO_2K + C_{19}H_{39}\cdot CO_2K + H_2$$

When heated with phosphorus and hydriodic acid, it is converted into behenic acid $C_{21}H_{43}\cdot CO_2H$, and when heated with dilute nitric acid, it is converted into its isomeride *brassidic acid*, which is a solid melting at 40°.

## MONOBASIC ACIDS FROM MONOHYDRIC ALCOHOLS OF THE ACETYLENE SERIES

**93. Propiolic, or Sorbic, Series.**—The most important members of this series are:

Propiolic acid
Tetrolic acid
Sorbic acid
Linoleic acid
Palmitolic acid
Stearolic acid
Behenolic acid

These acids may be prepared from the acids of the oleic series by the abstraction of 2 atoms of hydrogen, which is accomplished by the action of potash on the chlorine or bromine compounds or derivatives of these acids. For instance:

$$\underset{\text{bromocrotonic acid}}{C_4H_5BrO_2} + KOH = KBr + H_2O + \underset{\text{tetrolic acid}}{C_4H_4O_2}$$

$$\underset{\text{dibromocrotonic acid}}{C_4H_6Br_2O_2} + 2KOH = 2KBr + 2H_2O + \underset{\text{tetrolic acid}}{C_4H_4O_2}$$

**94. Propiolic Acid.**—Propiolic acid $CH⋮C \cdot CO_2H$ corresponds with propargyl alcohol. It is obtained as its potassium salt by heating an aqueous solution of potassium hydrogen acetylene dicarboxylate:

$$CO_2H \cdot C⋮C \cdot CO_2K = CO_2 + HC⋮C \cdot CO_2K$$

It melts at 6°, boils at 144°, and yields explosive metallic derivatives.

**95. Tetrolic Acid.**—Tetrolic acid $C_3H_3 \cdot CO_2H$ is produced as mentioned in Art. **93** by heating chlorocrotonic acid at 100° with potash dissolved in alcohol:

$$C_3H_4Cl \cdot CO_2H + 2KOH = C_3H_3 \cdot CO_2K + KCl + 2H_2O$$

or it may also be prepared by heating sodium allylide in carbon dioxide:

$$C_3H_3Na + CO_2 = C_3H_3 \cdot CO_2Na$$

It crystallizes in rhombic plates, and is easily soluble in alcohol as well as ether. It melts at 76.5° and boils at 203°.

**96. Sorbic Acid.**—Sorbic acid $C_5H_7CO_2H$ is obtained by distilling the juice of the unripe berries of the mountain ash (*Sorbus aucuparia*); the juice passes over, together with water, as a yellow fragrant oil, which becomes a crystalline solid on either boiling with strong hydrochloric acid or fusing with $KOH$ and precipitating with an acid. It crystallizes in long needles, melts at 134.5°, and is decomposed when distilled, unless in presence of steam. It is nearly insoluble in cold water, very sparingly soluble in hot water, and dissolves in alcohol. Nascent hydrogen converts it into *hydrosorbic acid* $C_6H_{10}O_2$.

**97. Linoleic Acid.**—Linoleic acid $C_{15}H_{27}\cdot CO_2H$ occurs as a glyceride in linseed oil and a few other drying oils. The oil is saponified with potash, the aqueous solution is precipitated by $CaCl_2$, and the calcium linoleate extracted by ether. It is a yellowish oil.

*Palmitolic Acid* $C_{16}H_{28}O_2$ is an isomeride. It may be prepared from dibromide of hypogæic acid, and it crystallizes in shining needles, which melt at 42°.

**98. Stearolic Acid.**—Stearolic acid $C_{17}H_{31}\cdot CO_2H$ is prepared from the dibromide of oleic acid. It crystallizes in long needles, melts at 48°, and can be distilled without decomposition. It is insoluble in water, and soluble in alcohol and ether.

**99. Behenolic Acid.**—Behenolic acid $C_{21}H_{39}\cdot CO_2H$ is prepared from the dibromide of erucic acid. It crystallizes in shining needles, which melt at about 75°.

**100.** As has been already stated in Art. **93,** all these acids may be prepared from the halogen derivatives of the acids of the oleic series by the action of $KOH$ dissolved in alcohol. The acids of the sorbic series combine with 2 and 4 atoms of bromine, and by treating them with nitric acid, they take up 2 atoms of oxygen and are thus converted into new acids.

## MONOBASIC ACIDS FROM THE MONOHYDRIC ALCOHOLS OF THE BENZENE SERIES

**101. Aromatic, or Benzoic, Series.**—These acids may, according to their construction, be divided into two classes; namely:

1. Those in which the group $COOH$ is attached to the benzene nucleus; as, for instance, *benzoic acid* $C_6H_5\cdot CO_2H$ and *toluic acid* $C_6H_4(CH_3)\cdot CO_2H$. These acids can be obtained by oxidizing the hydrocarbons containing side chains.

2. Those acids that contain the group $COOH$ as part of their side chain. They may be regarded as open-chain acids,

in which $C_6H_5$, $C_6H_4(CH_3)$, etc. have replaced $H$, as in *phenylacetic acid* $C_6H_5 \cdot CH_2 \cdot COOH$ and *tolylacetic acid* $C_6H_4(CH_3) \cdot CH_2 \cdot COOH$. This second class of acids may be prepared by the hydrolysis of the corresponding cyanides; as, for instance :

$$\underset{\substack{\text{benzyl cyanide}\\ \text{or}\\ \text{phenyl acetonitrile}}}{C_6H_5 \cdot CH_2 \cdot CN} + 2H_2O = \underset{\text{phenylacetic acid}}{C_6H_5 \cdot CH_2 \cdot CO_2H} + H_3N$$

**102. Benzoic Acid.**—Benzoic acid $C_6H_5 \cdot CO_2H$ was discovered in 1608, and prepared from animal's urine by Scheele in 1785 ; its composition was established in 1832 by the researches of Liebig and Wöhler. It was originally extracted from *gum benzoin*, a resinous exudation from the tree *Styrax Benzoin*, growing in the Malay Islands. Benzoic acid occurs also in nature in dragon's blood (a resin), in Peru and Tolu balsams, in cranberries, etc. It is present in the urine of horses, in combination with glycocoll, as hippuric acid, from which it is obtained by boiling with hydrochloric acid. Benzoic acid is also present in coal tar. It is obtained on a large scale as a by product in the manufacture of oil of bitter almonds from benzyl chloride or benzal chloride. The acid may also be obtained by heating benzo-trichloride with water to a high temperature :

$$C_6H_5CCl_3 + 2H_2O = C_6H_5 \cdot CO_2H + 3HCl$$

Benzoic acid crystallizes in shining needles or in feathery scales. It is an inodorous acid when cold, but acquires a faint odor when gently warmed ; it melts at 120°, and sublimes at a temperature a little above this ; it boils at 250°, and volatilizes without decomposition when boiled with water. It dissolves in about 200 parts of cold and 24 parts of hot water, and is very readily soluble in alcohol. Potash and ammonia also dissolve it, from which solutions it is precipitated again by an acid.

All the benzoates are more or less soluble, with the exception of ferric benzoate, which is obtained as a buff-colored precipitate when ferric chloride is added to a neutral benzoate.

By distillation with an excess of lime, benzoic acid is decomposed into benzene, as may be observed from the following equation :

$$C_6H_5 \cdot CO_2H + CaO = CaCO_3 + C_6H_6$$

When vapor of benzoic acid is passed over heated zinc dust, it is converted into bitter-almond oil (benzoic aldehyde):

$$C_6H_5 \cdot CO_2H + Zn = C_6H_5 \cdot CHO + ZnO$$

When boiled with strong nitric acid, benzoic acid is converted into nitrobenzoic acid $C_6H_4(NO_2) \cdot CO_2H$. Phosphorus pentachloride converts it into *benzoyl chloride* $C_6H_5 \cdot COCl$. This chloride bears the same relation to benzoic acid as acetyl chloride bears to acetic acid ; the radicals benzoyl and acetyl being related in a similar way to benzyl and ethyl:

| | |
|---|---|
| Ethyl $C_2H_5$ ; Acetyl $C_2H_3O''$ | Benzyl $C_7H_7$; Benzoyl $C_7H_5O''$ |
| Ethyl hydride (ethane) $C_2H_6$ | Benzyl hydride (toluene) $C_7H_8$ |
| Ethyl hydroxide (alcohol) $C_2H_5 \cdot OH$ | Benzyl hydroxide $C_7H_7 \cdot OH$ |
| Acetyl hydride (aldehyde) $C_2H_4O$ | Benzoyl hydride $C_7H_6O$ |
| Acetyl hydroxide (acetic acid) $C_2H_4O_2$ | Benzoyl hydroxide $C_7H_6O_2$ |

*Benzoic anhydride*, or *dibenzoyl oxide* $(C_6H_5 \cdot CO)_2O$, is obtained by the action of benzoyl chloride on potassium benzoate:

$$C_7H_5O(OK) + C_7H_5OCl = (C_6H_5 \cdot CO)_2O + KCl$$

The mass is washed with water and dissolved in alcohol, from which the anhydride crystallizes out. It fuses at 42° and boils at 310°. Boiling with water converts it into benzoic acid.

When benzoyl chloride is heated with dry sodium acetate, *benzo-acetic anhydride* is obtained:

$$C_6H_5 \cdot COCl + CH_3 \cdot COONa$$
$$= (C_6H_5 \cdot CO)(CH_3 \cdot CO)O + NaCl$$

*Benzoic peroxide* $(C_6H_5 \cdot CO)_2O_2$ is prepared by the action of barium dioxide on benzoyl chloride under water:

$$2C_6H_5 \cdot COCl + BaO_2 = (C_6H_5 \cdot CO)_2O_2 + BaCl_2$$

The product, when recrystallized from ether, yields large shining crystals, which explode when heated. Alkalies resolve it into benzoic acid and oxygen.

**103. Toluic Acids.**—Toluic acid, or *methyl benzoic acid* $C_6H_4(CH_3)\cdot CO_2H$, exists in three isomeric modifications. They are prepared by oxidizing the three corresponding xylenes, $C_6H_4(CH_3)_2$, with nitric acid diluted with 3 parts of water.

*Orthotoluic acid* crystallizes in needles, which melt at 102°. It is moderately soluble in water and distils easily with aqueous vapors. Its calcium salt $(C_8H_7O_2)_2Ca, 2H_2O$ and its barium salt $(C_8H_7O_2)_2Ba$ form needle-shaped crystals, which are readily soluble in water.

*Metatoluic acid* is more readily dissolved in water than its two isomerides. It crystallizes from hot water in needle-shaped crystals, which melt when exposed to a temperature of about 110°. It distils easily without decomposition with aqueous vapor. Its calcium salt $(C_8H_7O_2)_2Ca, 3H_2O$ crystallizes from alcohol in needles, which are readily soluble in water.

*Paratoluic acid* is obtained by oxidation of 1 : 4-xylene with dilute nitric acid; it crystallizes in needles melting at 178°. Its calcium salt $(C_8H_7O_2)_2Ca, 2H_2O$ crystallizes in needles, which are readily soluble in water.

**104. Mesitylenic Acid.** — Mesitylenic acid 1:3:5 $C_6H_3(CH_3)_2CO_2H$ is prepared by oxidizing mesitylene with dilute nitric acid. It is a crystalline volatile acid, fusing at 166°, and soluble in boiling water and in alcohol.

**105. Cuminic Acid.**—Cuminic acid, or *isopropyl benzoic acid* 1:4 $C_6H_4(C_3H_7)\cdot CO_2H$, is prepared from the aldehyde existing in *Roman cumin oil;* by boiling it with an alcoholic solution of potash, which converts it into cuminic alcohol and potassium cuminate, the cuminic acid is precipitated and may be crystallized from alcohol. It fuses at 116° and can be sublimed.

**106.** All the acids belonging to the benzoic or aromatic series of acids are crystalline, volatile, sparingly soluble in water, and readily soluble in alcohol as well as in ether. When distilled with excess of lime, they yield hydrocarbons of the benzene series, $CO_2$ being abstracted.

### MONOBASIC ACIDS OF THE CINNAMIC SERIES

**107. Cinnamic Acid.**—Cinnamic acid $C_6H_5 \cdot CH : CH \cdot CO_2H$ is prepared by boiling storax with soda, decomposing the solution of sodium cinnamate with $HCl$, which precipitates the cinnamic acid in feathery crystals like benzoic acid, fusing at 133°, boiling at 290°, and subliming undecomposed. It is soluble in boiling water and in alcohol.

Cinnamic acid is also known as *phenyl acrylic acid*, and its connection with acrylic acid is shown by fusing it with potash, which yields acetate and benzoate of potassium, while acrylic acid yield acetate and formate:

$$C_6H_5 \cdot CH : CH \cdot CO_2H + 2KOH$$
$$= CH_3 \cdot CO_2K + C_6H_5 \cdot CO_2K + H_2$$

Oxidizing agents convert cinnamic acid into benzoic aldehyde (bitter-almond oil):

$$C_6H_5 \cdot CH : CH \cdot CO_2H + 2O_2$$
$$= C_6H_5 \cdot CHO + 2CO_2 + H_2O$$

When distilled with excess of lime, it yields cinnamene, or phenyl ethylene. Nascent hydrogen converts it into phenyl propionic acid:

$$C_6H_5 \cdot CH : CH \cdot CO_2H + 2H = C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CO_2H$$

Cinnamic acid is prepared synthetically by the action of sodium acetate on bitter-almond oil in presence of acetic anhydride, which probably acts as a dehydrating agent:

$$CH_3 \cdot CO_2Na + C_6H_5 \cdot CHO = C_6H_5 \cdot CH : CH \cdot CO_2Na + H_2O$$

*Atropic acid*, or *a-phenyl acryl acid*, is produced when atropine, the alkaloid of deadly nightshade, is boiled with either baryta or $HCl$. It fuses at 106°.

The other members of the cinnamic series are of no, or very little, practical importance. They may be prepared from benzoic aldehyde or cuminic aldehyde, as cinnamic acid is, by treatment with the anhydrides and sodium salts of members of the acetic series.

### MONOBASIC ACIDS FROM POLYHYDRIC ALCOHOLS

**108.** As already stated in Art. **35**, these acids may be alcohol acids, or aldehyde acids, if the polyatomic alcohol is a glycol, and ketone acids, or even ketone alcohol acids or ketone-aldehyde acids, if the alcohol is polyhydric, in which case it must contain primary as well as secondary alcohol groups.

Alcohol acids are generally called *hydroxy acids*, a title that they may justly claim, since they can be prepared from the chloro-substituted open-chain acids of the previous series by treatment with silver oxide and water, showing that the $Cl$ has been substituted by $OH$; as, for instance, when monochloracetic acid is converted into glycollic acid:

$$2CH_2Cl\cdot COOH + Ag_2O + H_2O$$
$$= 2CH_2OH\cdot COOH + 2AgCl$$

It will be found that the hydrogen of the hydroxyl group in a hydroxy acid is capable of replacement by a metal, just as it is in the hydroxyl group of an alcohol, so that the acid possesses the functions of both an alcohol and an acid. Thus, the monobasic hydroxy acids may contain two or more $H$ atoms, replaceable by a metal, although they are strictly monobasic, since they contain only one $CO_2H$ group; hence, they are sometimes termed *diatomic* (*triatomic*, *etc.*) *monobasic acids.*

The simplest hydroxy acid, hydroxy formic acid $HO\cdot COOH$, does not exist in the free state, probably for the reason given in Art. **34**; it would possibly be identical with carbonic acid.

**109. Glycollic Acid.**—Glycollic acid, or *hydroxy acetic acid* $CH_2OH\cdot CO_2H$, was first obtained by Strecker in 1848.

It may be considered as a product of the oxidation of glycol $CH_2OH \cdot CH_2OH$ by diluted nitric acid, but it is better prepared by oxidizing alcohol with nitric acid. The mode of preparation is as follows:

In a cylindrical glass, about 2 inches in diameter, 118 cubic centimeters of 80-per-cent. alcohol are poured; a long funnel tube, the lower end of which is drawn to a point, is inserted to the bottom of the vessel, and 50 cubic centimeters of water are carefully poured in so as to form a layer beneath the alcohol. Then 126 cubic centimeters of nitric acid, having a specific gravity of 1.35, are poured into the vessel in the same manner, and thus form a new layer beneath the water. The vessel is put aside without disturbing the layers, and allowed to stand for 5 days in a place where a constant temperature of about 20° is maintained, when the three layers will have mixed. The liquid is then changed to a syrupy consistency by evaporating small portions of it, say 20 cubic centimeters at a time, over a water bath, diluted with 10 volumes of water, boiled, and neutralized with calcium carbonate. To the crystalline paste which forms when the mass cools down, an equal volume of alcohol is added and the precipitate filtered off. The precipitate is boiled with water, and, while boiling, is filtered in order to remove all particles of undissolved calcium oxalate. On cooling, the filtrate deposits calcium glyoxalate, while calcium glycollate remains in solution; this is boiled with a little lime in order to decompose any glyoxalate, and the filtered solution is evaporated and treated with oxalic acid, in order to precipitate the calcium as calcium oxalate, thus leaving glycollic acid in solution.

The action of nitric acid on alcohol is of a representative character. Ethyl alcohol $C_2H_5 \cdot OH$ is derived from methyl alcohol $CH_3OH$ by the substitution of the methyl group $CH_3$ for $H$, so that ethyl alcohol should be written $CH_2 \cdot CH_3 \cdot OH$ or $CH_3 \cdot CH_2 \cdot OH$. Now the groups $CH_3$ and $CH_2 \cdot OH$, under the influence of oxidizing agents, are converted into $CHO$, characteristic of the aldehydes, and $CO \cdot OH$, characteristic of the acids, respectively. Accordingly, we find, among the products of the above operation, acetic aldehyde $CH_3\cdot CHO$, acetic acid $CH_3\cdot CO\cdot OH$, glyoxal $CHO\cdot CHO$, glyoxylic acid $CHO\cdot CO\cdot OH$, glycollic, or hydroacetic, acid $CH_2\cdot OH\cdot CO\cdot OH$, and oxalic acid $CO\cdot OH\cdot CO\cdot OH$.

Glycollic acid occurs in nature in unripe grapes, in leaves of the wild vine, and in other plants. It has an extremely sour taste, dissolves readily in water, alcohol, and ether, melts at 80°, and volatilizes at 100°.

It is converted into oxalic acid by oxidizing agents. When heated with sulphuric acid, it yields formic aldehyde and formic acid:

$$CH_2\cdot OH\cdot CO_2H = H\cdot CHO + H\cdot CO_2H$$

The formic aldehyde is converted into formic paraldehyde $(HCOH)_2$ and most of the formic acid is decomposed into $H_2O$ and $CO$. When glycollic acid is heated with hydrochloric acid, it yields monochloracetic acid, according to the equation:

$$CH_2\cdot OH\cdot CO_2H + HCl = CH_2Cl\cdot CO_2H + H_2O$$

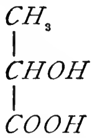
This may, however, be reconverted into glycollic acid by boiling with $KOH$, which replaces the $Cl$ by $OH$.

Hydriodic acid reduces glycollic acid to acetic acid, as seen from the equation:

$$CH_2OH\cdot CO_2H + 2HI = CH_3\cdot CO_2H + H_2O + I_2$$

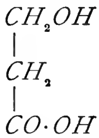
All the glycollates are more or less soluble and crystallizable. *Calcium glycollate* $(C_2H_3O_3)_2Ca, 2H_2O$ is slightly soluble in cold water, and crystallizes in needles. *Silver glycollate* $(C_2H_3O_3Ag)_2H_2O$ is also sparingly soluble in water. Both these salts, however, dissolve quite readily in boiling water.

**110. Lactic Acids, or Hydroxypropionic Acids.**—Of these acids having the composition $C_2H_4(OH)\cdot CO_2H$ there are two isomeric modifications; namely,



$$\begin{array}{l} CH_3 \\ | \\ CHOH \\ | \\ COOH \end{array}$$

α-lactic acid,
or
ethidene lactic acid



$$\begin{array}{l} CH_2OH \\ | \\ CH_2 \\ | \\ CO\cdot OH \end{array}$$

β-lactic acid,
or
ethene lactic acid

*Ethidene lactic acid* $CH_3 \cdot CHOH \cdot COOH$, which is sometimes called *ethylidene lactic acid*, or *fermentation lactic acid*, is obtained by a fermentation process known as *lactous fermentation.* Various kinds of sugar and dextrin, when subjected to the action of particular ferments, are converted into lactic acid, the change consisting in a resolution of the molecule, preceded in some cases by the assumption of the elements $H$ and $O$, in the form of water:

$$\underset{\text{glucose}}{C_6H_{12}O_6} = \underset{\text{lactic acid}}{2C_3H_6O_3}$$

$$\underset{\text{milk sugar}}{C_{12}H_{22}O_{11} + H_2O} = \underset{\text{lactic acid}}{4C_3H_6O_3}$$

This fermentation, which is, as has been previously stated, known as lactous fermentation, requires a temperature between 20° and 40° and the presence of water and certain ferments, namely, albuminous substances in a peculiar state of decomposition, such as casein, glutin, or animal membranes, especially the coating of the stomach or the bladder of certain animals. Pasteur investigated this peculiar fermentation, and he came to the opinion, which is shared by many others, that it depends on the presence of a minute living organism of the fungus family, known as *Penicillium glaucum*, but whether this effect is due to the fungi themselves or to the peculiar state of the albuminous matter in which they occur, is still an open question.

The following is a good method for preparing the acid in larger quantities: A mixture of 3 kilograms of raw sugar dissolved in 13 liters of water, 4 kilograms of sour milk, 100 grams of old cheese, and 1.5 kilograms of pulverized chalk, is exposed to a temperature of from 30° to 35°. After the expiration of a week, the whole mass has solidified to calcium lactate. The salt thus obtained is purified by crystallization, and is exactly decomposed by dilute sulphuric acid. The calcium sulphate is separated by filtration, and the acid liquid is boiled and saturated with zinc carbonate. It is then filtered and allowed to cool. The zinc lactate crystallizes, and its solution being decomposed by hydrogen sulphide, zinc sulphide and lactic acid are obtained. The latter is separated by filtration and its solution concentrated on the water bath.

For the preparation of lactic acid on a smaller scale, advantage is taken of the fact that some sugars (glucose, fructose) on being heated with alkalies, yield considerable quantities of the acid.

Lactic acid is a colorless, syrupy, strongly acid liquid, with a specific gravity of 1.215. Subjected to heat, it begins to lose water at about 130° and is converted, slowly and little by little, into a yellow, amorphous mass, insoluble in water, but soluble in alcohol as well as in ether. The amorphous body thus obtained is known as *dilactic acid* $C_6H_{10}O_5$:

$$2C_3H_6O_3 = C_6H_{10}O_5 + H_2O$$

At 230° it disengages a small quantity of carbon monoxide and carbon dioxide, and a product distils, which very often solidifies on cooling. This body is *lactide*, or *dilactic anhydride* $C_6H_8O_4$, and is derived directly from dilactic acid:

$$C_6H_{10}O_5 = \underset{\text{lactide}}{C_6H_8O_4} + H_2O$$

Lactide occurs in colorless crystals, which are soluble in water and in alcohol. It possesses the property of combining directly with the elements of water, lactic acid being again formed.

When lactic acid is heated to 130° with dilute sulphuric acid, in a sealed tube, it yields aldehyde and formic acid:

$$C_2H_5O\cdot CO_2H = CH_3\cdot CHO + H\cdot CO_2H$$

With strong sulphuric acid, the formic acid is converted into water and carbon monoxide. Oxidation with $K_2Mn_2O_8$ converts the variety of lactic acid now under consideration into *pyruvic acid* $CH_3\cdot CO\cdot COOH$. Nitric acid oxidizes lactic acid to oxalic acid, and oxidation with chromic acid converts it into acetic acid, $CO_2$, and $H_2O$:

$$C_2H_5O\cdot CO_2H + O_2 = CH_3\cdot CO_2H + CO_2 + H_2O$$

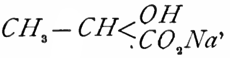
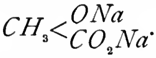
Since lactic acid is really hydroxypropionic acid, it may be reduced to propionic acid by strong hydriodic acid:

$$C_2H_4(OH)\cdot CO_2H + 2HI = C_2H_5\cdot CO_2H + H_2O + I_2$$

and, conversely, propionic acid may be converted into lactic acid by the following steps:

$$(1)\quad CH_3\cdot CH_2\cdot CO_2H + Br_2 = CH_3\cdot CHBr\cdot CO_2H + HBr$$

$$(2)\quad CH_3CHBr\cdot CO_2H + KOH = CH_3\cdot CH\cdot OH\cdot CO_2H + KBr$$

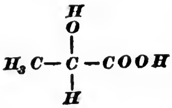
**Lactates.**—The best defined of these salts are represented by the formulas $M'C_3H_5O_3$ and $M''(C_3H_5O_3)_2$. They are, as a class, only sparingly soluble in water, effloresce rapidly from their solutions, and are, all of them, insoluble in ether. *Sodium lactate* $C_3H_5O_3Na$, or  $CH_3-CH<\begin{smallmatrix}OH\\CO_2Na\end{smallmatrix}$, obtained by neutralizing the acid with sodium carbonate, is an amorphous mass, which, when heated with metallic sodium, is converted into *disodic lactate*  $CH_3<\begin{smallmatrix}ONa\\CO_2Na\end{smallmatrix}$. *Calcium lactate* $(C_3H_5O_3)_2Ca, 5H_2O$ is obtained in the process of preparing lactic acid previously described. *Zinc lactate* $(C_3H_5O_3)_2Zn, 3H_2O$ gives off its water of crystallization when heated to 100°, it dissolves in 6 parts of boiling water and 5.75 parts of cold water, and is nearly entirely insoluble in alcohol. *Ferrous lactate* is precipitated in small yellowish crystals on mixing ammonium lactate with either ferrous chloride or ferrous sulphate.

**111. Stereo-isomerism as Illustrated by Ethylidene Lactic Acid.**—Besides the various places of occurrence of ethylidene lactic acid mentioned in Art. **110,** it is also found in the juice of flesh (its presence has been proved in Liebig's extract of meat), in bile, and in the urine of persons suffering from phosphorus poisoning. This lactic acid has been termed *sarcolactic*, or *paralactic*, acid, owing to the fact that it cannot be considered exactly identical with ethylidene lactic acid of fermentation so far described. The difference, as far as the chemical properties are concerned, is only very slight, consisting mainly in a greater solubility of zinc sarcolactate (which crystallizes with $2H_2O$) than of zinc fermentation lactate (which crystallizes with $3H_2O$), and the decrease of solubility of the calcium salt ($4H_2O$ against $5H_2O$ in the fermentation salt). It is in their physical properties where the greatest difference prevails. The fermentation acid is optically inactive, that is, it exerts no influence on polarized light, while the sarcolactic acid rotates the plane of polarization to the right. (See Double Refraction and Circular Polarization, *Physics.*) This difference in physical property leads to the distinct titles *inactive ethylidene lactic acid*, for the fermentation of lactic acid, and *dextro-ethylidene lactic acid*, for the sarcolactic acid. Dextro-ethylidene lactic acid is converted into an anhydride when kept out of contact with atmospheric moisture and drying it in a desiccator; the solution of this anhydride is found to be levorotary. The salts of the dextro-acid are levorotary.

When cane sugar is fermented by means of certain bacilli, a *levo-ethylidene lactic acid* is produced, whose salts are dextrorotary.

It appears that there are three ethylidene lactic acids, which may be distinguished as *inactive*, *dextro-* and *levo-ethylidene lactic acid*, respectively. But, when equal weights of the *d-* and *l*-acids are mixed together, the product is found to be optically inactive; from which we may draw the conclusion that the *i*, or inactive, acid is composed of an equal number of *d-* and *l*-acid molecules, which neutralize each other, so that in building up a theory to account for the existence of these three acids, it becomes only necessary to attempt to explain the isomerism of the dextro- and levo-modifications. The theory of position isomerism, already mentioned, will not be sufficient to furnish an explanation, because the only possible position isomeride of ethylidene lactic acid, according to the theory, is ethylene lactic acid, from which both the *d-* and the *l*-acids differ chemically.

The examination of a large number of optically active compounds has shown that each contains one or more carbon atoms, to which are attached four different elements or radicals; thus, in ethylidene lactic acid $CH_3 \cdot CHOH \cdot COOH$, the middle carbon has each of its bonds satisfied by a different atom or radical, as is seen from Fig. 7. Such a carbon is said to be *asymmetric*, and it is generally believed that *an optically active compound is one that possesses one or more asymmetric carbon atoms*, and that the property of being either dextro- or levorotary depends on the arrangement in the space of the four different atoms or radicals grouped about the asymmetrical carbon atom.



$$\begin{array}{c} H \\ O \\ | \\ H_3C-C-COOH \\ | \\ H \end{array}$$

FIG. 7

No hypothesis has been suggested so far upon which it becomes possible to foretell whether a given compound, containing an asymmetric carbon atom, will be dextro- or levorotary. This subject will receive further attention after the isomerides of tartaric acid have been considered.

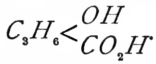
It is only possible to explain the existence of dextro- and levo-ethylidene lactic acids by assuming that the four groups attached to the asymmetric carbon atom are differently arranged in space.

If the carbon atom is considered to occupy the center of a tetrahedron in space, then it will be found that no essentially different structures can be made, unless each corner of the tetrahedron has a different radical attached to it. For, if two tetrahedra are constructed, the corners of which are represented by *A–A–A–B*, or *A–A–B–B*, or *A–A–B–C*, or any combination of four letters, two of which are the same, it will be found to be always possible to put the one tetrahedron inside the other in such a manner that the four letters on the corners of the one shall coincide with the four letters on the corners of the other. If, however, the four corners of each are represented by four different letters, say *A–B–C–D*, it will be found possible to arrange these letters so that the one tetrahedron cannot be introduced into the other in such a manner that the four corners correspond. The arrangement necessary will be understood from the statement that, if the observer is opposite those faces of the tetrahedra that are similarly lettered, the order of the letters on the one face will be the reverse of the order of the letters on the other face; if the letters *A–B–C*, for instance, are in the order of the motion of the hands of a clock on the face of one tetrahedron, they will be in the reverse order *C–B–A* on the face of the other. Such an arrangement is shown in Fig. 8, from which it will be seen that the two arrangements bear the same relationship to each other as an object bears to its image. If the compound, which is arranged in the clockwise manner in Fig. 8, is dextrorotary, then that which is counter-clockwise must be levorotary.

FIG. 8

**112. Ethylene Lactic Acid, or β-Hydroxypropionic Acid.**—Ethylene lactic acid $CH_2(OH)\cdot CH_2\cdot CO_2H$ occurs in the juice of flesh, and is prepared by treating β-iodopropionic acid $CH_2I\cdot CH_2\cdot CO_2H$ with moist silver oxide, or is obtained by heating acrylic acid with aqueous sodium hydroxide. The free acid yields a non-crystallizable, thick syrup. When heated alone, or when boiled with sulphuric acid (diluted with 1 part of $H_2O$), it loses water and forms acrylic acid; hence, it is sometimes called *hydracrylic acid.* Hydriodic acid again changes it to β-iodopropionic acid. It yields oxalic acid and carbon dioxide when oxidized with chromic acid or nitric acid.

The sodium salt $C_3H_5O_3Na$, melting at 142°–143°, and the calcium salt $(C_3H_5O_3)_2Ca,2H_2O$, fusing at 145°, when heated above their melting points, pass into the corresponding acrylates. The zinc salt $(C_3H_5O_3)_2Zn,4H_2O$ is soluble in water and alcohol.

**113. Hydroxybutyric Acids.**—Hydroxybutyric acid has the general formula $C_4H_8O_3$ =  $C_3H_6<\begin{matrix}OH\\CO_2H\end{matrix}$ Five modifications of this acid are theoretically possible, although only four are so far known.

1. *α-hydroxybutyric acid* $CH_3\cdot CH_2\cdot CH(OH)\cdot CO_2H$ is obtained by heating α-bromobutyric acid with moist silver

oxide. It is crystalline, melts at 43°–44°, and is very deliquescent. Its salts are crystalline compounds, the zinc salt $(C_4H_7O_3)_2Zn$ forming white needles, which are slightly soluble in water.

2. *β-hydroxybutyric acid* $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CO_2H$ is produced by boiling β-bromobutyric acid with silver oxide, and in various other ways. The free acid is an uncrystallizable syrupy liquid. Its calcium salt $(C_4H_7O_3)_2Ca$ crystallizes only with difficulty.

3. *γ-hydroxybutyric acid* $CH_2OH : CH_2 \cdot CH_2 \cdot CO_2H$, also known as *normal hydroxybutyric acid*, is prepared from succinic acid $CO_2H \cdot CH_2 \cdot CH_2 \cdot CO_2H$.

4. *a-hydroxyisobutyric acid* $(CH_3)_2 : C(OH) \cdot CO_2H$ crystallizes in slender prisms, which are soluble in water and in ether. It sublimes at 50°, melts at 79°, and distils at 212°.

5. *β-hydroxyisobutyric acid* $(CH_3)(CH_2OH) : CH \cdot CO_2H$ is, as has been already stated, obviously possible, but not known so far.

### POLYHYDROXY MONOBASIC ACIDS

**114. Glyceric Acid.**—Glyceric acid $CH_2OH \cdot CHOH \cdot CO_2H$ is obtained by oxidizing glycerol with nitric acid, or by treating it with bromine and water. It is also formed by the spontaneous decomposition of nitroglycerin. It is a thick, yellow syrup, which is soluble in water and alcohol.

A number of different polyhydric monobasic acids is produced by the oxidation of the sugars; these are known as *hexonic acids* $CH_2OH \cdot (CHOH)_4 \cdot CO_2H$. They are stereoisomerides of each other, being either *d*-, *l*-, or *i*-acids. They will be treated in detail with the sugars.

**115. Glyoxylic Acid.**—Glyoxylic acid, also known as *glyoxalic acid* $CHO \cdot CO_2H$, is a product of the oxidation of glycol and alcohol. It is a syrupy and very acid liquid. It has the properties both of an acid and of an aldehyde, as is indicated by its formula. Its solution reduces ammoniacal silver nitrate. When heated with sulphuric acid, it disengages carbon monoxide.

*Glycuronic acid* $CHO\cdot(CHOH)_4\cdot CO_2H$ is obtained by reducing saccharic acid with sodium amalgam; it is a syrupy liquid.

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### MONOBASIC HYDROXY ACIDS FROM BENZENE HYDROCARBONS

**116.** The $OH$ groups in these acids may be attached either to the benzene nucleus, when the acids are *phenol acids* but not alcohol acids, or they may occur in the side chain, in which case the acid is an alcohol acid; thus, salicylic acid is a phenol acid $C_6H_4(OH)\cdot COOH$, while phenyl-glycollic acid is an alcohol acid $C_6H_5\cdot CHOH\cdot COOH$.

The most important general reactions by which the phenolic acids are obtained are:

1. The sodium phenols are heated with $CO_2$.
2. The phenols are boiled with carbon tetrachloride $CCl_4$ and $KOH$; as, for instance,

$$C_6H_5OH + CCl_4 + 5KOH$$
$$= C_6H_4(OH)\cdot COOK + 4KCl + 3H_2O.$$

3. The homologues of phenol are oxidized by fusion with $KOH$; as, for instance,

$$C_6H_4(OH)\cdot CH_3 + 2KOH = C_6H_4(OK)\cdot COOK + 3H_2$$

Like the alcohol acids, the phenol acids yield two classes of salts, e. g., $C_6H_4(OH)\cdot CO_2Na$ and $C_6H_4(ONa)\cdot CO_2Na$.

**117. Hydroxybenzoic Acids.**—Hydroxybenzoic acid has the formula $C_6H_4(OH)\cdot CO_2H$ and occurs in three modifications. The most important is the 1:2-acid, known as *salicylic acid.* It was first prepared synthetically by Kolbe and Lautemann by passing carbon dioxide into phenol in which sodium was dissolved:

$$C_6H_5\cdot OH + CO_2 = C_6H_4(OH)CO_2H$$

The process was later improved, and large quantities of salicylic acid are now manufactured by treating dry sodium phenol with carbon dioxide under pressure, and heating the product to 130°. Sodium phenyl carbonate $C_6H_5O\cdot COONa$ is first formed, and, upon heating under pressure, this is converted into sodium salicylate:

$$\underset{\text{sodium phenol}}{2C_6H_5ONa} + CO_2 = \underset{\text{phenol}}{C_6H_5\cdot OH} + \underset{\text{sodium salicylate}}{C_6H_4(ONa)CO_2Na}$$

After removing the excess of phenol by distillation, the mass is exhausted with water, and the solution is treated with hydrochloric acid, which sets free the salicylic acid.

It was formerly extracted from the essential oil of wintergreen (*Gaultheria procumbens*).

Salicylic acid crystallizes from its alcoholic solution in large monoclinic prisms, and from water in needles. It requires, approximately, 1,800 parts of cold water to dissolve it, but it is much more soluble in hot water and in alcohol. Its solution gives an intense violet color with ferric chloride. It melts at 155°, gives off phenol at a higher temperature, and, when heated with quicklime, is completely resolved into carbon dioxide and phenol. It is distinguished from both its isomerides by its behavior with ferric chloride, its very slight solubility in water, and its lower melting point. It possesses powerful antiseptic properties, and is used for the preservation of meat and other food articles, being both tasteless and odorless.

The salicylates of $K$ and $Na$ are crystallizable; barium salycilate $[C_6H_4(OH)CO_2]_2Ba,2H_2O$ also crystallizes, and, when boiled with baryta water, yields a sparingly soluble salt $C_6H_4BaOCO_2,2H_2O$, in which the dyad $Ba$ replaces the $H$ of the hydroxyl, as well as that of carboxyl.

**118. Anisic Acid.**—Anisic acid, or *paramethyl oxybenzoic acid* $C_6H_4(OCH_3)\cdot CO_2H$, is obtained by oxydizing anisic aldehyde $C_8H_8O_2$, which is obtained by treating the oils of anise, of fennel, etc. with nitric acid. It is obtained artificially from salicylic acid by heating its potassium salt to 220°, when it yields dipotassium parahydroxybenzoate, which is converted into potassium anisate when treated successively with methyl iodide and caustic potash:

$$2[C_6H_4(OH)\cdot CO_2K] = C_6H_5\cdot OH + CO_2 + C_6H_4(OK)\cdot CO_2K$$

$$C_6H_4(OK)\cdot CO_2K + 2CH_3I = \underset{\text{methyl anisate}}{C_6H_4(OCH_3)\cdot CO_2CH_3} + 2KI$$

$$C_6H_4(OCH_3)\cdot CO_2CH_3 + KOH$$
$$= \underset{\text{potassium anisate}}{C_6H_4(OCH_3)\cdot CO_2K} + CH_3\cdot OH$$

Hydrochloric acid precipitates the anisic acid, which may be dissolved in alcohol and crystallized in prisms. It melts at 185°, and distils without decomposition at 280°.

**119. Protocatechuic Acid.**—Protocatechuic acid, or *dihydroxybenzoic acid* $C_6H_3(OH)_2\cdot CO_2H$, is produced by the action of fused soda on bodies belonging to the class of *gum resins.* The acid obtained its name from its production in this way from *catechu*, a substance extensively used in dyeing black. It crystallizes from water in shining needles containing 1 molecule of $H_2O$. It is soluble in hot water, ether, alcohol, and sparingly soluble in cold water. The crystals melt at 199°, and decompose into $CO_2$ and $C_6H_4(OH)_2$(pyrocatechol) at a higher temperature. Ferric chloride colors the solution green, changing, on addition of a very weak solution of sodium carbonate, to blue and finally to red.

**120. Vanillic Acid.**—Vanillic acid, or *methyl protocatechuic acid* $C_6H_3(OH)(OCH_3)\cdot CO_2H$, is formed by oxidation of vanillin, when that substance is exposed to the moist atmosphere. It may also be prepared by oxidizing coniferin (a glucoside) with potassium permanganate. It crystallizes in plates or shining white needles, fusing at 211°, and subliming without decomposition. It is sparingly soluble in cold water, and readily soluble in hot water and in alcohol. When heated together with hydrochloric acid in a sealed tube at 150°, it is decomposed into protocatechuic acid and methyl chloride:

$$C_6H_3(OH)(OCH_3)\cdot CO_2H + HCl$$
$$= C_6H_3(OH)_2\cdot CO_2H + CH_3Cl$$

**121. Gallic Acid.**—Gallic acid $C_6H_2(OH)_3 \cdot CO_2H$ is obtained artificially by treating di-iodosalicylic acid with alkalies:

$$\underset{\text{di-iodosalicylic acid}}{C_7H_4I_2O_3} + 2KOH = 2KI + \underset{\text{gallic acid}}{C_7H_4(OH)_2O_3}$$

It results from the hydrolysis of the tannin in gallnuts (*gallotannic acid*):

$$C_{13}H_9O_7 \cdot CO_2H + H_2O = 2C_6H_2(OH)_3 \cdot CO_2H$$

It is therefore usually prepared by exposing coarsely powdered and moistened gallnuts to the air, renewing the water as it evaporates. At the expiration of two or three months a black liquid is separated from the mass by pressure, and the solid residue is exhausted with hot water. The liquid is then purified by repeated crystallization. It crystallizes in fine silky needles, with 1 molecule of water, which melt at about 200°, and, if the temperature is further increased to about 210°, it is decomposed into $CO_2$ and $C_6H_3(OH)_3$ (pyrogallol). Gallic acid is soluble in 100 parts of cold water and 3 parts of hot water; it dissolves very readily in alcohol, but less freely in ether. A solution of gallic acid gradually absorbs oxygen from the air, becoming colored and disengaging $CO_2$. If a recently boiled solution of gallic acid is passed up into a tube filled with mercury and containing no air, and some recently boiled baryta water is then added, a white precipitate is formed, which at once changes to blue, if a little oxygen is allowed to bubble through. The change of color indicates the oxidation of the gallic acid. Ferric salts give a bluish-black precipitate.

When gallic acid is heated with 4 parts of strong sulphuric acid to about 75°, a dark-red solution is obtained, and if this is cooled and poured into water, a red precipitate is obtained. This precipitate has the composition $C_{14}H_8O_8, 2Aq$, or twice the composition of gallic acid minus $2H_2O$; it was formerly called *rufigallic acid*, but is really a compound called *hexahydroxyanthraquinone* $C_{14}H_2(OH)_6O_2$.

**122. Ellagic Acid.** — Ellagic acid $C_{13}H_7O_7 \cdot CO_2H$ is obtained by the action of an oxidizing agent—such as arsenic anhydride, silver oxide, etc.—on gallic acid. It is a constituent of the bezoar stones, the calculi sometimes found in the intestines of a certain Persian species of the goat. It is a yellowish, crystalline powder, which is insoluble in water, and only slightly soluble in alcohol.

**123. Tannic Acid.**—Tannic acid and *tannin* are the names generally applied to certain slightly acid compounds, which are found widely diffused through the vegetable kingdom, and which have the two following characteristic properties: (1) They produce a bluish- or greenish-black color with the ferric salts, which is the basis of writing ink; and (2) they precipitate gelatine and albuminous matter—hence their property of more or less completely tanning hide to leather.

The only one of these acids that has been thoroughly investigated is *gallotannic acid* $C_{13}H_9O_7 \cdot CO_2H, 2H_2O$. It is most readily prepared by exhausting finely pulverized gallnuts with a mixture of alcohol and ether in a percolator (see Fig. 9) having its mouth loosely closed with a lid and its neck plugged with cotton wool. The ethereal solution that passes through is collected in a receiver, and in the course of a day or two separates into two or sometimes three layers, or strata. The lowest layer is a very concentrated solution of gallotannic acid in water, while the upper one consists of ether, holding in solution gallic acid, coloring matter, and other impurities. The aqueous solution of gallotannic acid is evaporated to dryness at a low temperature. The acid has also been prepared by the action of a dehydrating agent such as $POCl_3$ on gallic acid; hence, it is believed to be digallic acid $C_6H_2(OH)_3 \cdot CO \cdot O \cdot C_6H_2(OH)_2 \cdot COOH$, which represents 2 molecules of gallic acid from which 1 molecule of water has been removed.

FIG. 9

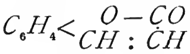
Gallotannic acid, or tannin, thus obtained is a slightly yellowish, amorphous mass, which is very readily soluble in water, but only slightly so in alcohol and ether. Its melting point is at 212°-215°. Its solution is slightly acid and astringent. A solution of tannic acid produces with ferric salts a bluish-black precipitate, which constitutes ink. It does not color ferrous salts, but the mixture soon blackens on exposure to the air by absorbing oxygen.

Gallnuts are very rich in tannin as we have seen, and a very good writing ink may be prepared in the following manner: One kilogram of finely powdered gallnuts is exhausted with 14 liters of water, and the solution is filtered; a solution of 500 grams of gum arabic is then added, and afterward a solution of 500 grams of ferrous sulphate; the whole mixture is then thoroughly stirred, and exposed to the air until it acquires a deep black color.

Besides albumin and gelatine, starch and most of the alkaloids are also precipitated by tannic acid. $NaCl$ causes the separation of tannic acid from its solution. Lead acetate precipitates it as a basic tannate, which is insoluble in acetic acid. Copper sulphate also precipitates it immediately. Alum and potash added to tannic acid give a precipitate that is insoluble in cold potash solution. If potash or ammonia is added to a solution of tannic acid, it acquires a brownish color, owing to the absorption of oxygen.

If, to an alcoholic solution of tannic acid, an alcoholic solution of potash is added, a precipitate of *potassium tannate* $C_{13}H_9O_7 \cdot CO_2K$ is obtained, and if this precipitate is dissolved in water and a solution of $BaCl_2$ added, a precipitate, which is *barium tannate* $(C_{13}H_9O_7 \cdot CO_2)_2Ba$, is produced.

The tannic acids, or tannins, used in the arts, in the form of extracts of various parts of different plants, slightly vary in properties and, possibly, in composition. Pending a more exact knowledge as to their constitution, they are distinguished by names implying the sources from which they are derived; thus, *quercitannic acid* is obtained from the bark of the oak tree, *quinotannic acid* from cinchona bark, *caffeotannic acid* from coffee, etc.

**124. Coumaric Acid.**—Coumaric acid, or *1 : 2-hydroxy cinnamic acid* $C_6H_4(OH) \cdot CH : CH \cdot CO_2H$, occurs in *faham* *leaves*, and is readily prepared from *coumarin*, its anhydride, by boiling with potash. Coumarin  $C_6H_4<\begin{matrix}O-CO\\CH:CH\end{matrix}$ is that substance which causes the well known odor of hay and of the Tonka bean (*Coumaroma odorata*). Coumarin is extracted from these plants by boiling with alcohol, and crystallizes in slender, shining needles. It has been prepared artificially by heating sodio-salicylic aldehyde with sodium acetate and acetic anhydride.

**125. Caffeic Acid.**—Caffeic acid, or *dihydroxy cinnamic acid* $C_6H_3(OH)_2\cdot CH:CH\cdot CO_2H$, is prepared by boiling, with caustic soda, the residue obtained by evaporating the coffee beverage and precipitating the solution with $HCl$. It crystallizes in slightly yellowish plates, or prisms, and is readily soluble in hot water and alcohol.

**126. Quinic Acid.**—Quinic, or *kinic*, acid, or *tetrahydroxy benzoic hexanhydride* $C_6H\cdot H_6\cdot(OH)_4\cdot CO_2H$, occurs in cinchona bark, in coffee, and in various other plants, and is obtained as a by-product in the manufacture of quinine.

Quinic acid forms transparent colorless prisms, which are easily soluble in water, but only very slightly soluble in alcohol. It melts at 162°, and is decomposed at a higher temperature. By means of oxidizing agents ($MnO_2$ and $H_2SO_4$), it is converted into *quinone* $C_6H_4O_2$, and carbonic and formic acids. By fusion with potash, it yields protocatechuic acid.

## DIBASIC ACIDS FROM PARAFFIN HYDROCARBONS

**127. Oxalic, or Succinic, Series.**—The acids of this important series may be considered as being derived from the hydrocarbons by the substitution of two $COOH$ groups for two atoms of $H$. They may evidently be obtained by oxidation of diprimary glycols. The general formula of the series is $C_nH_{2n}(COOH)_2$. The acids of this series are solid, crystallizable, and non-volatile bodies; most of them are easily soluble in water, and all have a strong acid reaction.

They are characterized by their behavior when heated. Those that contain the $COOH$ groups attached to different carbon atoms, tend to form internal anhydrides by loss of water, while those that have the $COOH$ group attached to one and the same carbon atom, yield $CO_2$ and an acid of the acetic series. When fused with $KOH$, they yield $K_2CO_3$ and a salt of the acetic series. Many of these acids are produced by the action of powerful oxidizers on a variety of organic bodies; thus, succinic, adipic, pimelic, and suberic acids are produced by treating various fatty and resinous bodies with nitric acid.

**128. Oxalic Acid.**—This important acid $(CO_2H)_2$, occurs in many plants, and, chiefly as potassium salt, in the different varieties of *Oxalis* and *Rumex*. The calcium salt is often found in plant cells; it is also met in the animal economy. Urine frequently deposits little crystals of calcium oxalate, and the salt is sometimes found in the bladder, where it forms rough concretions, known to medical science as *mulberry calculi*.

Oxalic acid is, as a rule, prepared, on the small scale, by oxidizing sugar with nitric acid, and, on the large scale, by the oxidation of sawdust with potash.

*Preparation.*—1. By the oxidation of sugar with nitric acid:

$$C_{12}H_{22}O_{11} + 9O_2 = 6C_2H_2O_4 + 5H_2O$$

One part of sugar is gently heated in a retort with 5 parts of concentrated nitric acid, specific gravity 1.42. The light is removed when the action commences, and copious red fumes are seen to disengage. When the action slackens, heat may again be applied to the vessel, and the liquid concentrated by distilling off the superfluous nitric acid, until it deposits crystals on cooling. These are drained, redissolved in a small quantity of hot water, and the solution set aside and allowed to dry by exposure to air.

2. By heating sawdust with caustic alkalies: Common pine sawdust is made into a thick paste with a solution containing $KOH + 2NaOH$, and having a specific gravity of

1.35. This is spread on iron plates and gradually heated, care being taken to keep it in motion by constantly stirring. The action of the heat expels a quantity of water, and the mixture is kept for some hours at a temperature of about 204°, without allowing the mass to become charred, which would cause a loss of oxalic acid. The final product thus obtained is a gray powder; this is then treated with water at about 15.5°, which leaves the sodium oxalate undissolved. The supernatant liquid is drawn off, evaporated to dryness, and heated in furnaces to recover the alkalies, which are causticized and used for new operations. The sodium oxalate is washed and decomposed by boiling with slaked lime, and the resulting calcium oxalate is decomposed by means of sulphuric acid. The liquid decanted from the calcium sulphate is evaporated to crystallization in leaden vessels, and the crystals are purified by recrystallization.

**Properties.**—Oxalic acid crystallizes from its aqueous solution in monoclinic prisms with 2 molecules of water, which effloresce at 20° in dry air. Large quantities of oxalic acid, from about 10 grams upwards, introduced into the system are poisonous. It acts on the heart, retarding its movements, and on the nerve centers, of which it rapidly depresses the functions. Its antidote is chalk or precipitated calcium carbonate. It is soluble in 9 parts of water of medium temperature, and dissolves quite easily in alcohol. It melts in its water of crystallization at 98°, begins to disengage gases at 132°, and, between 155° and 160°, decomposes into formic acid and carbon dioxide, and also into $CO_2$, $CO$, and $H_2O$; both reactions take place at the same time, as shown in the following two equations:

$$(1) \qquad C_2H_2O_4 = CH_2O_2 + CO_2$$

$$(2) \qquad C_2H_2O_4 = CO_2 + CO + H_2O$$

When heated with sulphuric acid, it is decomposed into carbon monoxide, carbon dioxide, and water. An aqueous oxalic-acid solution under the influence of light decomposes into $CO_2$, $H_2O$, and, with sufficient oxygen access, $H_2O_2$. If a solution of oxalic acid, or, better, ammonium oxalate, is added to a solution of calcium chloride, a white precipitate of calcium oxalate is formed. This precipitate is formed even in very dilute solutions, and is insoluble in acetic acid.

If a small quantity of silver oxalate $C_2O_4Ag_2$ is quickly heated in a small test tube, it explodes violently.

All these reactions characterize oxalic acid.

Oxalic acid is largely used in calico printing, in dyeing and bleaching, in cleaning brass, and in removing iron stains from linen.

**129. Oxalates.**—The oxalates, except those of the alkali metals, are almost insoluble in water. *Sodium oxalate* $Na_2C_2O_4$ occurs in various plants growing in salt marshes. *Normal potassium oxalate* $K_2C_2O_4 \cdot 2H_2O$ is moderately soluble. *Hydropotassium oxalate*, also known as *potassium binoxalate* $KHC_2O_4 \cdot 2H_2O$, is sometimes called *salt of sorrel* and very often *essential salt of lemons*, which latter name is, however, wrong, as lemons contain no oxalic acid whatever. *Trihydro-potassium oxalate*, or *potassium quadroxalate* $KHC_2O_4 \cdot C_2H_2O_4 \cdot 2H_2O$, is more commonly sold as salt of sorrel. *Ammonium oxalate* $(NH_4)_2C_2O_4 \cdot 2H_2O$ occurs in Peruvian guano. It finds employment in analysis from the precipitation of calcium it produces (see *Qualitative Analysis*). It crystallizes in needles from a solution of oxalic acid that has been neutralized with ammonia. *Calcium oxalate* $CaC_2O_4 \cdot 4H_2O$ occurs crystallized in plant cells, and certain plants growing in soil rich with limestone contain sometimes as much as half their entire weight of calcium oxalate. As has been previously mentioned, it is occasionally found in abnormal urine and in calculi. *Ferrous oxalate* $(CO_2)_2Fe$ occurs as *oxalite* in coal; *ferric oxalate* $(CO_2)_6Fe_2$, when exposed to sunlight in the presence of water, evolves $CO_2$ and deposits a yellow crystalline precipitate of $(CO_2)_2Fe, 2Aq$. Ferric oxalate is used in photography. *Potassium ferrous oxalate* $(CO_2)_4FeK_2$ is prepared by adding potassium oxalate in excess to ferrous sulphate; it is a very powerful reducing agent, and is used as such quite frequently in photography. *Potassium chromic oxalate* $(CO_2)_6K_3Cr, 3H_2O$ is obtained in crystals of dark-blue, or nearly black, color, by dissolving in water 1 part of potassium dichromate, 2 parts of hydropotassium oxalate, and 2 parts of oxalic acid. Neither the oxalic acid nor the $Cr_2O_3$ can be precipitated from this salt by the usual tests. *Manganese oxalate* $(CO_2)_2Mn$ is used, mixed with drying oils, in the manufacture of varnishes, etc.

**130. Malonic Acid.**—Malonic acid $CH_2(CO_2H)_2$ is the next higher homologue of oxalic acid. It was discovered in 1858 by Dessaignes, on oxidizing malic acid $CO_2H\cdot CH(OH)\cdot CH_2\cdot CO_2H$ with potassium bichromate and sulphuric acid. It occurs as calcium salt in sugar beets. It is usually prepared from monochloracetic acid $CH_2Cl\cdot CO_2H$ by converting it into the potassium salt, and boiling this with potassium cyanide, when potassium cyanacetate $CH_2(CN)\cdot CO_2K$ is formed. This is boiled with potash, which converts it into potassium malonate:

$$CH_2(CN)\cdot CO_2K + H_2O + KOH = CH_2(CO_2K)_2 + NH_3$$

The excess of potash is neutralized by $HCl$, and calcium chloride added, which precipitates calcium malonate; by boiling this with oxalic acid, the calcium is left as oxalate, and the solution deposits tabular crystals of malonic acid.

Malonic acid melts at 132°, and crystallizes in triclinic plates. It is easily soluble in water and alcohol. Above its melting point, it decomposes into $CO_2$ and acetic acid.

*Barium malonate* has the formula $(C_3H_2O_4)Ba, 2H_2O$. The *calcium salt* $C_3H_2O_4Ca, 2H_2O$ dissolves with difficulty in cold water. The *silver salt* $C_3H_2O_4Ag_2$ is a white crystalline compound, which is insoluble.

**131. Succinic Acids.** — Succinic acid $C_2H_4(CO_2H)_2$ exists in two modifications; namely,

| $CO_2H\cdot CH_2\cdot CH_2\cdot CO_2H$ | $CH_3\cdot CH(CO_2H)_2$ |
|---|---|
| ethylene succinic acid | ethylidene succinic acid |

Ethylene succinic acid, or common succinic acid, may be produced by the fermentation of tartaric acid, the latter acid being considered as dihydroxysuccinic acid $C_2H_2(OH)_2(CO_2H)_2$, which in this way becomes reduced to succinic acid.

The diluted tartaric acid is neutralized with ammonia, and mixed with a little magnesium sulphate, potassium phosphate, and calcium chloride, these three compounds being added for the purpose of serving as mineral food for the bacteria, which cause the fermentation and which soon grow if the flask is kept in a warm room (about 25°), and carefully corked to exclude air. The fermentation proceeds slowly but steadily, and, after the expiration of about two months, the ammonium tartrate in the flask has been converted into ammonium succinate and carbonate; this mixture is boiled to expel the latter, milk of lime is added, and the whole is again boiled as long as $NH_3$ is expelled; the calcium succinate is then decomposed by sulphuric acid, and the liquid is filtered from the calcium sulphate and evaporated to crystallization.

Succinic acid forms large colorless crystals, which remain unaltered when exposed to the air, but, when heated, they begin to emit vapors at 120° and to fuse at 180°. At 235°, succinic acid boils and breaks up into succinic anhydride and water, according to the equation:

$$\underset{\substack{\text{succinic}\\\text{acid}}}{C_4H_6O_4} = \underset{\substack{\text{succinic}\\\text{anhydride}}}{C_4H_4O_3} + H_2O$$

The vapors of succinic acid provoke coughing in a remarkable degree, thus affording a sure, but rather disagreeable, test for this acid. Succinic acid dissolves in 20 parts of cold water and 3 parts of hot water; it is moderately soluble in alcohol, but only sparingly in ether. Fusion with $KOH$ converts it into potassium carbonate and potassium propionate, as is seen from the equation:

$$C_2H_4(CO_2H)_2 + 3KOH = CO(OK)_2 + C_2H_5 \cdot CO_2K + 2H_2O$$

*Calcium succinate* $C_2H_4(CO_2)_2Ca$ crystallizes with 3 molecules of water from a hot solution, and with 1 molecule of water from a cold solution; it is rather sparingly soluble in water. It occurs in nature in the bark of the mulberry tree. When ammonium succinate is added to a solution containing a ferric salt, all the iron is precipitated as a reddish-brown *basic ferric succinate* $Fe_2(C_4H_4O_4)_2(OH)_2$ (used in analytical chemistry in the separation of iron from aluminum).

Succinic acid is manufactured by the dry distillation of refuse amber, which contains it ready formed, in iron retorts, and by purifying the solid product of this distillation.

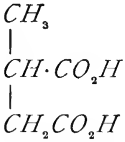
Malic acid is hydroxysuccinic acid, and is reduced by fermentation to succinic acid. Both malic and tartaric acids are reduced to succinic acid by the action of hydriodic acid. Succinic acid has been obtained synthetically by boiling ethene dibromide with potassium cyanide dissolved in alcohol, and then boiling the ethene cyanide thus obtained with $KOH$ dissolved in alcohol:

$$(1)\quad C_2H_4Br_2+2KCN = C_2H_4(CN)_2+2KBr$$
$$(2)\quad C_2H_4(CN)_2+2KOH+2H_2O = C_2H_4(CO_2K)_2+2NH_3$$

Succinic acid is always produced in small quantities in the fermentation of sugar, and is consequently always to be found in fermented beverages, such as wine and beer. It occurs in unripe grapes, while ripe grapes contain tartaric acid (dihydroxysuccinic acid). It occurs in various plants, such as lettuce, poppies, wormwood, etc., and it is also found in the urine of the horse, the dog, and the rabbit.

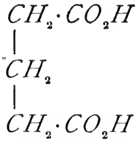
*Ethylidene succinic acid*, or *isosuccinic acid* $CH_3\cdot CH(CO_2H)_2$, which is isomeric with succinic acid, is obtained by boiling with potassium hydrate the cyanide of ethylidene $CH_3\cdot CH(CN)_2$. It crystallizes in needles, fuses at 130°, and is more soluble in water than succinic acid.

**132. Pyrotartaric Acid.**—Pyrotartaric acid $C_5H_8O_4$ exists in four modifications; namely,



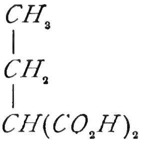
$$\begin{array}{l} CH_3 \\ | \\ CH\cdot CO_2H \\ | \\ CH_2CO_2H \end{array}$$

pyrotartaric acid, or methylsuccinic acid



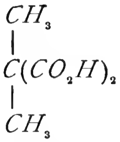
$$\begin{array}{l} CH_2\cdot CO_2H \\ | \\ CH_2 \\ | \\ CH_2\cdot CO_2H \end{array}$$

glutaric acid



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH(CO_2H)_2 \end{array}$$

ethylmalonic acid

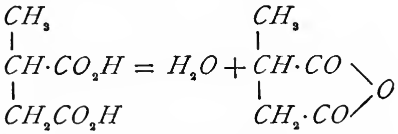


$$\begin{array}{l} CH_3 \\ | \\ C(CO_2H)_2 \\ | \\ CH_3 \end{array}$$

dimethylmalonic acid

*Methylsuccinic acid* is obtained by the dry distillation of tartaric acid mixed with an equal weight of powdered pumice stone. The distillate is mixed with water, filtered from oily matter, evaporated on the water bath, and finally crystallized from alcohol.

It crystallizes in small rhombic prisms, and is readily soluble in water, ether, and alcohol. It melts at 112°, and, when rapidly heated, it is resolved into water and methylsuccinic anhydride:



The remaining acids of this series are not of sufficient technical importance to warrant their description here; the names and sources of the most important among the great many isomerides will be found in Table XII.

### DIBASIC ACIDS FROM OLEFINE HYDROCARBONS

**133. Fumaric Series.**—The acids of this series are unsaturated acids; their general formula may be represented as $C_nH_{2n-2}(CO_2H)_2$, and they are capable of taking up 2 atoms of bromine to become dibromo derivatives of the acids of the preceding series.

Fumaric acid is the first acid of this series, its formula is $C_2H_2(CO_2H)_2$, and might, consequently, exist in two modifications; namely, $CO_2H \cdot CH : CH \cdot CO_2H$ and $CH_2 : C(CO_2H)_2$. Fumaric acid and maleic acid have exactly the same composition and molecular formula, but there is not sufficient evidence to show that these two acids are position isomerides; they appear rather to be stereo-isomerides.

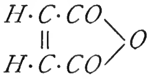
**134. Fumaric Acid.** — Fumaric acid $C_2H_2(CO_2H)_2$ exists, in the free state, in many plants, in Iceland moss, in *Fumaria officinalis* (common fumitory), and in some fungi. It is prepared by heating malic acid strongly as long as water distils over:

$$C_2H_3(OH)(CO_2H)_2 = C_2H_2(CO_2H)_2 + H_2O$$

The residue is treated with cold water to extract unaltered malic acid, and the fumaric acid is obtained by crystallization from either hot water or alcohol. When heated to 200°, it partly sublimes undecomposed and the rest decomposes into water and maleic anhydride. If fumaric acid is heated to about 150° with a large excess of water, it is reconverted into malic acid.

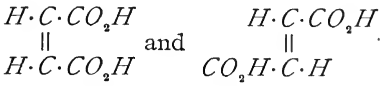
The *fumarates of barium, calcium,* and *lead* are sparingly soluble; the silver salt $C_4H_2O_4Ag_2$ is very insoluble and explodes when heated.

**135. Maleic Acid.**—Maleic acid, which is, as has been already stated, isomeric with fumaric acid, may be prepared by the rapid heating of malic acid, or by the action of $PCl_5$ on the same acid, and in various other ways. Maleic acid crystallizes in large prisms or plates, is very easily soluble in cold water, and possesses a peculiar, disagreeable taste. The crystals melt at 130°, and boil at 160° with decomposition into maleic anhydride,



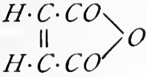
Its silver salt $C_4H_2O_4Ag_2$ is a finely divided precipitate, which gradually changes into large crystals. Its barium salt $C_4H_2O_4Ba, H_2O$ is soluble in hot and cold water and crystallizes well.

**136.** In order to be able to form a tangible idea of, and to account for, the isomerism between fumaric and maleic acids, it is assumed that the $CO_2H$ groups are differently situated with regard to a plane drawn through the two nuclear carbon atoms of the molecule. On the plane of the paper, the assumed difference may be represented by the two formulas:



$$\begin{array}{c} H\cdot C\cdot CO_2H \\ \| \\ H\cdot C\cdot CO_2H \end{array} \quad \text{and} \quad \begin{array}{c} H\cdot C\cdot CO_2H \\ \| \\ CO_2H\cdot C\cdot H \end{array}$$

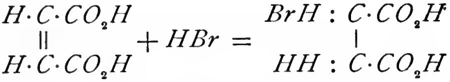
The first of these two formulas is known as the *plane-symmetrical,* or *cis, formula,* while the second is called the *axial-symmetrical, centri-symmetrical,* or *trans,* *formula.* Since maleic acid very readily forms an anhydride,



$$\left.\begin{array}{l}H\cdot C\cdot CO\\ \quad\|\\ H\cdot C\cdot CO\end{array}\right\rangle O,$$

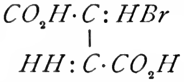
it may be supposed to have the first formula, because the formation of an anhydride would occur the more easily the nearer the $CO_2H$ groups are to each other. Many cases of stereo-isomerism are believed to be explicable by formulas resembling those given above, so that the expressions *maleinoid* and *fumaroid structure* are frequently used.

It has been shown in a preceding Section that doubly linked carbon atoms might be supposed to occupy each the center of a tetrahedron, which tetrahedra have one edge in common. When maleic acid is treated with $HBr$, the double linking is opened up, a change that may be presented thus:



$$\begin{array}{l}H\cdot C\cdot CO_2H\\ \quad\|\\ H\cdot C\cdot CO_2H\end{array} + HBr = \begin{array}{l}BrH : C\cdot CO_2H\\ \qquad\quad\ |\\ HH : C\cdot CO_2H\end{array}$$

The formula of this bromo-succinic acid must be regarded as formed of two tetrahedra with a solid angle in common (see Fig. 26, *Organic Chemistry*, Part 2). It is assumed that tetrahedra having one edge in common cannot rotate with regard to one another, but that those having only a solid angle in common can rotate in this manner. Now, if this is the case, the bromo-succinic acid shown above may rotate and become



$$\begin{array}{l}CO_2H\cdot C : HBr\\ \qquad\qquad |\\ \quad HH : C\cdot CO_2H\end{array}$$

rather than remain as previously represented, because the radicals $CO_2H$ and $H$ and $Br$ may be expected to attract one another. By treating this bromo-succinic acid with alkalies, it is possible to remove $HBr$ from it, and if this is done, the acid that remains should be fumaric acid, not maleic acid. This is actually found to be the case, so that the formula given above for fumaric acid is, to some extent, confirmed.

**137.** As is seen from Table XIII there are three isomeric acids having the formula $C_3H_4(CO_2H)_2$; namely, *itaconic*, *citraconic*, and *mesaconic acid.*

*Itaconic* and *citraconic acids* are formed by the action of heat on citric and aconitic acids; they both are, by dehydration, converted into citraconic anhydride. Citraconic acid is converted into mesaconic acid when it is boiled with dilute nitric acid, or when heated to 100° with concentrated hydrochloric acid. The three acids, itaconic, citraconic, and mesaconic, are unsaturated and can combine with nascent hydrogen, forming pyrotartaric acid:

$$C_5H_6O_4 + 2H = C_5H_8O_4$$

*Itaconic acid* crystallizes in rhombic octahedrons, dissolves in 17 parts of water at 10°, melts at 161°, and is resolved by distillation into water and citraconic anhydride.

*Citraconic acid* crystallizes in four-sided prisms which melt at 80°. It is much more soluble in water than itaconic acid, and deliquesces on exposure to the air. Its anhydride $C_5H_4O_3$ forms an oily liquid, which readily recombines with water to form the acid.

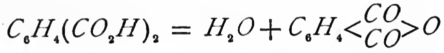
*Mesaconic acid* forms shining prisms, which are only sparingly soluble in cold water. It melts at 208° and sublimes without decomposition.

The isomerism of citraconic and mesaconic acids is analogous to that of maleic and fumaric acids.

## DIBASIC ACIDS FROM HYDROCARBONS CONTAINING A BENZENE NUCLEUS

**138.** These acids are obtained, as their class name indicates, from benzene hydrocarbons. Thus, the most important of these acids, phthalic acid $C_6H_4(CO_2H)_2$, may be prepared by the oxidation of one of the three xylenes $C_6H_4(CH_3)_2$.

**139. Phthalic Acids.**—Phthalic acid $C_6H_4(CO_2H)_2$ is formed by the action of nitric acid on naphthalene, or naphthalene tetrachloride. It crystallizes in brilliant scales or in short, thick prisms, which are only slightly soluble in cold water, but readily dissolve in hot water, alcohol, and ether. It fuses at 185°, and is resolved at a higher temperature into water and phthalic anhydride $C_8H_4O_3$:



$$C_6H_4(CO_2H)_2 = H_2O + C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>O$$

phthalic anhydride

When heated with an excess of calcium hydrate, phthalic acid is decomposed into $2CO_2$ and benzene, but when exactly 2 molecules of it are heated with 1 molecule of $Ca(OH)_2$, it yields calcium benzoate:

$$2C_8H_6O_4 + Ca(OH)_2 = (C_7H_5O_2)_2Ca + 2CO_2 + 2H_2O$$

Chromic acid oxidizes phthalic acid completely into $CO_2$ and $H_2O$.

Barium chloride added to a solution of ammonium phthalate precipitates barium phthalate $C_8H_4O_4Ba$, which is only very slightly soluble in water.

Phthalic acid is found among the products of oxidation of alizarine and purpurine with nitric acid, as is seen from the subjoined equations:

$$\underset{\text{alizarine}}{C_{14}H_8O_4} + 2H_2O + 5O_2 = \underset{\substack{\text{phthalic}\\ \text{acid}}}{C_8H_6O_4} + \underset{\substack{\text{oxalic}\\ \text{acid}}}{3C_2H_2O_4}$$

$$\underset{\text{purpurine}}{C_{14}H_8O_4} + 2H_2O + 5O_2 = \underset{\substack{\text{phthalic}\\ \text{acid}}}{C_8H_6O_4} + \underset{\substack{\text{oxalic}\\ \text{acid}}}{3C_2H_2O_4}$$

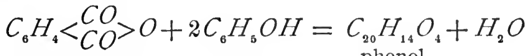
*Isophthalic acid*, or 1:3-phthalic acid, crystallizes in needle-shaped crystals. It is soluble in hot water and sparingly soluble in cold water. It yields no anhydride when heated, but sublimes unchanged. Its barium salt dissolves easily in water, so that the acid is not precipitated by barium chloride from the solution of its ammonium salt, which distinguishes it from its two isomerides.

*Terephthalic acid*, or 1:4-phthalic acid, is difficult to crystallize, and is generally obtained as a white powder. It is insoluble in water, so that it is precipitated from its solution in alkali by adding acid. The *barium phthalate* is only sparingly soluble. This acid does not yield an anhydride.

These differences in the properties of the three different phthalic acids are of importance, as the production of one or the other frequently helps to decide the constitution of a benzene derivative.

*Phthalic anhydride* $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>O$ is obtained by heating phthalic acid, as has been previously mentioned. It forms long shining needles, which fuse at 128° and boil at 284°. Phthalic anhydride, when heated with phenols, combines with them directly, with the elimination of the elements of water, and compounds are obtained that are designated as *phthaleins.*

Thus, when phthalic anhydride is heated with ordinary phenol, 2 molecules of phenol combine with 1 molecule of phthalic anhydride, 1 molecule of water is expelled, and *phthalein of phenol* is obtained:



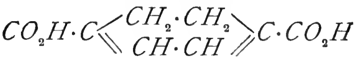
$$\underset{\text{phthalic anhydride}}{C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>O} + \underset{\text{phenol}}{2C_6H_5OH} = \underset{\text{phenol phthalein}}{C_{20}H_{14}O_4} + H_2O$$

Phthalic anhydride is used in the preparation of various dyes, which will be treated later.

**140.** By treating phthalic acids with nascent hydrogen, a large number of hydrogen addition products, *hydrophthalic acids*, e. g., $C_6H_4 \cdot H_4 \cdot (COOH)_2$, has been obtained. These acids are remarkable for the numerous cases of isomerism they exhibit, the cause of which has been traced to the existence of *cis* and *trans* forms, as in the case of maleic and fumaric acids, and also to the different positions of the double linking between the carbon atoms of the benzene nucleus; thus, the two following dihydroterephthalic acids are found to be isomeric:

$$CO_2H \cdot C \genfrac{}{}{0pt}{}{\diagup CH_2 CH \diagdown\!\diagdown}{\diagdown\!\diagdown CH \cdot CH_2 \diagup} C \cdot CO_2H$$

and



$$CO_2H \cdot C \genfrac{}{}{0pt}{}{\diagup CH_2 \cdot CH_2 \diagdown}{\diagdown\!\diagdown CH \cdot CH \diagup\!\diagup} C \cdot CO_2H$$

The nomenclature used to express this isomerism is the insertion of the symbol △ before the number of that carbon atom which is doubly linked to the one following it; thus, △2 would imply a benzene ring in which carbon atom No. 2 is doubly linked to carbon atom No. 3. The formulas given above are, according to this nomenclature, given as follows: △3, 6 dihydroterephthalic acid, and △4, 6 dihydroterephthalic acid, respectively:

**141. Isouvitic acid** $C_7H_6\cdot(CO_2H)_2$ is obtained by fusing gamboge (a gum resin) with potash. It crystallizes in short prisms, which fuse at 160°. It is sparingly soluble in hot water, but dissolves readily in alcohol and in ether.

**Cumidic acid** $C_6H_2(CH_3)_2\cdot(CO_2H)_2$ is prepared by boiling durene $C_6H_2(CH_3)_4$ with dilute nitric acid. It crystallizes in long transparent prisms; it is sparingly soluble in water, but dissolves readily in alcohol.

**Cumilic acid** $C_6H_2(CH_3)_3\cdot CO_2H$ is formed at the same time as cumidic acid. It fuses at 150° and sublimes in needles, while cumidic acid does not fuse and sublimes in scales.

**142. Dibasic Hydroxy Acids.**—The acids of this series may be regarded as oxidation products of diprimary polyhydric alcohols, or, in the case of those having a benzene nucleus, as dicarboxylic acids from phenol.

**143. Tartronic Acid.**—Tartronic acid, or *hydroxymalonic acid* $CH(OH)(CO_2H)_2$, is formed by the action of nascent hydrogen on mesoxalic acid:

$$\underset{\text{mesoxalic acid}}{CO(CO_2H)_2} + 2H = \underset{\text{tartronic acid}}{CH(OH)(CO_2H)_2}$$

It is also obtained by spontaneous decomposition of dinitrotartaric acid, when its aqueous solution is left to evaporate, the decomposition being attended with the evolution of carbon dioxide and nitrogen trioxide:

$$\underset{\text{dinitrotartaric acid}}{C_2H_2(O\cdot NO_2)_2(CO_2H)_2} = \underset{\text{tartronic acid}}{CH(OH)(CO_2H)_2} + CO_2 + N_2O_3$$

This acid forms large prismatic crystals, which are easily soluble in water, alcohol, and ether. The crystals melt at

175°, and are resolved, at a higher temperature, into carbon dioxide, water, and glycollide $C_2H_2O_3$, which is an amorphous substance, and an anhydride of glycollic acid.

**144. Malic Acid.**—Malic acid, or *hydroxysuccinic acid* $C_2H_3(OH)(CO_2H)_2$, is one of the chief natural vegetable acids, and was first extracted by Scheele, in 1785, from apple juice. It is mostly prepared from the unripe berry of the mountain ash. The juice of these berries is extracted by pressure, boiled, filtered, and neutralized with milk of lime. Calcium malate is deposited, which is converted into the acid, or hydrocalcium, malate by being dissolved in hot nitric acid diluted with ten times its weight of water; on cooling hydrocalcium malate, $[C_2H_3(OH)(CO_2H)\cdot CO_2]_2Ca,8H_2O$ crystallizes out. This is converted into malate of lead by decomposition with lead acetate. The precipitated lead malate is suspended in pure water and decomposed by hydrogen sulphide, when $PbS$ is precipitated and malic acid is found in solution. The liquid is at last filtered and the acid obtained by evaporation.

Malic acid crystallizes in little needles grouped in rounded grains, which deliquesce when exposed to the air. It fuses at 100°, and, at a higher temperature, yields a feathery sublimate of maleic and fumaric acids and of maleic anhydride. When boiled for a considerable time with hydrochloric acid, it is converted into fumaric acid and water. Hydriodic acid reduces it to succinic acid:

$$C_2H_3(OH)(CO_2H)_2+2HI = C_2H_4(CO_2H)_2+H_2O+I_2$$

Oxidation by chromic acid converts malic acid into malonic acid.

Malic acid presents three isomerides. Their solutions have a sour taste; one of them, the natural acid, rotates the plane of polarized light to the left, another to the right, and the third is optically inactive. They are identical in structure and must be regarded as stereo-isomeric.

**145. Tartaric Acid.**—Tartaric acid, or *dihydroxysuccinic acid* $CO_2H\cdot CHOH\cdot CHOH\cdot CO_2H$, or $C_4H_6O_6$, or

$C_2H_2(OH)_2(CO_2H)_2$, is one of the most widely distributed vegetable acids. It was discovered, like malic acid, by Scheele, in 1769, in the *tartar*, or *argol*, which is deposited in casks in which wine has been stored. It is mostly prepared from the purified tartar, known as *cream of tartar*, which is *hydropotassium tartrate.* The hydropotassium tartrate is dissolved in boiling water, and powdered chalk is added as long as effervescence is produced, or as long as the liquid exhibits an acid reaction; calcium tartrate and potassium tartrate are thereby produced, and the latter is separated from the former, which is insoluble in water, by filtration. The solution of potassium tartrate is then mixed with excess of calcium chloride, which precipitates all the remaining potassium tartrate in the form of calcium salt; this is washed and added to the former portion, and the whole is digested with a sufficient quantity of dilute sulphuric acid and heated, when calcium sulphate is precipitated, and the tartaric acid is obtained by evaporating the filtered solution. The crude acid thus obtained is dissolved in water, decolorized by animal charcoal, and recrystallized; a little sulphuric acid is most always added, in order to promote the formation of large crystals. The following equations represent the various stages in the manufacture of the acid:

$$\text{(1)} \quad 2C_4H_4O_6KH + CaCO_3 = C_4H_4O_6K_2 + C_4H_4O_6Ca + H_2O + CO_2$$

$$\text{(2)} \quad C_4H_4O_6K_2 + CaCl_2 = C_4H_4O_6Ca + 2KCl$$

$$\text{(3)} \quad C_4H_4O_6Ca + H_2SO_4 = C_4H_4O_6H_2 + CaSO_4$$

Tartaric acid forms colorless, transparent prisms, which are very often of quite considerable size; they are permanent in air, odorless, and dissolve readily in water, either cold or hot, and in alcohol. The solution of tartaric acid reddens litmus strongly and has a pure acid taste. When crystallized tartaric acid is rapidly heated to 170°, it fuses and becomes an amorphous, deliquescent mass of *metatartaric acid*, which is isomeric with it. At 145°, it becomes *tartralic acid* $C_8H_{10}O_{11}$, 2 molecules of the acid having lost a molecule of water; at 180°, it yields *tartrelic acid* $C_8H_8O_{10}$

and *tartaric anhydride*, which is isomeric with it. All these compounds may be readily reconverted into tartaric acid by digestion with water. On further heating, it undergoes destructive distillation, yielding *acetic*, *pyroracemic* $C_3H_4O_3$, *pyrotartaric* $C_5H_8O_4$, *pyrotritartaric* $C_7H_8O_3$, and *formic acids*, together with *dipyrotetracetone* $C_8H_{12}O_2$, which is characterized by its peculiar odor, closely resembling that of burned sugar.

Fused $KOH$ converts tartaric acid into acetate and oxalate. When distilled with sulphuric acid and $MnO_2$ or $K_2Cr_2O_7$, it yields formic acid and $CO_2$, and when boiled with nitric acid, it is converted into oxalic acid.

When a strong aqueous solution of hydriodic acid and tartaric acid are heated together to 120° in a closed tube, the tartaric acid is reduced to malic acid, and the latter in its turn to succinic acid, as is seen from the two equations:

$$\underset{\text{tartaric acid}}{C_2H_2(OH)_2(CO_2H)_2}+2HI = \underset{\text{malic acid}}{C_2H_3(OH)(CO_2H)_2}+H_2O+I_2$$

$$\underset{\text{malic acid}}{C_2H_3(OH)(CO_2H)_2}+2HI = \underset{\text{succinic acid}}{C_2H_4(CO_2H)_2}+H_2O+I_2$$

Conversely, tartaric acid may be produced synthetically from dibromo-succinic acid.

Tartaric acid is, as has been previously stated, one of the most important vegetable acids, and it occurs in most fruits, closely associated with malic acid. Tartaric acid is a dibasic acid, and forms an acid potassium salt, which is remarkable for being sparingly soluble, and which is precipitated in minute crystals when almost any salt of potassium is added to tartaric acid and stirred with a glass rod. The natural tartaric acid, just described, is dextrorotary.

**146. Tartrates.**—*Hydropotassium tartrate* $HKC_4H_4O_6$ is commonly known as *cream of tartar*. It is prepared by recrystallizing argol from hot water, which dissolves about $\frac{1}{15}$ of its weight, but only retains $\frac{1}{200}$ on cooling. It forms irregular groups of small, translucent, or transparent, prismatic crystals, which grate between the teeth. It has a decidedly acid reaction and a sour taste. When heated, it evolves a characteristic smell of burned sugar, and leaves a residue consisting of a mass of black charcoal mixed with potassium carbonate. It is nearly insoluble in alcohol, which precipitates it from its aqueous solution, which explains its separation from the grape juice ; as the proportion of alcohol increases while the process of fermentation is going on. It dissolves readily in acids and in alkalies, which convert it into *normal potassium tartrate* $K_2C_4H_4O_6$. *Potassium sodium tartrate* $KNaC_4H_4O_6,4Aq$ is much used in medicine as a purgative; it was discovered in 1672 by Seignette, a pharmacist of Rochelle, hence, it is often called *Rochelle salt* or *Seignette salt.* It is prepared by neutralizing a boiling solution of cream of tartar with sodium carbonate, and evaporating this solution. On cooling, the double salt is obtained in fine, rhombic prisms. It has a mild saline taste. *Calcium tartrate* $CaC_4H_4O_6,4Aq$ occurs in grape and senna leaves. It is only sparingly soluble in water, and precipitates when $CaCl_2$ is added to an ammoniacal solution of a tartrate. *Cupric tartrate* $CuC_4H_4O_6,3Aq$ is sparingly soluble in water, but dissolves in alkalies to a deep-blue solution, in which 2 atoms of the alkali metal have displaced 2 atoms of hydrogen. This alkaline cupric solution, generally known as *Fehling's solution,* is frequently used in analytical chemistry for the detection of sugar. *Silver tartrate* $Ag_2C_4H_4O_6$ is precipitated by silver nitrate from a normal tartrate, and the solution deposits metallic silver when heated. *Potassium antimonyl tartrate* $K(SbO)C_4H_4O_6$, or *tartar emetic,* is readily prepared by boiling antimony trioxide in a solution of cream of tartar ; it is deposited from a hot and concentrated solution in rhombic prisms, which dissolve, without being decomposed, in 15 parts of cold water and 3 parts of boiling water, and have an acrid, disagreeable, metallic taste. The solution is decomposed by both acids and alkalies, the former precipitate a mixture of cream of tartar and antimony trioxide, and the latter precipitate the trioxide, which is again dissolved by great excess of the reagent. Hydrogen sulphide separates all the antimony as antimony trisulphide. Dry potassium antimonyl tartrate heated with the blowpipe on charcoal, yields a bead of metallic antimony. The crystals of potassium antimonyl tartrate have the composition $2K(SbO)C_4H_4O_6, Aq$, the group $SbO$ acting as a univalent radical, and replacing 1 atom of hydrogen. When dried at 100°, these crystals cast off their water of crystallization, and at 200° an additional molecule of water, leaving the compound $K(SbO)C_4H_2O_5$, which has the constitution of a salt of tartrelic acid; but when dissolved in water, the crystals again take up the elements of water, and reproduce the original salt.

**147.** *Racemic acid*, isomeric with tartaric acid, was discovered in 1822 by Kestner, and has been thoroughly investigated by Berzelius and Pasteur. It is prepared by heating tartaric acid with one-tenth of its weight of water in a sealed tube at 175° for about 30 hours. It is distinguished from tartaric acid by the form of its crystals, which are triclinic prisms, by having 1 molecule of water of crystallization, and by being much less soluble in water and less easily fusible. Moreover, it does not change the plane of polarized light, while tartaric acid is dextrorotary. The solution of racemic acid precipitates solutions of sulphate, nitrate, and chloride of calcium, a property that tartaric acid does not possess. Racemic acid is found mixed with tartaric acid extracted from certain samples of argol, and its crystals may be distinguished from those of tartaric acid by the cloudy appearance they assume at 100°, due to the loss of their water of crystallization.

**148.** *Calcium racemate* $CaC_4H_4O_6, 4Aq$ differs from calcium tartrate in being insoluble in acetic acid and only difficultly soluble in ammonium chloride. *Hydropotassium racemate* is more soluble than cream of tartar. *Sodium-ammonium racemate* $NaNH_4C_4H_4O_6$ has the same crystalline form as the corresponding tartrate, but while the crystals of the latter compound are exactly alike, the crystals of the former compound show certain irregularities, that is, they differ from one another in the position of certain unsymmetrical faces, which faces occupy, in different crystals of the racemate, not similar, but opposite positions, the one kind of crystal being, as it were, the reflected image of the other. The two different crystals are shown in Fig. 10, and they are said to be *enantiomorphous.* When these crystals are picked out, and each class separately dissolved in water, solutions are obtained, which, at the same degree of concentration, exert equal but opposite action on polarized light, the right-handed crystals (*a*) deflecting the planes of polarization to the right, and the left-handed crystals (*b*) deflecting an equal amount to the left.

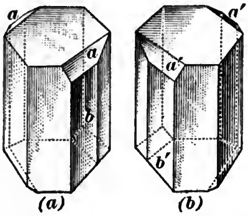


FIG. 10

Furthermore, the solutions of right-handed crystals when evaporated yield right-handed crystals only, while by the evaporation of a solution of left-handed crystals new left-handed crystals only are obtained; by mixing the solutions of these two varieties of crystals with calcium chloride, calcium salts are obtained, which, when decomposed by sulphuric acid, yield acids that agree with each other in composition and in all other respects, except that their crystalline forms exhibit the previously mentioned difference, and their solutions, when brought to the same degree of concentration, exert equal and opposite effects on polarized light. One of these solutions, in fact, is dextro-tartaric acid, while the other is levo-tartaric acid; and, if equal weights of dextro-tartaric and levo-tartaric acids in solution are mixed, heat is evolved. The mixture loses its entire effect on polarized light and is in every respect identical with racemic acid.

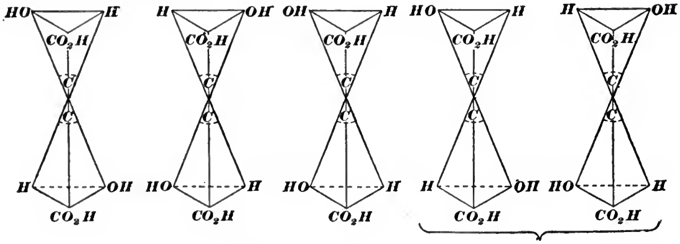
**149.** *Mesotartaric*, or *inactive tartaric*, *acid* is isomeric with tartaric acid, and while, like racemic acid, optically inactive, it has properties different from those of racemic acid. It is most easily prepared by heating ordinary tartaric acid with a little water in a sealed tube at 165° for 48 hours. The mass is dissolved in water, when racemic acid crystallizes out first. The unaltered tartaric acid is precipitated as hydropotassium tartrate, thus leaving the more soluble mesotartrate in solution. Mesotartaric acid crystallizes in rectangular tables with 1 molecule of water of crystallization. It is more soluble than racemic acid and rather less than ordinary tartaric acid. Neither the normal nor the hydropotassium salts crystallize.

*Calcium mesotartrate* $CaC_4H_4O_6,3H_2O$ is at first a flocculent precipitate, which, however, soon becomes crystalline. Free mesotartaric acid is not precipitated by calcium sulphate. When heated to 170°, it is converted into dextro-tartaric acid.

**150.** We have studied, in the preceding articles, four varieties of tartaric acid, which are stereo-isomeric to one another. If we consider carefully what has been said concerning stereo-isomerism in Art. **111,** we are well able to account for the existence of a dextro-, a levo-, and an optically inactive tartaric acid, by the presence of an asymmetric carbon atom; but the existence of a fourth variety, i. e., a second inactive acid, requires further explanation, which may here be given.

A great number of experiments have proved beyond any doubt that, according to whatever method tartaric acid is synthetically prepared, only the inactive but never the active forms of the acid have been obtained. This seems reasonable on the theory that the inactive form consists of an equal number of molecules of dextro- and levo-forms, for it is an equal chance whether the clockwise form or the anticlockwise form be produced, so that both forms are produced in equal amounts and the resulting compound, consequently, is inactive. It may, in fact, be considered as a general rule, that all artificial compounds, i. e., compounds synthetically produced, are optically inactive.

We have seen in Art. **146** that racemic acid can be split up into the dextro- and levo-acids, but the other inactive variety, *mesotartaric acid*, cannot be so split up. From these facts the conclusion has been drawn that racemic acid is composed of an equal number of molecules of dextro- and levo-acids, or that it is, as it is generally expressed, an *externally compensated compound*, and that mesotartaric acid is optically inactive from another cause, namely, because it is *internally compensated.* To explain this, reference must be made to the figures of tetrahedra shown in Fig. 26, *Organic Chemistry*, Part 2; tartaric acid belongs to the type of two tetrahedra having one solid angle in common, and to the other solid angles of each tetrahedron there must be three different radicals $H$, $OH$, and $CO_2H$ attached. It is evident that these three radicals must be either similarly or differently arranged around each tetrahedron. If they are similarly arranged, then it will be possible on severing the tetrahedra to place one inside the other, so that each solid angle shall correspond; if they are differently arranged, this will, of course, be impossible. It is supposed that when the radicals are similarly arranged, the tartaric acid is either dextro- or levo-rotary, according as the arrangement is clockwise or anticlockwise; but, if they are differently arranged, the dextrorotary power of one tetrahedron will annul the levorotary power of the other, and an optically inactive compound must result. Fig. 11 will illustrate what has been explained.



Levo-tartaric acid

Dextro-tartaric acid

Internally compensated or meso-tartaric acid

Externally compensated tartaric acid or racemic acid

FIG. 11

**151. Saccharic Acid.**—Saccharic acid $CO_2H \cdot (CHOH)_4 \cdot CO_2H$ is produced by the action of dilute nitric acid on cane sugar, glucose, milk sugar, and mannite. It is made by heating sugar with 3 parts of nitric acid (Sp. Gr. 1.3) until violent action begins. When the reaction seems terminated and no more red fumes evolve, it is kept at a temperature of 50° for about 3 hours; then it is diluted with 2 or 3 volumes of water, neutralized with $K_2CO_3$, and strongly acidified with acetic acid. On standing, hydropotassium saccharate $C_4H_8O_4(CO_2)_2HK$ crystallizes out; this is dissolved in a little potash solution and precipitated by cadmium chloride. The cadmium saccharate thus obtained is dissolved in water and decomposed by hydrogen sulphide. The precipitated $CdS$ is filtered off, and the filtrate, holding the saccharic acid in solution, is evaporated to a syrupy consistence, from which the acid crystallizes slowly in long, colorless needles. It has a sour taste, is soluble in water and alcohol, and forms soluble salts with lime and baryta. When mixed with silver nitrate, it gives no precipitate, but on the addition of ammonia, a white, insoluble substance separates, which, on gently warming the whole, is reduced to metallic silver, the vessel being lined with a smooth and brilliant coating of the metal. Nitric acid converts saccharic acid into oxalic and tartaric acids.

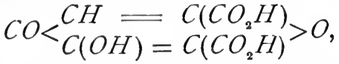
*Calcium saccharate* $C_4H_8O_4(CO_2)_2Ca,H_2O$ is a crystalline compound, which is nearly insoluble in water, but which readily dissolves in acetic acid.

**152. Mucic Acid.**—Mucic acid $CO_2H\cdot(CHOH)_4CO_2H$ was discovered by Scheele in 1780. It is isomeric with saccharic acid, and is produced, along with a small quantity of oxalic acid, by the action of dilute nitric acid on sugar and gum. It may be readily prepared by heating together in a flask 1 part of milk sugar or gum, 4 parts of nitric acid, and 1 part of water· the mucic acid is afterwards collected on a filter, washed, and dried. It forms a white, crystalline powder, which is only very sparingly soluble in cold water and in alcohol. It has a slightly sour taste, and reddens vegetable colors.

The mucates differ greatly from the saccharates, most of them being insoluble; the acid *potassium mucate* is more soluble than the normal salt. By boiling mucic acid with water for some time, it is converted into *paramucic acid*, which is isomeric with it, but is more readily soluble in alcohol. Hydriodic acid reduces saccharic and mucic acid to *adipic acid:*

$$C_4H_8O_4(CO_2H)_2+8HI = C_4H_8(CO_2H)_2+4H_2O+4I_2$$

**153.** *Pyromucic acid*, also known as *furfane monocarboxylic acid* $C_4H_3O\cdot CO_2H$, is produced by the dry distillation of mucic acid, or by boiling furfurol with water and recently prepared silver oxide; the silver is precipitated by hydrochloric acid, the filtrate evaporated, and the pyromucic acid that is thus obtained purified by recrystallization from alcohol. Pyromucic acid forms prismatic crystals, which are easily soluble in hot and cold water, and sparingly soluble in alcohol. It melts at 134°, and may be sublimed. The pyromucates are very soluble.

**154. Meconic Acid.**—Meconic acid, or *hydroxypyrone dicarboxylic acid*  $CO\!<\!\begin{matrix}CH = C(CO_2H)\\ C(OH) = C(CO_2H)\end{matrix}\!>\!O$, is one of the more important constituents of opium, from which it may be extracted by digesting with hot water, neutralizing the solution with calcium carbonate, and adding calcium chloride, which precipitates *acid calcium meconate* $HCaC_7HO_7, H_2O$ from which meconic acid may be obtained by dissolving the salt in hot hydrochloric acid, wherefrom, on cooling, the acid crystallizes out. It crystallizes in mica-like plates, and is easily soluble in boiling water, but only difficultly soluble in cold water. The crystals, $C_7H_4O_7\cdot 3H_2O$, give off their water of crystallization when heated to 100°, and the dehydrated acid melts at 150°. A solution of meconic acid gives a fine red color with ferric chloride, which is not bleached by mercuric chloride.

**155. Comenic acid** $C_6H_4O_5$ is a decomposition product of meconic acid, being obtained when an aqueous or a hydrochloric-acid solution of meconic acid is boiled, carbon dioxide being evolved; the remaining solution contains the comenic acid, which, being only very difficultly soluble in water, readily crystallizes out on cooling.

**156. Chelidonic acid** $C_7H_4O_6$, which is closely related to meconic acid by its composition and origin, occurs as calcium salt, together with malic and fumaric acids, in celandine (*Chelidonium majus*), a plant that belongs to the same botanical order as the opium poppy, which yields the meconic acid. It is prepared by boiling the juice, filtering, adding nitric acid, precipitating with lead nitrate, and decomposing the resulting lead salt with hydrogen sulphide. It crystallizes in needles with 1 molecule of water of crystallization, and is only sparingly soluble in cold water and alcohol.

**157. Citric Acid.**—Citric, or *hydroxytricarballylic*, acid $C_3H_4(OH)(CO_2H)_3$, which was discovered by Scheele in 1784, occurs widely diffused in nature. It exists in lemons, oranges, limes, currants, raspberries, cherries, etc. in conjunction with malic acid. It is readily prepared from lemon juice, which is first allowed to stand until it begins to ferment, and is then filtered, and saturated with chalk while boiling. The precipitate of calcium citrate is washed with boiling water, and decomposed by a slight excess of dilute sulphuric acid. The liquid separated from the calcium sulphate yields crystals of citric acid.

It may be prepared synthetically from acetone by the following steps:

1. $$\underset{\text{acetone}}{CH_3\cdot CO\cdot CH_3} + Cl_4 = 2HCl + \underset{\text{dichloracetone}}{CH_2Cl\cdot CO\cdot CH_2Cl}$$

2. By heating the dichloracetone with strong hydrocyanic acid, it is converted into dichloracetone cyanhydrate $CH_2Cl\cdot C(OH)(CN)\cdot CH_2Cl$.

3. This last, acted on by hydrochloric acid and water, yields $NH_4Cl$ and dichloracetonic acid

$$CH_2Cl\cdot C(OH)(CO_2H)CH_2Cl.$$

4. On treating this with potassium cyanide, it gives $2KCl$ and dicyanacetonic acid $CH_2CN\cdot C(OH)(CO_2H)CH_2CN$.

5. By the action of $2HCl$ and $4H_2O$, this is converted into $NH_4Cl$ and citric acid $CO_2H\cdot C(OH):(CH_2\cdot CO_2H)_2$.

The whole synthetical process may be expressed shortly by the following equations:

$$(1)\quad \underset{\text{acetone}}{CH_3\cdot CO\cdot CH_3} + Cl_4 = 2HCl + \underset{\text{dichloracetone}}{CH_2Cl\cdot CO\cdot CH_2Cl}$$

$$(2)\quad \underset{\text{dichloracetone}}{CH_2Cl\cdot CO\cdot CH_2Cl} + \underset{\text{hydrocyanic acid}}{HC\vdots N}$$

$$= \underset{\text{dichloracetone cyanhydrate}}{CH_2Cl\cdot C(OH)(CN)\cdot CH_2Cl}$$

$$(3)\quad \underset{\text{dichloracetone cyanhydrate}}{CH_2Cl\cdot C(OH)(CN)\cdot CH_2Cl} + HCl + 2H_2O$$

$$= NH_4Cl + \underset{\text{dichloracetonic acid}}{CH_2Cl\cdot C(OH)(CO_2H)CH_2Cl}$$

$$(4)\quad \underset{\text{dichloracetonic acid}}{CH_2Cl\cdot C(OH)(CO_2H)CH_2Cl} + 2KCN$$

$$= 2KCl + \underset{\text{dicyanacetonic acid}}{CH_2CN\cdot C(OH)(CO_2H)CH_2CN}$$

$$(5)\quad \underset{\text{dicyanacetonic acid}}{CH_2CN\cdot C(OH)(CO_2H)CH_2CN} + 2HCl + 4H_2O$$

$$= 2NH_4Cl + \underset{\text{citric acid}}{CO_2H\cdot C(OH):(CH_2\cdot CO_2H)_2}$$

Citric acid crystallizes in two different forms. The crystals that separate by spontaneous evaporation from a cold saturated solution are trimetric prisms containing $C_6H_8O_7, H_2O$, while those that are deposited from a hot solution have a different form and contain $C_6H_8O_7, 2H_2O$. This acid has a pure and agreeable acid taste and is very soluble in water, and fairly so in alcohol; the solution strongly reddens litmus. Citric acid fuses at 100° and loses its water of crystallization at 130°; heated further to 170°, it loses another molecule of $H_2O$ and becomes *aconitic acid* $C_3H_3(CO_2H)_3$, and, when still further heated, this loses $CO_2$ and *itaconic acid* distils over:

$$C_3H_3(CO_2H)_3 = CO_2 + C_3H_4(CO_2H)_2$$

This crystallizes in the neck of the retort. The liquid portion of the distillate contains *citraconic acid*, which is isomeric with itaconic acid. Fused potassium hydrate converts citric acid into oxalic and acetic acids.

Citric acid is frequently adulterated with tartaric acid, which is readily detected by dissolving the acid in a little cold water, and adding to the solution a small quantity of potassium acetate. If tartaric acid should be present, a white crystalline precipitate of cream of tartar is produced on agitation. Citric acid is further distinguished from tartaric acid by the characteristics of its calcium salt. An aqueous solution of citric acid is not precipitated by lime water in the cold, but, on boiling, a precipitate will be formed that consists of *tricalcic citrate*, which is insoluble in potash lye. Calcium tartrate, on the other hand, dissolves in alkalies, and is precipitated therefrom as a jelly, on boiling.

The citrates of the alkali metals are soluble and crystallize with greater or less facility; those of barium, strontium, calcium, lead, and silver are insoluble. *Ferric citrate* $Fe_2(C_6H_5O_7)_2, 6H_2O$ and *ferric ammonio citrate* $Fe_2(NH_4)_3(C_6H_5O_7)_3$ are used in medicine.

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## KETONES

**158.** The members of this series of organic compounds may be regarded as being formed from the acids by the removal of the radical $OH$ from the group $CO \cdot OH$, characteristic of the acids, and by substituting for it another radical, which is, as a rule, one of the hydrocarbon radicals of the alcohols. Thus, for instance, if we remove the hydroxyl radical $OH$ from acetic acid $CH_3 \cdot CO \cdot OH$ and substitute for it methyl $CH_3$, we obtain a compound $CH_3 \cdot CO \cdot CH_3$, or *acetone*. This replacement can take place through the action of a metallic alkyl compound on the chloride of the acid, as is seen from the following equation:

$$CH_3 \cdot CO \cdot Cl + CH_3Na = CH_3 \cdot CO \cdot CH_3 + NaCl$$

The student will notice that the formula of acetone, however, contains the group $CO$, or carbonyl, which is also present and prominent in the aldehydes, and it has been found that the ketones are really the aldehydes of the so called secondary alcohols, which, as has been previously shown, contain the group: $C<^{H}_{OH}$, and that these secondary alcohols may be converted into ketones by partial oxidation, just as a primary alcohol is converted into an aldehyde, and that a ketone yields secondary alcohol with nascent hydrogen, just as an aldehyde would yield primary alcohol under similar treatment.

It has been previously stated that the aldehyde of any acid can generally be obtained by the distillation of a salt of this acid with a formate. The salts of the alkali metals are, however, owing to their greater stability, less suitable for this purpose than the calcium salts. Acetic aldehyde, for instance, may be prepared by the distillation of calcium acetate and calcium formate, as is seen from the following equation:

$$(CH_3 \cdot CO_2)_2Ca + (H \cdot CO_2)_2Ca = 2(CH_3CO \cdot H) + 2(CaO \cdot CO_2)$$

If calcium acetate is distilled with calcium acetate—that is, by itself—acetone and calcium carbonate will result, as is seen from the equation:

$$\begin{aligned}&(CH_3 \cdot CO_2)_2Ca + (CH_3 \cdot CO_2)_2Ca\\ &= 2(CH_3 \cdot CO \cdot CH_3) + 2(CaO \cdot CO_2)\end{aligned}$$

The formulas of the aldehydes show that in these compounds 1 atom of $H$ is connected with an alcohol radical through the carbonyl group $CO$, while the formulas of the ketones show that their two alcohol radicals are connected through this $CO$ group. The two alcohol radicals in the ketone compounds may be either similar or different, and the ketones with two similar alcohol radicals are known as *simple ketones*, and those with dissimilar alcohol radicals as *mixed*, or *double*, *ketones*. Thus, for instance, if calcium acetate and propionate are distilled together, a ketone known as *acetone propione* results, as is expressed in the subjoined equation:

$$(CH_3 \cdot CO_2)_2Ca + (C_2H_5CO_2)_2Ca$$
$$= 2CH_3 \cdot CO \cdot C_2H_5 + 2CaO \cdot CO_2$$

When acted on by oxidizing agents, the aldehydes as well as the ketones yield acids; but, while an aldehyde only yields one acid, a ketone, containing two hydrocarbon radicals, yields two acids. Thus, acetone $CH_3 \cdot CO \cdot CH_3$ yields acetic acid $CH_3 \cdot CO \cdot OH$ and formic acid $H \cdot CO \cdot OH$, and propione $C_2H_5 \cdot CO \cdot C_2H_5$ yields propionic acid $C_2H_5 \cdot CO \cdot OH$ and acetic acid $CH_3 \cdot CO \cdot OH$. The ketones of the acetic series all yield acetic acid as one of the acids produced by their oxidation, showing that these ketones all contain the group $CH_3$.

The ketones are neutral bodies. The lower members of the series are volatile, ethereal-smelling liquids, while the higher members are solids.

**159. Acetone.**—Acetone, or *dimethyl ketone* $CH_3 \cdot CO \cdot CH_3$, has been known for a long time, its formula was determined by Liebig and Dumas, in 1832. It occurs in small quantities in the blood and in normal urine, while in the urine of those suffering from diabetes, it is present in considerable quantities. It is produced in the dry distillation of tartaric acid, citric acid, sugar, wood, etc.; hence, it is also found in crude wood alcohol. Technically, it is prepared by distilling dry calcium acetate in clay retorts. The vapors given off are condensed in a well cooled receiver, and the liquid obtained is distilled on a water bath with an excess of calcium chloride.

Acetone is a colorless, mobile, and peculiar-smelling liquid, having a specific gravity of .792 at 20°. It is miscible with water, alcohol, and ether. It is inflammable and burns with a luminous flame. On adding solid potash or calcium chloride to its aqueous solution, the acetone separates and rises to the surface. It is an excellent solvent for many carbon compounds, especially for certain gums and resins. It is not as powerful a reducing agent as aldehyde, and does not reduce silver nitrate. When oxidized by $K_2Mn_2O_8$ or by $K_2Cr_2O_7$ and $H_2SO_4$, it yields acetic and carbonic acids.

When acted on by dehydrating agents, such as sulphuric acid, hydrochloric acid, quicklime, etc., acetone loses the elements of water, and yields *condensation products* richer in carbon; thus, 2 molecules of $(CH_3)_2CO$ losing $H_2O$ give $(CH_3)_2C:CH\cdot CO\cdot CH_3$, *mesityl oxide*, a liquid that possesses a strong odor of peppermint, and boils at 130°. Three molecules of $(CH_3)_2CO$ losing $2H_2O$ yield $[(CH_3)_2C:CH]_2CO$, which is a crystalline compound, known as *phorone;* it has an odor resembling that of geranium and boils at 196°. The loss of another molecule of water produces $C_9H_{12}$, or *mesitylene.*

**160.** Up to the present time, none of the other ketones have found any practical application in the arts, and they will not be considered in detail in this paper. The following tables enumerate the principal single and mixed ketones, their formulas, and their melting and boiling points:

### TABLE XVIII

#### SINGLE KETONES

| Name | Formula | Melting Point | Boiling Point |
|---|---|---|---|
| Di-ethyl ketone ............. | $CO(C_2H_5)_2$ | | 103° |
| Di-propyl ketone, or butyron. | $CO(C_3H_7)_2$ | | 144° |
| Di-isopropyl ketone ......... | $CO[CH(CH_3)_2]_2$ | | 124° |
| Caprone.................... | $CO(C_5H_{11})_2$ | 14.6° | 226° |
| Tetra-ethyl acetone ......... | $CO[CH(C_2H_5)_2]_2$ | | 203° |
| Œnanthone ................. | $CO(C_6H_{13})_2$ | 30° | 263° |
| Caprylone.................. | $CO(C_7H_{15})_2$ | 40° | |
| Caprinone.................. | $CO(C_8H_{17})_2$ | 48° | |
| Laurone ................... | $CO(C_{11}H_{23})_2$ | 69° | |
| Myristone.................. | $CO(C_{13}H_{27})_2$ | 76° | |
| Palmitone.................. | $CO(C_{15}H_{31})_2$ | 83° | |
| Stearone .................. | $CO(C_{17}H_{35})_2$ | 88° | |

## TABLE XIX

### MIXED KETONES

| Name | Formula | Melting Point | Boiling Point |
|---|---|---|---|
| Methyl ethyl ketone...... | $CH_3 \cdot CO \cdot C_2H_5$ | | 81° |
| Methyl propyl ketone..... | $CH_3 \cdot CO \cdot C_3H_7$ | | 102° |
| Methyl isopropyl ketone.. | $CH_3 \cdot CO \cdot CH(CH_3)_2$ | | 96° |
| Pinacoline ............ .... | $CH_3 \cdot CO \cdot C(CH_3)_3$ | | 106° |
| Methyl œnanthone....... | $CH_3 \cdot CO \cdot C_6H_{13}$ | | 171° |
| Methyl nonyl ketone...... | $CH_3 \cdot CO \cdot C_9H_{19}$ | 15° | 225° |
| Methyl decyl ketone...... | $CH_3 \cdot CO \cdot C_{10}H_{21}$ | 21° | 247° |
| Methyl undecyl ketone, from lauric acid........ | $CH_3 \cdot CO \cdot C_{11}H_{23}$ | 28° | 263° |
| Methyl dodecyl ketone.... | $CH_3 \cdot CO \cdot C_{12}H_{25}$ | 34° | (207°) |
| Methyl tridecyl ketone, from myristic acid..... | $CH_3 \cdot CO \cdot C_{13}H_{27}$ | 39° | (224°) |
| Methyl tetradecyl ketone.. | $CH_3 \cdot CO \cdot C_{14}H_{29}$ | 43° | (231°) |
| Methyl pentadecyl ketone, from palmitic acid...... | $CH_3 \cdot CO \cdot C_{15}H_{31}$ | 48° | (244°) |
| Methyl hexadecyl ketone, from margaric acid..... | $CH_3 \cdot CO \cdot C_{16}H_{33}$ | 52° | (252°) |
| Methyl heptadecyl ketone, from stearic acid....... | $CH_3 \cdot CO \cdot C_{17}H_{35}$ | 55° | (265°) |

The boiling points, inclosed in parenthesis, were determined under 100 millimeters pressure.

**161.** There remain to be considered the *ketone alcohols*, *ketone aldehydes*, *ketone acids*, and *ketone ketones*, or *diketones*, all of which may be regarded as derivatives of polyhydric alcohols.

**Ketone Alcohols, or Ketols.**—These may be defined as alcohols containing a ketone group $:CO$, and may be regarded as derived from polyhydric alcohols containing a secondary alcohol group. *Acetone alcohol*, also known as *acetol*, or *acetyl carbinol* $CH_3 \cdot CO \cdot CH_2OH$, is an example.

**Ketone Aldehydes.**—These compounds are exemplified by *pyroracemic aldehyde*, or *methyl glyoxal* $CH_3 \cdot CO \cdot CHO$, a yellow volatile oil.

**Ketone Acids.**—The most important compounds of this class are: *Pyroracemic acid* $CH_3 \cdot CO \cdot CO_2H$, which is prepared by the dry distillation of tartaric, or racemic, acid. It is a liquid boiling at about 167° and is soluble in water. *Aceto-acetic acid* $CH_3 \cdot CO \cdot CH_2 \cdot CO_2H$, which may be regarded as acetic acid in which acetyl $CH_3CO$ has replaced $H$. It is a liquid compound, which dissolves in water and readily decomposes into acetone and $CO_2$ when heated. *Levulinic acid* $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$ is a product of the action of acids on various carbohydrates. *Benzoyl formic acid*, or *phenyl glyoxylic acid* $C_6H_5 \cdot CO \cdot CO_2H$, is a product of the oxidation of mandelic acid $C_6H_5 \cdot CH(OH) \cdot CO_2H$.

**Diketones.**—The simplest example is *diacetyl* $CH_3 \cdot CO \cdot CO \cdot CH_3$, which is prepared by boiling isonitroso-methyl acetone $CH_3 \cdot C(NOH) \cdot CO \cdot CH_3$ with acid. It is a greenish-yellow liquid, smelling of quinone, and boiling at 87°.

## ETHERS

**162.** The ethers may be regarded as compounds that are derived from the alcohols by the substitution of an alcohol radical for the hydrogen in the $OH$ group. The following example will clearly show this transformation process: If methyl alcohol $CH_3 \cdot OH$ is treated with sodium, the hydroxyl hydrogen atom in the alcohol is displaced by an atom of sodium, and sodium methoxide $CH_3 \cdot ONa$ results. If this product is acted on by methyl iodide, the sodium atom in $CH_3 \cdot ONa$ will be displaced by the group $CH_3$, and methyl ether $CH_3 \cdot O \cdot CH_3$ results, as is seen from the following equation:

$$CH_3 \cdot ONa + CH_3I = CH_3 \cdot O \cdot CH_3 + NaI$$

It will be evident that a similar reaction between sodium methoxide and ethyl iodide $C_2H_5I$ would produce methyl ethyl ether $CH_3 \cdot O \cdot C_2H_5$, so that the number of ethers obtainable would exceed that of the alcohols.

Ethers are neutral, volatile bodies, nearly insoluble in water. The lowest members are gases, the next higher are liquids, and the highest are solids. The boiling points are very much lower than those of the corresponding alcohols. Like the ketones, ethers containing two similar alcohol radicals are termed *simple ethers*, while those with different radicals are known as *mixed ethers*. Ethers, as a rule, offer more resistance to the attacks of other bodies than the alcohols. They are, in general, convertible into the corresponding alcohols by the action of water at high temperature, the $HOH$ exchanging 1 atom of $H$ for 1 of the alcohol radicals. With hydrogen haloid acids, especially with hydriodic acid, they yield haloid compounds, imitating, though with considerably less energy, the reactions of those acids with the alkaline oxides, such as $K_2O$, which resemble the ethers in constitution, thus:

$$K_2O + 2HI = H_2O + 2KI$$

and $$(CH_3)_2O + 2HI = H_2O + 2CH_3I$$

**163. Ether.**—*Ethyl ether*, *sulphuric ether*, or, for short, *ether* $C_2H_5 \cdot O \cdot C_2H_5$, and its production from sulphuric acid and alcohol, were already known in the 16th century. They were described by Valerius Cordus, a German physician. Ether is prepared in the arts, as has been stated, by distilling alcohol with sulphuric acid. If a mixture of 9 parts of concentrate sulphuric acid and 5 parts of 90-per-cent. alcohol is distilled, ether and water pass over together, and if alcohol is added from time to time, a small quantity of sulphuric acid is quite sufficient to etherify a comparatively large quantity of alcohol. The alcohol is first converted into *hydrogen ethyl sulphate*, or *sulphethylic acid*, as is seen from the following equation:

$$H_2SO_4 + C_2H_5 \cdot OH = HC_2H_5SO_4 + H_2O$$

When this process of heating is continued with more alcohol, until 140° is reached, hydrogen ethyl sulphate is decomposed into ether, and sulphuric acid which acts in the same way on further quantities of alcohol:

$$HC_2H_5SO_4 + C_2H_5 \cdot OH = C_2H_5 \cdot O \cdot C_2H_5 + H_2SO_4$$

As this process is a continuous one, it is generally known as the *continuous etherification process*, and is carried on most conveniently in the following manner with the apparatus below :

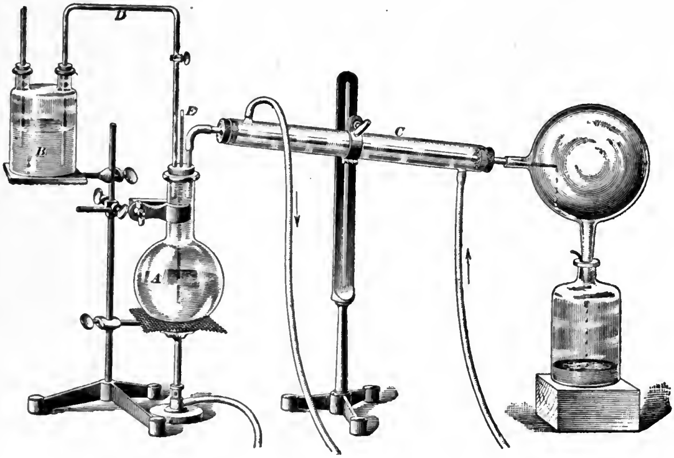

FIG. 12

Alcohol having a specific gravity of .83 is added, with continued stirring, to an equal volume of concentrate sulphuric acid that has been well cooled by standing in a basin filled with ice water. When the mixture has thoroughly cooled down it is poured in a flask *A* (see Fig. 12), which is connected with a reservoir of alcohol *B* and a well cooled Liebig's condenser *C*. The mixture is quickly heated to approximately 140°, and fresh alcohol is then allowed to pass in slowly from the siphon tube *D*, which is furnished with a stop-cock and which connects the alcohol reservoir with the distilling flask; the flow of the alcohol being so regulated into the latter as to keep as nearly as possible at a constant level in *A*, in order to keep the temperature as constant as possible at 140°. This is rendered easier by arranging a thermometer *E*, which dips into the liquid, as shown in the illustration. When the total quantity of alcohol used amounts to six or seven times that originally taken, the process must be stopped, because secondary reactions, attended by carbonization, have used up much of the sulphuric acid. The liquid collected in the receiver contains about two-thirds of its weight of ether, with about one-sixth of water, an equal quantity of alcohol, and a little sulphurous acid. It separates, as a rule, into two layers, the upper one of which being the ether. The whole is introduced into a narrow stoppered bottle and shaken with cold water, added in small portions, as long as the layer of ether on the surface increases in volume; a little potash is then added to fix $SO_2$, and, after shaking, the upper layer of ether is drawn off into a flask containing lumps of fused calcium chloride, to remove water and alcohol. After standing for some hours, the ether is distilled off in a water bath at as low a temperature as possible. To free it entirely from water, it must be again rectified, after digestion with powdered quicklime, and finally with sodium, till no more hydrogen bubbles are visible. In the arts, the operation is conducted on the large scale in apparatus of an analogous character and construction.

*Theory of Etherification.*—The process of preparing ether just described had been in use a long time before a real satisfactory explanation of it was arrived at. One of the earliest views regarded the formation of ether as a mere removal of water, by means of sulphuric acid, from alcohol, assuming alcohol to be a compound of water and ether; but against this spoke the fact that the water was not retained by the acid, but distilled over with the ether, and that the same acid would etherify successive additions of alcohol. Leaving the theory of catalytic action, or decomposition by contact, entirely out of question, we arrive at the important observation that the first product of the action of sulphuric acid on alcohol is sulphethylic acid, which is decomposed, when distilled with more alcohol at 140°, into ether, water, and sulphuric acid, as shown in the equations previously given. Very strong evidence in favor of this view is furnished by the following experiment: Amyl alcohol $C_5H_{11}\cdot OH$ is converted by sulphuric acid into sulphamylic acid $C_5H_{11}\cdot SO_4H$, which is heated in the distilling flask (Fig. 12), while ethyl alcohol $C_2H_5 \cdot OH$ is allowed to flow in from the reservoir; this decomposes the sulphamylic acid, yielding sulphuric acid and amyl ethyl ether:

$$C_5H_{11} \cdot SO_4H + C_2H_5 \cdot OH = C_5H_{11} \cdot O \cdot C_2H_5 + H_2SO_4$$

If the process is continued after all the amyl ethyl ether has passed over, only ethyl ether is obtained.

**164. Properties of Ether.**—Ether is a colorless, mobile liquid with a strong and peculiar odor, and specific gravity at 0° of .736. Ether boils at a temperature of 35° and bears, without freezing, the greatest cold. When dropped on the hand, it produces the sensation of cold, owing to its rapid vaporization. It is very combustible and burns with a whitish flame, generating water and carbon dioxide Although ether is one of the lightest substances, its vapor has a specific gravity of 2.59. It is but slightly miscible with water, on the surface of which it forms a separate layer; 9 parts of water dissolve 1 part of ether, 36 parts of ether dissolve 1 part of water. Ether dissolves in all proportions in alcohol. In 1846, Dr. William T. G. Morton, of Boston, discovered the fact that ether vapor, when inhaled, produces unconsciousness and anesthesia. This discovery has been of inestimable value in surgery, and while other anesthetics, such as chloroform, laughing gas, etc., have been introduced, ether appears to have the general preference. It is also much used in laboratories as a solvent, especially for fatty substances and alkaloids, and by the photographer in dissolving collodion.

**165. Other Methods of Preparing Ether.**—The mode of preparing ether mentioned in Art. **163** is not the only existing one, and, although these other methods are not used for the economical preparation of ether in the arts, they greatly assist the explanation of its constitution and confirm the modern theory of etherification. Thus, for instance, ethyl iodide heated with sodium oxide, in a sealed tube, at 180°, yields ether and sodium iodide:

$$2C_2H_5I + Na_2O = (C_2H_5)_2 : O + 2NaI$$

Silver oxide $Ag_2O$ is very frequently substituted for $Na_2O$, this compound effecting the conversion more rapidly. Alcohol, heated with ethyl bromide and potash, yields ether, water, and potassium bromide:

$$C_2H_5 \cdot OH + C_2H_5Br + KOH = (C_2H_5)_2 : O + HOH + KBr$$

Ethyl iodide acted on by sodium ethoxide, yields ether and sodium iodide:

$$C_2H_5I + C_2H_5ONa = (C_2H_5)_2 : O + NaI$$

Ethyl iodide, heated with a small quantity of water, under pressure, yields first alcohol, and afterwards ether:

$$C_2H_5I + HOH = C_2H_5 \cdot OH + HI$$
$$C_2H_5I + C_2H_5 \cdot OH = C_2H_5 \cdot O \cdot C_2H_5 + HI$$

Other acids besides sulphuric acid may be used in the etherification process, especially those that are non-volatile and polybasic; as, for instance, phosphoric, arsenic, and boracic acids could probably be successfully substituted for $H_2SO_4$. But certain salts, such as zinc chloride and aluminum sulphate, also generate ether from alcohol, and the explanation of this is not quite as simple. It will be found that such salts are capable of decomposition by water, with formation of basic salt and free acid; thus,

$$ZnCl_2 + H_2O = ZnClOH + HCl$$

or with aluminum sulphate:

$$Al_2(SO_4)_3 + 4H_2O = Al_2SO_4(OH)_4 + 2H_2SO_4$$

If these reactions take place with alcohol $C_2H_5 \cdot OH$ instead of with $HOH$, the products will be $C_2H_5Cl$ instead of $HCl$, and $C_2H_5 \cdot HSO_4$ instead of $H_2SO_4$, and we know that either of these would react with the excess of alcohol to produce ether.

When ether is heated with water and some sulphuric acid at 180°, in a sealed tube, it is reconverted into alcohol, and probably passes through the same stages, but in an inverse order, as in the preparation with the aid of sulphuric acid; viz.,

$$(C_2H_5)_2 : O + 2H_2SO_4 = 2C_2H_5 \cdot HSO_4 + H_2O$$
$$C_2H_5 \cdot HSO_4 + H_2O = C_2H_5 \cdot OH + H_2SO_4$$

When ether is acted on by hydriodic-acid gas, in the cold, it yields alcohol and ethyl iodide:

$$(C_2H_5)_2O+HI = C_2H_5\cdot OH+C_2H_5I$$

If a *mixed ether*, such as ethyl amyl ether, is treated in this way, the radical containing the most carbon is the one converted into alcohol:

$$C_2H_5\cdot O\cdot C_5H_{11}+HI = C_5H_{11}\cdot OH+C_2H_5I$$

Ether forms crystalline compounds with various substances, e. g., the chlorides and bromides of $Sn$, $Al$, $P$, $Sb$, and $Ti$, being present in them as ether of crystallization.

When dropped upon platinum black it takes fire, and when poured into chlorine gas an explosion results, hydrochloric acid being set free. In the dark, however, and in the cold, substitution by chlorine is possible, the final product of substitution, perchloro-ether $C_4Cl_{10}O$, is a solid with an odor resembling that of camphor.

**166. Methyl Ether.**—Methyl ether $CH_3\cdot O\cdot CH_3$, also known as *dimethyl oxide*, may be prepared by heating 1 part of methyl alcohol and 4 parts of sulphuric acid; and passes over as a colorless gas, which may be collected over mercury. It is condensed by pressure and cold to a liquid that begins to vaporize at $-21°$. It has an ethereal odor, and burns with a pale and feebly luminous flame. Cold water dissolves about 33 times its volume of this gas, acquiring thereby its characteristic odor and taste; on boiling the solution, the gas is again liberated. Alcohol, wood spirit, and sulphuric acid dissolve it in still larger quantities.

**167.** By referring to Table XX, the student will notice that the ethers derived from the alcohols belonging to the series $C_nH_{2n+2}$, form an homologous series isologous* with the alcohols, that each ether is metameric† with the isologous alcohol, and that the simple ethers of this series all have an

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* *Isologous* may briefly be defined as "having similar differences in composition."

† *Metameric* means "having the same percentage composition and the same molecular weight."

even number of carbon atoms; while the mixed ethers of this series are distinguished by an odd number of carbon atoms.

TABLE XX

| Alcohols | Formula | Ethers | Formula |
|---|---|---|---|
| Ethyl..... | $C_2H_5 \cdot OH$ | Methyl ether........ | $CH_3 \cdot O \cdot CH_3$ |
| Propyl.... | $C_3H_7 \cdot OH$ | Methyl ethyl ether.. | $CH_3 \cdot O \cdot C_2H_5$ |
| Butyl..... | $C_4H_9 \cdot OH$ | Ethyl ether......... | $C_2H_5 \cdot O \cdot C_2H_5$ |
| Amyl..... | $C_5H_{11} \cdot OH$ | Ethyl propyl ether.. | $C_2H_5 \cdot O \cdot C_3H_7$ |
| Caproyl... | $C_6H_{13} \cdot OH$ | Propyl ether........ | $C_3H_7 \cdot O \cdot C_3H_7$ |

**168.** The ethers of the glycols or dihydric alcohols are formed from these alcohols by the replacement of the hydroxyl hydrogen by a radical; thus, glycol, or ethene alcohol $C_2H_4(OH)_2$, yields $C_2H_4 \cdot O_2 \cdot C_2H_4$, diethene dioxide, or glycol ether. To prepare this compound from glycol, the latter is saturated with $HCl$ gas and distilled, when it yields *glycol chlorhydrin*, or *chloride of ethylene hydrate*, according to the equation:

$$C_2H_4(OH)_2 + HCl = C_2H_4 \cdot OH \cdot Cl + H_2O$$

When this is distilled with potash, it gives ethylene oxide:

$$C_2H_4 \cdot OH \cdot Cl + KOH = C_2H_4 : O + KCl + H_2O$$

When ethylene oxide is treated with bromine, it is converted into $(C_2H_4O)_2Br_2$, from which mercury removes the bromine, leaving $(C_2H_4)_2O_2$. The ether thus obtained is a liquid, which boils at 102°, and is miscible with water, alcohol, and ether in all proportions.

**169. Glycerine Ether.**—Glycerine ether $C_3H_5 \vdots O_3 \vdots C_3H_5$ represents glycerine $C_3H_5(OH)_3$ in which glyceryl $C_3H_5$ has replaced three atoms of $H$ in the three hydroxyl groups. It is formed when glycerine is distilled with calcium chloride. It is an inodorous colorless liquid, which boils at about 170° and has a specific gravity of 1.16; it mixes with water.

**170.** *Benzyl ether* $C_7H_7 \cdot O \cdot C_7H_7$ is prepared by distilling benzyl alcohol with boric oxide $B_2O_3$, which removes the elements of water:

$$2C_7H_7OH - HOH = C_7H_7 \cdot O \cdot C_7H_7$$

It is a colorless liquid, which does not dissolve in water, and which only boils above 300°.

**171.** The principal ethers are given in Table XXI.

TABLE XXI

| Name of Ether | Formula | Boiling Point |
|---|---|---|
| Methyl ether | $CH_3 \cdot O \cdot CH_3$ | $-21°$ |
| Methyl ethyl ether | $CH_3 \cdot O \cdot C_2H_5$ | $+11°$ |
| Ethyl ether | $C_2H_5 \cdot O \cdot C_2H_5$ | 35° |
| Methyl propyl ether | $CH_3 \cdot O \cdot C_3H_7$ | 39° |
| Ethyl propyl ether | $C_2H_5 \cdot O \cdot C_3H_7$ | 64° |
| Propyl ether | $C_3H_7 \cdot O \cdot C_3H_7$ | 91° |
| Ethyl butyl ether | $C_2H_5 \cdot O \cdot C_4H_9$ | 92° |
| Butyl ether | $C_4H_9 \cdot O \cdot C_4H_9$ | 141° |
| Cetyl ether | $C_{16}H_{33} \cdot O \cdot C_{16}H_{33}$ | 300° |
| Glycol ether | $C_2H_4 \cdot O_2 \cdot C_2H_4$ | 102° |
| Monoethyl glycol ether | $C_2H_4 \cdot OH \cdot OC_2H_5$ | 134° |
| Diethyl glycol ether | $C_2H_4 : (OC_2H_5)_2$ | 124° |
| Glycerine ether | $C_3H_5 \vdots O_3 \vdots C_3H_5$ | 171° |
| Ethyl glycerine ether | $C_3H_5(OH)_2 \cdot O \cdot C_2H_5$ | 230° |
| Diethyl glycerine ether | $C_3H_5 \cdot OH(OC_2H_5)_2$ | 191° |
| Triethyl glycerine ether | $C_3H_5 \vdots O_3(C_2H_5)_3$ | 185° |
| Allyl ether | $C_3H_5 \cdot O \cdot C_3H_5$ | 94° |
| Methyl allyl ether | $CH_3 \cdot O \cdot C_3H_5$ | 46° |
| Ethyl allyl ether | $C_2H_5 \cdot O \cdot C_3H_5$ | 63° |
| Ethyl propargyl ether | $C_2H_5 \cdot O \cdot C_3H_3$ | 80° |
| Benzyl ether | $C_7H_7 \cdot O \cdot C_7H_7$ | 298° |
| Methyl benzyl ether | $CH_3 \cdot O \cdot C_7H_7$ | 168° |
| Ethyl benzyl ether | $C_2H_5 \cdot O \cdot C_7H_7$ | 185° |
| Phenyl benzyl ether | $C_6H_5 \cdot O \cdot C_7H_7$ | 287° |

# ORGANIC CHEMISTRY

## (PART 5)

## DERIVATIVES OF HYDROCARBONS

### HALOGEN DERIVATIVES

**1. Chemical Reaction.**—Chemical reaction is usually divided into two classes; namely, *complete reaction* and *reversible reaction.* Complete reaction includes those changes in which all the reacting substances are converted into the products of the reaction; for example, when a mixture of equal volumes of hydrogen and chlorine is fired, the two gases combine completely and are converted into the stable compound, hydrochloric acid. A reversible reaction, on the other hand, is of such a nature that the products of the reaction, under slightly altered conditions, react with each other to reform the original substances. Thus, for example, when steam and iron are heated together, a reaction occurs which may be expressed by the following equation:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

but it is equally true that, when hydrogen and black oxide of iron are heated together, a reaction takes place, which may be expressed as follows:

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O$$

Either of these two reactions may, of course, be carried to approximate completion under suitable conditions; thus, by passing steam over red-hot iron, the whole of the iron can be converted into $Fe_3O_4$; so, also, by passing hydrogen over $Fe_3O_4$ at high temperatures, the whole of the oxide can be converted into metallic iron. If, however, iron and steam are heated together in a closed vessel, the iron will never be completely oxidized, owing to a reversible action; that is to say, as soon as any $Fe_3O_4$ and $H$ are produced, these tend to react with each other to reform $H_2O$ and $Fe$. In other words, the reaction

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$$

can take place in either direction at the same time, a fact that is expressed by the substitution of the sign $\rightleftarrows$ for the sign $=$ in such an equation.

It has been seen, however, that, by passing steam over red-hot iron, the latter can be completely oxidized; that is to say, the equation $3Fe + 4H_2O = Fe_3O_4 + 4H_2$ can be realized. This, however, is only possible because one of the products of the reaction—hydrogen in this case—is in such a physical condition that it can be removed from the actual sphere of action—the tube in which the reaction is performed. Indeed, for the complete oxidation of the iron, a large excess of steam over that indicated in the equation (72 parts of steam for 168 parts of iron) must be passed through the apparatus containing the iron, in order to sweep away the hydrogen. If the gas could not be removed in this manner, the complete reaction would be impossible. The same remarks apply to the complete reduction of $Fe_3O_4$ by hydrogen.

A reversible reaction can only become complete when one of the products of the reaction is removed from the sphere of the action. Under any other conditions the vessel in which the reaction is proceeding will contain some of each of the reacting substances and some of each of the products of the reaction.

## HALOGEN DERIVATIVES FROM OPEN-CHAIN HYDROCARBONS

**2.** While studying the previous Sections on *Organic Chemistry*, the student will have noticed that, in many cases, halogen derivatives result from the direct action of the halogens on the hydrocarbons. While chlorine and bromine thus react frequently by metalepsis, iodine can hardly do so, unless an absorbent for $HI$ (as, for instance, $HgO$) is present; this is because the metalepsis is reversible; for instance:

$$CH_4 + I_2 \rightleftarrows CH_3I + HI$$

Since the unsaturated hydrocarbons generally combine with the halogen to form addition products that are either identical or isomeric with the halogen-substituted saturated hydrocarbons, some other method must be resorted to in order to prepare halogen-substitution products of unsaturated hydrocarbons. They are, consequently, usually prepared either by treating the halogen-substituted saturated hydrocarbons with reagents that will remove halogen hydride, as, for instance,

$$C_2H_4Cl_2 - HCl = C_2H_3Cl$$

or by only partially saturating still more unsaturated hydrocarbons, as, for instance,

$$C_2H_2 + Cl_2 = C_2H_2Cl_2$$

The halogen-substitution products from all hydrocarbons are obtained by the interaction of the alcohols with phosphorus halides (a halide is an ide compound of a halogen with another element, as, for example, phosphorous iodide, potassium chloride, etc.), or, what is equivalent, with phosphorus and a halogen. Examples of this mode of preparation will be met frequently in the succeeding articles. In a great many cases the simple treatment of an alcohol with a halogen hydride, especially in the presence of a dehydrating agent, will produce the halogen-substitution product. The reaction may be expressed through the following general formula:

$$R \cdot OH + HX = RX + HOH$$

**3. Methyl Chloride.**—Methyl chloride, or *monochlormethane* $CH_3Cl$, is formed when a mixture of equal volumes of methane (marsh gas) and chlorine is exposed to reflected sunlight. It is more easily prepared, however, by passing $HCl$ gas into a boiling solution of zinc chloride in methyl alcohol, contained in a flask connected with a reversed condenser. The final result of the reaction may be expressed by the equation:

$$CH_3 \cdot OH + HCl = CH_3Cl + H_2O$$

It may also be prepared by heating a mixture of 1 part wood spirit, 2 parts common salt $NaCl$, and 3 parts concentrated sulphuric acid. Methyl chloride has found use in freezing machines lately, and is prepared on a large scale from trimethyl amine, obtained by distilling the refuse of the beet-sugar factories; this is neutralized with hydrochloric acid, and heated to 260°, when it is decomposed into trimethyl amine, ammonia, and methyl chloride.

Methyl chloride is a colorless gas, with a peculiar but agreeable odor and a sweetish taste. When exposed to 0° it may be liquefied by a pressure of 2½ atmospheres. The liquid boils at $-22°$ at ordinary pressure. It is only slightly soluble in water. When heated for a considerable time with a concentrated solution of $KOH$, it is converted into methyl alcohol. Liquid methyl chloride is employed in the arts in the production of cold, and also, to a very great extent, in the manufacture of dyestuffs.

**4. Ethyl Chloride.**—Ethyl chloride, or *monochlorethane* $C_2H_5Cl$, also sometimes called *hydrochloric ether*, may be prepared in the same way as methyl chloride, except that, instead of using a solution of zinc chloride in methyl alcohol, a solution of zinc chloride in ethyl alcohol is employed. It may also be prepared by heating in a retort 3 parts oil of vitriol, 2 parts alcohol, and 4 parts dry common salt. In either case, the vapor of ethyl chloride should be conducted through a little tepid water in a wash bottle, and thence into a small receiver that is thoroughly cooled by being packed in ice and salt. Below 12.5°, its boiling point, ethyl chloride is a thin, colorless, and excessively volatile liquid, of a penetrating, aromatic, and somewhat alliaceous odor. It is soluble in 10 parts of water, and burns with a flame tinged with green.

**5. Bromide and Iodide of Methyl.**—Methyl bromide $CH_3Br$ and methyl iodide $CH_3I$ are formed by the action of phosphorus and iodine or bromine on methyl alcohol.

Methyl bromide boils at 4.5°, burns feebly, and has an odor resembling that of chloroform. Methyl iodide has a pleasant and agreeable odor; it boils at 44°, and is insoluble in water, but soluble in alcohol. It is used in the manufacture of aniline dyes.

**6. Ethyl Bromide.**—Ethyl bromide $C_2H_5Br$, also known as *hydrobromic ether*, is prepared by distilling a mixture of 8 parts bromine, 1 part amorphous phosphorus, and 39 parts alcohol. The distillate is washed with water, and the oily ethyl bromide is separated and dried with potassium carbonate. It is a very volatile, colorless, refracting liquid, smelling like chloroform, and having a burning taste. It is soluble in alcohol as well as in ether, but is totally insoluble in water. It boils at 41°. It has been employed as an anesthetic.

**7. Ethyl Iodide.**—Ethyl iodide $C_2H_5I$, also known as *hydriodic ether*, is prepared by treating 5 parts red phosphorus, 70 parts alcohol, and 100 parts iodine, in a retort. The phosphorus is introduced first, covered with part of the alcohol, and heated to fusion. The rest of the alcohol is poured upon the iodine, and the solution thus obtained is allowed to flow gradually through a funnel into the retort. The brown liquid is at once decolorized, and ethyl iodide distils over, which is condensed by a good cooling apparatus. The distillate, consisting of alcohol and ethyl iodide, is again poured on the residuary iodine, which is thus rapidly dissolved, introduced into the retort, and ultimately entirely converted into ethyl iodide. The latter is washed with water to remove the alcohol, digested with calcium chloride, and rectified.

Ethyl iodide is a colorless liquid with a pleasant odor, and has a specific gravity of 1.93. It boils at 93°, and becomes brown on keeping, especially on exposure to light, iodine being liberated and butane formed:

$$2C_2H_5I = C_4H_{10} + I_2$$

It is sparingly soluble in water, but quite freely soluble in alcohol and ether. It is an important and frequently used reagent in organic researches, being used to introduce the group $C_2H_5$ into the place of other radicals.

**8.** The monohalogen-substitution derivatives of the paraffins, higher in the series than ethane, exist in isomeric forms that are exactly analogous to the isomeric alcohols (see isomerism among monohydric alcohols), a halogen being substituted for the group $OH$.

**9.** Dihalogen derivatives of ethane can obviously exist in two modifications: $CH_2X \cdot CH_2X$, or *ethylene halides*, and $CH_3 \cdot CHX_2$, or *ethylidene halides*. The former are prepared by the simple addition of the desired halogen to ethylene, while the latter are obtained from an aldehyde by treatment with a phosphorus pentahalide.

**10. Ethylene and Ethylidene Chlorides.**—Ethylene chloride $C_2H_4Cl_2$, or *ethene dichloride*, has long been known by the name of *oil of the Dutch chemists*, having been discovered by four Dutch chemists in 1795. It may be obtained by the distillation of glycol with phosphorus pentachloride, as may be seen from the following equation:

$$C_2H_4(OH)_2 + 2PCl_5 = C_2H_4Cl_2 + 2POCl_3 + 2HCl$$

It is, however, usually prepared by causing dry ethene gas and dry chlorine gas to combine in a good-sized glass globe (see Fig. 1) having a narrow neck at the lower part, dipping into a bottle to receive the product. The gases are conveyed by separate tubes to the globe and are allowed to mix there, the ethene gas being kept a little in excess. The combination takes place quite rapidly, and the liquid product trickles down the sides of the globe into the receiver. When a considerable quantity has been collected, it is agitated, first with water, and afterwards with concentrated sulphuric acid, and at last purified by distillation.

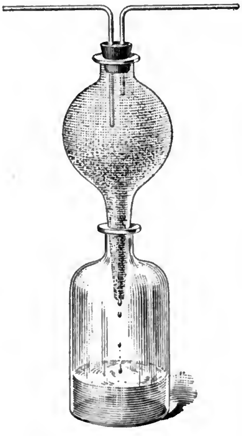

FIG. 1

Ethylene chloride (Sp. Gr. 1.28) is a thin colorless liquid that has the sweet, characteristic odor and taste of chloroform. It boils at 83.5°, is inflammable, and burns with a smoky greenish flame. It is nearly insoluble in water, but dissolves in alcohol and ether.

Ethylidene chloride $CH_3 \cdot CHCl_2$ is mostly prepared by the action of $COCl_2$ on $CH_3 \cdot CHO$, carbon dioxide being liberated. It is a colorless liquid, smelling like chloroform, and having a specific gravity of 1.198, and a boiling point of 57°.

**11. Ethylene and Ethylidene Bromides.**—Ethylene bromide $CH_2Br \cdot CH_2Br$ is obtained by saturating bromine with olefiant gas. It is an oily fragrant liquid, and its specific gravity is 2.163 at 21°. It boils at about 131°. Ethylidene bromide $CH_3 \cdot CHBr_2$ is prepared similarly to the corresponding chloride. It boils at 110° to 114°, and decomposes when heated with water.

**12. Ethylene and Ethylidene Iodides.**—Ethylene iodide $CH_2I \cdot CH_2I$, also known as *ethene di-iodide*, is prepared by heating iodine in olefiant gas. It forms silky needles, which may be sublimed in this gas, but are easily decomposed into $C_2H_4$ and $I_2$. Ethylidene iodide $CH_3 \cdot CHI_2$ is obtained by heating the chloride with aluminum iodide:

$$3C_2H_4Cl_2 + 2AlI_3 = 2AlCl_3 + 3C_2H_4I_2$$

or by the addition of hydriodic acid to acetylene:

$$C_2H_2 + 2HI = C_2H_4I_2$$

It is a liquid that has a specific gravity of 2.84, and boils at 178°.

**13. Methene Di-Iodide.**—Methene di-iodide $CH_2I_2$ is prepared by the action of strong hydriodic acid on iodoform in a sealed tube at 130°:

$$CHI_3 + HI = CH_2I_2 + I_2$$

It is a yellow, highly refractive liquid, remarkable for its high specific gravity, which is 3.345. It is used for determining the specific gravity of precious stones. It solidifies at 2°, and boils at 182°.

**14. Chloroform.**—Chloroform $CHCl_3$, or *trichlormethane*, was discovered in 1831 by Soubeiran and Liebig. It is prepared by distilling dilute alcohol with chloride of lime at 65°. The distilled liquid, which consists chiefly of water and chloroform, separates in two layers; the chloroform, which forms the bottom layer, is drawn off, shaken with strong sulphuric acid to remove part of the impurities, and, when it has risen again to the surface, is separated and purified by distillation until it boils regularly at 61°. It is now mostly prepared by substituting acetone for alcohol.

Chloroform is a thin, colorless, very mobile liquid, having an agreeable but rather sweetish ethereal odor. Its specific gravity is 1.53, and its boiling point is 61°. It does not take fire when brought in contact with the flame. It is but slightly soluble in water, to which it imparts a sweet taste, but it is readily dissolved by ether, as well as by alcohol. It is very much used in the laboratory as a solvent, as it dissolves sulphur, phosphorus, fats, resins, a great number of the alkaloids, and, in general, organic matter that is rich in carbon. It is much used in surgery as an anesthetic. The inhalation of its vapor produces insensibility and loss of muscular action, apparently without any danger to life or health, provided the preparation is free from impurities. Strong sulphuric acid does not affect chloroform, nor is the acid colored by pure chloroform. The aqueous solution of potash does not decompose it, but the alcoholic solution converts it into potassium chloride and potassium formate, as is shown by the following equation:

$$CHCl_3 + 4KOH = 3KCl + HCO \cdot OK + 2H_2O$$

If the chloroform should be contaminated with ethylene chloride $C_2H_4Cl_2$, gaseous chlorethylene $C_2H_3Cl$ is evolved. When chloroform is heated with an alcoholic solution of potash and aniline, phenyl carbamine $H_5C_6 \cdot NC$ is formed; this compound has a very strong, characteristic odor, and thus forms a very delicate and easily recognizable test for chloroform. When chloroform and an alcoholic solution of ammonia are together heated at 180° in a sealed tube, ammonium chloride and ammonium cyanide are formed, according to the equation:

$$CHCl_3 + 5NH_3 = \underset{\text{ammonium chloride}}{3NH_4Cl} + \underset{\text{cyanide}}{NH_4 \cdot CN}$$

When heated with potassium amalgam, chloroform evolves acetylene:

$$2CHCl_3 + 3K_2 = C_2H_2 + 6KCl$$

and when heated with sodium ethoxide, it is converted into orthoformic ether.

$$CHCl_3 + 3NaOC_2H_5 = 3NaCl + CH(OC_2H_5)_3$$

**15. Iodoform.**—Iodoform $CHI_3$, also known as *triiodomethane*, is a solid, yellow, crystallizable substance that is formed by the simultaneous action of iodine and an alkaline hydrate on alcohol and many other organic substances. It is usually prepared by dissolving 2 parts of crystallized sodium carbonate in 10 parts of water and 1 part of alcohol; the solution is heated to 80°, and 1 part of iodine is added in small portions at a time. The iodoform thus formed separates in yellow scales. Iodoform crystallizes in brilliant, yellow, hexagonal scales; it has a peculiar and characteristic odor, resembling saffron. It fuses at about 115°, and may be sublimed with slight decomposition. It is insoluble in water, but dissolves in alcohol and ether. It is used in medicine and surgery as an antiseptic. When boiled with potash, it is partly volatilized with the steam, and partly decomposed, yielding potassium iodide and formate. The production of iodoform is, as has been previously mentioned, a very delicate test for alcohol, though it must not be forgotten that many other organic substances also yield it.

**16. Bromoform.**—Bromoform $CHBr_3$ is usually prepared by the action of bromine on some alkaline hydrate dissolved in either alcohol or acetone. Potassium hydrate is dissolved in its own weight of dilute alcohol, and to the solution, which is thoroughly cooled, bromine is added, in small portions at a time, until the liquid obtains a permanent color. The product is agitated with water, and the oily liquid that separates is washed, dried, and rectified. Bromoform is an oily liquid that, in most of its properties, resembles chloroform. It boils at about 150°, is insoluble in water, but dissolves in alcohol and ether.

**17.** *Chloriodoform* $CHICl_2$ is produced by distilling iodoform with $HgCl_2$. It is a yellow liquid that boils at 131°. *Trichlorpropane* $C_3H_5Cl_3$ exists in four modifications, which may be represented by the following formulas:

$$CH_3 \cdot CH_2 \cdot CCl_3$$
$$CH_3 \cdot CHCl \cdot CHCl_2$$
$$CH_3 \cdot CCl_2 \cdot CH_2Cl$$
$$CH_2Cl \cdot CHCl \cdot CH_2Cl$$

The last of these formulas represents a compound known as *glyceryl trichloride* or *trichlorhydrin*, which is the most important of them. It may be prepared by the action of phosphoric chloride on glycerine, as is seen from the following equation:

$$C_3H_5(OH)_3 + 3PCl_5 = C_3H_5Cl_3 + 3HCl + 3POCl_3$$

It is a liquid with an odor resembling that of chloroform; it has a specific gravity of 1.42 at 15°, and boils at 158°. It is sparingly soluble in water. *Tribromhydrin* $C_3H_5Br_3$ is a crystalline solid that is obtained by the action of bromine on allyl iodide:

$$C_3H_5I + 2Br_2 = IBr + C_3H_5Br_3$$

It crystallizes in shining prisms, melts at 16°, and boils at about 220°. The corresponding iodine compound, tri-iodohydrin, does not appear to be capable of existing.

**18. Allyl Compounds.**—*Allyl chloride* $CH_2 : CH \cdot CH_2Cl$ is obtained by the distillation of phosphorus trichloride with allyl alcohol. It is a liquid with a pungent odor, and is insoluble in water. Its specific gravity is .95, and its boiling point 46°. *Allyl bromide* $C_3H_5Br$ is obtained by distilling propene bromide $C_3H_6Br_2$ with an alcoholic solution of potash, and is obtained as a liquid having a specific gravity of 1.42. It boils at 62°. *Allyl tribromide* $C_3H_5Br_3$ is obtained by adding bromine to the monobromide. It is a liquid that solidifies below 10°; its specific gravity is 1.436, and its boiling point 217°. *Allyl iodide* $C_3H_5I$ is obtained by distilling glycerine with phosphorus tetriodide. It is a liquid with a very strong odor resembling that of leeks; it boils at 101°, and has a specific gravity of 1.85. It combines with mercury to yield *mercury allyl iodide* $Hg''C_3H_5I$, forming colorless crystals that, on exposure to light, change, however, readily to yellow, and with iodine yield $HgI_2$ and $C_3H_5I$. In the presence of water, $Ag_2O$ replaces the iodine by $OH$, producing *mercury allyl hydroxide* $HgC_3H_5 \cdot OH$.

## HALOGEN DERIVATIVES FROM CLOSED-CHAIN HYDROCARBONS

**19.** Halogen derivatives from closed-chain hydrocarbons may be either substitution or addition products, and the substitution or addition may either occur in the closed-chain nucleus or in the side-chain. Thus, while only one compound of the formula $C_6H_5X$ exists, there are two of the formula $C_7H_7X$; namely, $C_6H_4X \cdot CH_3$ and $C_6H_5 \cdot CH_2X$, etc. It has been found that, as a rule, those compounds that are formed by substitution into the nucleus are more stable than the open-chain substitution products. If, for instance, the open-chain substitution product $C_2H_5Cl$ is treated with $Ag_2O,H_2O$, the compound $C_2H_5 \cdot OH$ will be readily formed, while the closed-chain substitution product $C_6H_5Cl$ will remain unaltered under the same treatment with the same reagent. The side-chain substitution products are, however, less stable, and behave in the same manner as the open-chain derivatives. The direct action of halogens on benzene itself produces, chiefly, substitution products. In the case of its homologues, nuclear substitution (i. e., substitution into the closed chain or nucleus) occurs if the action takes place in the cold, and, preferably, in the dark, and with the addition of iodine; while, with the help of heat and light, side-chain substitution products are procured. Thus, toluene $C_6H_5\cdot CH_3$ yields $C_6H_4Br\cdot CH_3$ when treated with bromine at normal temperature, but $C_6H_5\cdot CH_2Br$ when thus treated at higher temperatures.

**20. Halogen Derivatives of Benzene.**—*Chlorobenzene* $C_6H_5Cl$, also known as *phenyl chloride*, may be obtained by passing chlorine through benzene, or by the action of phosphorus pentachloride on phenol $C_6H_5OH$, according to the equation:

$$C_6H_5\cdot OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl$$

It is a strongly refractive colorless liquid that boils at 132°. *Bromobenzene* $C_6H_5Br$ is prepared in a similar way to chlorobenzene; it boils at 156°.

*Iodobenzene* $C_6H_5I$ is obtained by heating benzene with iodine and iodic acid to about 225°. By dissolving iodobenzene in $CHCl_3$ and passing $Cl$ through the solution, *dichloroiodobenzene* $C_6H_5I{:}Cl_2$ is obtained. The student's attention may here be drawn to the fact that iodine in this compound is trivalent.

**21. Chlorine Derivatives of Toluene and Naphthalene.**—*Chlorotoluenes* $C_6H_4Cl\cdot CH_3$ are formed by the action of chlorine on cold toluene. *Benzyl chloride* $C_6H_5\cdot CH_2Cl$ is obtained by passing chlorine gas into boiling toluene. *Benzal chloride* $C_6H_5\cdot CHCl_2$ and *benzotrichloride* $C_6H_5\cdot CCl_3$ are formed similarly to benzyl chloride, the saturation with chlorine being continued until the weight of the particular compound has been reached. Benzal chloride boils at 206°, while benzotrichloride boils at 212°. Two of each of the mono-halogen substitution products of naphthalene are known; namely, *α-chloronaphthalene* $C_{10}H_7Cl$ and *β-chloronaphthalene.* α-chloronaphthalene is prepared by passing chlorine into boiling naphthalene; it is a colorless liquid that boils at 263°. β-chloronaphthalene is prepared by treating β-naphthol $C_{10}H_7\cdot OH$ with phosphorus pentachloride. It is a crystalline body that melts at 61° and boils at 257°.

When chlorine gas is passed into naphthalene at a low temperature (*chlorinated*, as it is usually called), *naphthalene tetrachloride* $C_{10}H_8Cl_4$ is obtained. This compound crystallizes in colorless rhombohedra; it melts at 182°, and is converted into $C_{10}H_6Cl_2$ by boiling with $KOH$.

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### HALOGEN DERIVATIVES OF ALDEHYDES AND ACIDS

**22.** Most of these derivatives are of minor interest in the arts, and only the most important of them can here be mentioned.

**23. Chloraldehydes.**—*Monochloraldehyde* $CH_2Cl \cdot CHO$ is only known in its aqueous solution. It is prepared by the action of concentrated sulphuric acid on chloracetal $CH_2Cl \cdot CH(OC_2H_5)_2$. It is a rather unstable compound that, by exposure to air or the action of silver oxide, is converted into chloracetic acid $CH_2Cl \cdot CO_2H$. *Dichloraldehyde* $CHCl_2 \cdot CHO$ is prepared similarly to monochloraldehyde, substituting only dichloracetal $CHCl_2 \cdot CH(OC_2H_5)_2$ for chloracetal. It is a liquid that boils between 88° and 90°, and, on being kept for some length of time, is slowly converted into two solid polymeric modifications. One is amorphous, and is reconverted into the liquid dichloraldehyde by heating it at 120°. The second variety is of crystalline structure, and crystallizes from alcohol, dichloraldehyde being insoluble in water; in large prisms, these melt at 130°, but the molten mass does not pass into the liquid modification until it is heated to 240°. The most important of the chloraldehydes is *trichloraldehyde* $CCl_3 \cdot COH$, popularly known as *chloral*. It was discovered in 1832 by Liebig, while engaged in studying the actions of chlorine on the alcohols. It is obtained by the prolonged action of chlorine on alcohol. To prepare it, dry chlorine is passed into absolute alcohol, the latter being placed in a vessel surrounded by ice or very cold water, at the beginning of the action. This precaution is necessary, because the absorption of the chlorine gas by the alcohol creates considerable heat. The passage of the chlorine into the alcohol is continued for several hours, and when the absorption of the gas begins to slacken, the alcohol is carefully heated to near its boiling point to accelerate the absorption, and the passage is only stopped when positively no more chlorine is absorbed. The product is agitated with three times its own volume of strong sulphuric acid, and the whole is then gently heated on the water bath, when the impure chloral begins to separate and soon floats as an oily liquid on the surface of the acid. It is then removed and purified by repeated distillation. The principal reaction involved in this process may be expressed by the following equation:

$$CH_3 \cdot CH_2 \cdot OH + 4Cl_2 = 5HCl + CCl_3 \cdot CHO$$

but the $HCl$ formed acts on part of the alcohol, forming ethyl chloride and water. Chloral has also been obtained from starch, by distillation with hydrochloric acid and manganese dioxide.

Chloral is a thin, oily, colorless liquid; its specific gravity is 1.5, and its boiling point 97°. It is nearly tasteless, but has a pungent, tear-exciting odor, and it irritates the skin when brought in contact with it. On exposure to air, it readily absorbs moisture, and is converted into crystalline chloral hydrate $CCl_3 \cdot CH(OH)_2$, which may be obtained at once by dropping a little water into chloral and stirring it. Chemically pure chloral can be preserved without undergoing transformation, but in the presence of impurities, especially sulphuric acid, it soon becomes opaque and is changed into a white mass of metachloral or insoluble chloral that is insoluble in water, alcohol, and ether, while chloral itself is freely soluble in alcohol, ether, and water. Chloral resembles aldehyde in forming crystalline compounds with hydrosodium sulphite, and in giving a mirror of silver with silver-ammonium nitrate. With ammonia, chloral forms $CCl_3 \cdot CH(NH_2)(OH)$, corresponding with aldehyde ammonia. Zinc and $HCl$ substitute $H_3$ for $Cl_3$, converting the chloral into aldehyde. By nitric acid, chloral is oxidized to *trichloracetic acid* $CCl_3\cdot CO_2H$, which is a colorless, extremely deliquescent substance, possessing a caustic taste and strong bleaching properties; it boils at 190°. When heated with $KCN$ and water, chloral yields *dichloracetic acid* $CHCl_2\cdot CO_2H$, according to the equation:

$$CCl_3\cdot COH + KCN + H_2O = CHCl_2\cdot CO_2H + KCl + HCN$$

The alkaline hydrates decompose chloral into chloroform, and a formate, as may be seen from the following equation:

$$\underset{\text{chloral}}{CCl_3\cdot COH} + \underset{\substack{\text{potassium}\\ \text{hydrate}}}{KOH} = \underset{\substack{\text{potassium}\\ \text{formate}}}{KCHO_2} + \underset{\text{chloroform}}{CHCl_3}$$

**24. Chloral Hydrate.**—Chloral hydrate $CCl_3\cdot CH(OH)_2$ results, as has been previously stated, from the union of chloral and water. It is technically prepared on a very extensive scale. It consists of large prismatic crystals that fuse at 57° and distil at 96° to 98°. Chloral hydrate is very soluble in water and alcohol, imparting to these liquids its peculiar odor and biting taste. When heated to 97°, it dissociates into chloral and steam, but reforms again on cooling. When taken internally it produces sleep, a property that was discovered by Liebreich in 1869. A compound obtained similarly to chloral hydrate is *chloral alcoholate* $CCl_3\cdot CH\cdot OH\cdot OC_2H_5$; it is produced when chloral is dissolved in alcohol.

**25. Aldehyde Derivatives.**—*Tribromaldehyde* $CBr_3\cdot CHO$, also known as *bromal*, is analogous to chloral. It boils at 172° to 173°, and, if heated with alkali hydrates, is decomposed into bromoform and a formate. Higher chlorine-substitution products of the aldehydes are: *chlorpropionic aldehyde* $CH_2Cl\cdot CH_2\cdot CHO$, prepared from acrolein $CH_2 : CH\cdot COH$ and hydrochloric acid; *chlorbutyral aldehyde* $CH_3\cdot CHCl\cdot CH_2\cdot CHO$, produced from crotonaldehyde $CH_3\cdot CH : CH\cdot CHO$ by the addition of hydrochloric acid; *trichlorbutyral aldehyde* $CH_3\cdot CHCl\cdot CCl_2\cdot CHO$, also known as *butylchloral*, which boils at 163° to 165°, and whose hydrate, *butylchloral hydrate* $CH_3CHCl\cdot CCl_2\cdot CH(OH)_2$, melts at 78°, and is decomposed by alkalies into formic acid, an alkali chloride, and dichlorpropylene $CH_3 \cdot CCl : CHCl$.

**26. Acid Haloids.**—The haloid anhydrides of the acids or acid haloids are those derivatives that arise in the replacement of the hydroxyl of acids by halogens; they are the halogen compounds of the acid radicals. They are analogous to certain inorganic compounds; thus, if in nitrous acid $NOOH$ the hydroxyl group is replaced by $Cl$, nitrosyl chloride $NOCl$ is obtained, and, if in acetic acid $CH_3 \cdot COOH$, the hydroxyl group is replaced by $Cl$, we obtain acetyl chloride $CH_3COCl$.

**27. Acetyl Chloride.**—Acetyl chloride $CH_3 \cdot COCl$, also known as *acetic chloride*, was discovered by Gerhardt in 1852. It is prepared by distilling sodium acetate with phosphorus pentachloride:

$$\underset{\text{sodium acetate}}{NaC_2H_3O_2} + PCl_5 = \underset{\text{acetyl chloride}}{CH_3 \cdot COCl} + NaCl + POCl_3$$

Acetyl chloride is a colorless liquid with an irritating odor, and fumes in the air. Its specific gravity is 1.11, and it boils at 55°. If poured into water, it sinks to the bottom of the vessel and rapidly decomposes into acetic and hydrochloric acids. If mixed with alcohol instead of water, ethyl acetate is produced, as is seen from the following reaction:

$$CH_3CO \cdot Cl + C_2H_5OH = CH_3 \cdot CO \cdot OC_2H_5 + HCl$$

**28. Homologues of Acetyl Chloride.**—Among the homologues of acetyl chloride that are known are: *propyonyl chloride* $C_2H_5 \cdot COCl$, *butyryl chloride* $C_3H_7 \cdot COCl$, *valeryl chloride* $C_4H_9 \cdot COCl$, and *palmityl chloride* $C_{15}H_{31} \cdot COCl$; likewise, *acetyl bromide* $CH_3 \cdot COBr$, and *acetyl iodide* $CH_3COI$. A chloride of formic acid which would have the formula $HCO \cdot Cl$ does not exist, the compound always breaking up as rapidly as formed, into $CO$ and $HCl$.

**29. Other Chlorides.**—*Benzoyl chloride* $C_6H_5 \cdot COCl$, also known as *benzoic chloride*, is prepared by distilling phosphorus pentachloride with benzoic acid:

$$C_6H_5 \cdot CO_2H + PCl_5 = POCl_3 + C_6H_5 \cdot COCl + HCl$$

It is a highly refractive liquid, with an irritating odor. Its specific gravity is 1.11, and its boiling point 199°. It is decomposed by water into benzoic and hydrochloric acids, as is seen from the following equation:

$$C_6H_5{\cdot}COCl + H_2O = C_6H_5{\cdot}CO_2H + HCl$$

Ammonia converts it into benzamide:

$$C_6H_5{\cdot}COCl + NH_3 = C_6H_5{\cdot}CONH_2 + HCl$$

The corresponding bromide and iodide are obtained from benzoyl chloride by heating it with $KBr$ or $KI$. *Cinnamic chloride* $C_8H_7{\cdot}COCl$ is obtained similarly to benzoyl chloride; it is an oily liquid that boils at 260°. Other similar compounds known are *lactic chloride* $C_2H_4Cl{\cdot}COCl$, *salicylic chloride* $C_6H_4Cl{\cdot}COCl$, *succinyl dichloride* $C_2H_4(COCl)_2$, *fumaryl dichloride* $C_2H_2(COCl)_2$, and *chloromaleic chloride* $C_2HCl(COCl)_2$, which is obtained by heating tartaric acid with phosphorus pentachloride.

## ETHEREAL SALTS

### ETHEREAL SALTS FROM ACIDS

**30.** Ethereal salts, also known as *esters*, form a large group of rather important salts. Their composition may be compared with that of the salts formed by the substitution of metals for hydrogen in acids, and which are obtained by analogous methods. Ethereal salts are formed from either inorganic or organic acids by any of the following three methods; namely,

1. By the direct action of the acid on the alcohol; for example,

$$C_2H_5{\cdot}OH + CH_3COOH = \underset{\text{ethylic acetate}}{C_2H_5{\cdot}O{\cdot}C_2H_3O} + H_2O$$

2. By the action of the acid chlorides on the alcohols or their sodium compounds; for example,

$$C_2H_3OCl + C_2H_5OH = C_2H_3O{\cdot}O{\cdot}C_2H_5 + HCl$$

3. By the action of the halogen derivatives of the hydrocarbon on the silver salt of the acid; for instance,

$$2C_2H_5I + Ag_2SO_4 = (C_2H_5)_2SO_4 + 2AgI$$

The ethereal salts, like the metallic salts, are decomposed by the hydrates of the alkali metals, forming an alcohol that corresponds with the radical of the ethereal salt, and a salt of the alkali metal; if, for instance, ethyl acetate is heated with $KOH$, ethyl alcohol and potassium acetate are formed, as is seen from the following equation:

$$CH_3 \cdot CO_2C_2H_5 + KOH = C_2H_5 \cdot OH + CH_3 \cdot CO_2K$$

A reaction of this kind is termed *saponification* of the ethereal salt, because the formation of soap is affected in a similar manner by the action of alkalies on the fats and oils, which are ethereal salts formed by glycerine with the higher members of the acetic series of acids.

**31. Methyl Hydrogen Sulphate.**—Methyl hydrogen sulphate $HCH_3SO_4$, which is also frequently called *methyl sulphuric acid* or *sulpho-methylic acid*, is prepared by carefully and slowly mixing 1 part by weight of methyl alcohol with 2 parts by weight of concentrated sulphuric acid, and heating until the mixture boils. After thoroughly cooling, it is diluted with water, neutralized with barium carbonate, which precipitates any free sulphuric acid as barium sulphate, and leaves barium sulpho-methylate in solution. After the precipitated barium sulphate is filtered off, the barium sulpho-methylate is evaporated, first over the water bath and at the end in vacuum, when the barium salt is obtained in beautiful, square, colorless crystals that have the composition $Ba(CH_3SO_4)_2, 2Aq$. These crystals effloresce in the dry air, and are very soluble in water. When they are dissolved in water and the barium precipitated with an equivalent amount of sulphuric acid, a solution of sulpho-methylic acid is obtained, which, on being allowed to evaporate in the air, forms a thick, syrupy liquid. The reaction taking place between methyl alcohol and sulphuric acid may be expressed by the following equation:

$$CH_3 \cdot OH + H_2SO_4 \rightleftarrows CH_3HSO_4 + H_2O$$

It should here be remarked that the reaction can never be complete, as it is a reversible one. Methyl sulphuric acid is a very unstable compound, being readily decomposed by heat. The basic hydrogen in methyl sulphuric acid may be replaced by an equivalent weight of a metal, forming sulpho-methylates; as, for instance, $CH_3KSO_4$ *potassium sulpho-methylate.* All sulpho-methylates are readily soluble in water.

**32. Methyl Sulphate.**—Methyl sulphate $(CH_3)_2SO_4$ is prepared by distilling a mixture of 8 parts of sulphuric acid and 1 part of strong alcohol. That portion which distils at 150° is agitated with water and purified by rectification from powdered anhydrous baryta. Methyl sulphate is a colorless, oily liquid, of alliaceous odor; its specific gravity is 1.32, and it boils at 188°. It is neutral to test paper, and does not dissolve in water, but is decomposed by that liquid—slowly in the cold, but rapidly and with violence at a boiling temperature—into methyl alcohol and sulpho-methylic acid. Many of its reactions resemble those of the inorganic salts; thus, if distilled with $NaCl$, it yields methyl chloride and $Na_2SO_4$. With sodium formate it yields methyl formate and $Na_2SO_4$.

**33. Sulphethylic Acid.**—Sulphethylic acid $HC_2H_5SO_4$, also known as *ethyl-sulphuric acid* or *sulphovinic acid,* which has the composition of sulphuric acid $H_2SO_4$ with half of the hydrogen replaced by ethyl, is prepared in a similar way to methyl-sulphuric acid, employing, however, equal weights of alcohol and sulphuric acid. It is a viscid liquid, with properties and reactions similar to those of methyl-sulphuric acid. The sulphethylates or ethyl sulphates are soluble and easily crystallizable salts. *Calcium ethyl sulphate* crystallizes in beautiful, colorless crystals, containing $Ca(C_2H_5)_2(SO_4)_2, 2H_2O$. They are soluble in water, and effloresce in dry air. *Barium ethyl sulphate* $Ba(C_2H_5)_2(SO_4)_2, 2H_2O$

is readily soluble in water, and forms remarkably handsome crystals. *Potassium ethyl sulphate* $KC_2H_5SO_4$, readily prepared by decomposing calcium ethyl sulphate with potassium carbonate, is anhydrous, very soluble in water and permanent in air.

**34. Ethyl Sulphate.**—Ethyl sulphate $(C_2H_5)_2SO_4$, which represents sulphuric acid in which both hydrogen atoms have been replaced by two ethyl groups, is formed when silver sulphate is heated with ethyl iodide, double decomposition taking place; thus:

$$Ag_2SO_4+2C_2H_5I = (C_2H_5)_2SO_4+2AgI$$

Ethyl sulphate is an oily, fragrant liquid; its specific gravity is 1.18, and it boils at 208°. It is insoluble in water, and is not decomposed by it at ordinary temperature, but when heated with it, it is decomposed into alcohol and ethyl sulphuric acid. When exposed to heat by itself, it is decomposed into ethene $C_2H_4$ and $H_2SO_4$. *Sulphamylic acid*, or *amyl sulphuric acid*, $HC_5H_{11}SO_4$ is similarly prepared.

**35. Potassium Phenyl Sulphate.**—Phenyl sulphuric acid does not exist, but *potassium phenyl sulphate* $SO_2\cdot OC_6H_5\cdot OK$ is obtained by the prolonged action of potassium bisulphate on phenol dissolved in potash:

$$C_6H_5\cdot OK+2SO_2OHOK=SO_2OC_6H_5\cdot OK+SO_2(OK)_2+H_2O$$

The product is extracted with hot alcohol, from which it crystallizes in tables that are soluble in water. It is decomposed when exposed to moist air, or by boiling with either water or dilute hydrochloric acid, yielding phenol and hydropotassium sulphate, as may be seen from the following equation:

$$SO_2OC_6H_5\cdot OK+H_2O = HOC_6H_5+SO_2\cdot OH\cdot OK$$

Potassium phenyl sulphate occurs in minute quantities in urine.

**36. Ethyl Nitrate.**—Ethyl nitrate $C_2H_5\cdot NO_3$, also known as *nitric ether*, is prepared by the direct action of chemically pure nitric acid on alcohol. Its preparation on a large scale is to be avoided, as it would most likely result in an explosion. It is prepared by heating 80 grams of nitric acid (Sp. Gr. 1.40) with about 2 grams of urea nitrate on a steam bath; the urea nitrate is added to decompose any nitrous acid present. When the acid has become perfectly cool, 15 grams more of urea nitrate and then 60 grams of alcohol (Sp. Gr. .81) are added. The mixture is carefully distilled, and collected. The nitric ether is separated from the alcohol in the distillate, by the addition of water, shaken with the addition of a very little potash, the lower layer separated, allowed to stand over fused calcium chloride, and distilled. The reaction between the alcohol and the nitric acid is as follows:

$$C_2H_5{\cdot}OH + HNO_3 = C_2H_5{\cdot}NO_3 + H_2O$$

The decomposition of the nitrous acid by the urea is expressed by the following equation:

$$2HNO_2 + CO(NH_2)_2 = CO_2 + N_4 + 3H_2O$$

When alcohol is mixed with ordinary nitric acid, which usually is more or less contaminated with nitrous acid, the latter oxidizes the alcohol to aldehyde and other products that act on the nitric acid in a very violent and even sometimes in an explosive manner; but when urea is present, the nitrous acid acts on this instead of on the alcohol, and ethyl nitrate is safely produced. Ethyl nitrate is a colorless, pleasant-smelling liquid, boiling at 86° and having a specific gravity of 1.112 at 15°. It is almost insoluble in water, and burns with a white flame. It will explode if suddenly exposed to a high temperature. Alcoholic solution of potash converts it into $KNO_3$ and alcohol.

**37. Ethyl Nitrite.**—Ethyl nitrite $C_2H_5NO_2$ is produced by the direct action of nitric acid on alcohol, the nitric radical $NO_3$ being reduced to the nitrous radical $NO_2$ by the conversion of part of the alcohol into aldehyde. Pure ethyl nitrite is prepared by mixing 50 cubic centimeters of a solution containing 23 grams of potassium nitrite with

25 cubic centimeters of alcohol, and allowing the mixture to run slowly into a cool mixture of 25 cubic centimeters of alcohol, 50 cubic centimeters of water, and 37½ cubic centimeters of sulphuric acid. The ethyl nitrite distils over by the heat of the reaction, and is condensed in a receiver packed in ice. It is purified by shaking with a little dry potassium carbonate. It is a mobile, yellowish liquid, of specific gravity .947 at 15°, and boils at 16°. It is insoluble in water, and has an odor resembling that of apples. It is the active ingredient of the so called *sweet spirit of niter* (*spiritus ætheris nitrosi*) used in medicine. When ethyl nitrite stands with water it gradually decomposes, nitrogen oxide being eliminated, and an explosion may eventually occur under suitable conditions. Hydrogen sulphide changes ethyl nitrite into ammonia and alcohol.

**38. Nitrate and Nitrite of Methyl.**—Methyl nitrate $CH_3NO_3$ is prepared by distilling 1 part of niter and 1 part of methyl alcohol with 2 parts of sulphuric acid. The application of external heat is not necessary, as the heat produced by the reaction is quite sufficient to make the methyl nitrate distil over. It is a colorless liquid of specific gravity 1.182, and boils at 60°. When struck with a hammer or heated to 150°, it explodes quite violently. Methyl nitrite $CH_3NO_2$ is produced by the action of nitrous acid on methyl alcohol. It is a gaseous body, of pleasant odor, that condenses at very low temperature to a yellowish liquid that boils at about $-120°$.

**39. Other Ethereal Salts.**—The ethereal salts formed by phosphoric acid are of little importance in the arts, and will not be considered here. *Ethyl arsenite* $(C_2H_5)_3AsO_3$ is obtained by the action of sodium ethoxide and arsenious chloride, as is seen from the following equation:

$$3C_2H_5ONa + AsCl_3 = (C_2H_5)_3AsO_3 + 3NaCl$$

*Ethyl borate* $(C_2H_5)_3BO_3$, also known as *boric ether*, is formed by the action of boron trichloride on absolute alcohol. It is a colorless limpid liquid that boils at 120°. Its vapor burns with a green flame. Water decomposes it into boric acid and alcohol. *Ethyl silicate* $(C_2H_5)_4SiO_4$, also known as *silicic ether*, is obtained by treating silicic chloride with a small quantity of anhydrous alcohol:

$$4C_2H_5 \cdot OH + SiCl_4 = (C_2H_5)_4SiO_4 + 4HCl$$

It is a colorless liquid with a rather pleasant odor, and a taste similar to that of pepper. Its specific gravity is .933, and it boils at 165°. Its vapor burns with a bright flame, evolving clouds of $SiO_2$. It is decomposed slowly by water, and rapidly by ammonia. *Ethyl orthocarbonate* $(C_2H_5)_4CO_4$, which boils at 159°, is formed by the action of sodium on an alcoholic solution of chloropicrin, as is shown by the following equation:

$$CCl_3NO_2 + 4C_2H_5OH + 4Na$$
$$= (C_2H_5)_4CO_4 + 3NaCl + NaNO_2 + H_4$$

*Ethyl carbonate* $(C_2H_5)_2CO_3$, also known as *carbonic ether*, boils at 126°, and is obtained by heating silver carbonate with ethyl iodide in a closed tube. Acted on by chlorine, it yields *perchlorethyl carbonate* $(C_2Cl_5)_2CO_3$, which is a crystalline solid. *Potassium ethyl carbonate* $KC_2H_5CO_3$ is precipitated in crystalline form when $CO_2$ is passed into a solution of $KOH$ in absolute alcohol. *Ethyl perchlorate* $C_2H_5ClO_4$ is obtained by distilling barium perchlorate with barium sulphethylate. It is a liquid that boils at 74° and easily explodes with violence.

**40. Amyl Nitrite.**—Amyl nitrite $C_5H_{11}NO_2$ is prepared by passing nitrous vapors, made by the action of nitric acid on starch, into amyl alcohol, and distilling the carefully washed product. It is a pale yellow liquid of specific gravity .9 and boiling point 96°; it possesses a peculiar odor, resembling that of apples. Its vapor when inhaled produces dilatation of the capillary system and violent, but soon disappearing, headache. It is used in the medical science. It has been recommended as a remedy against seasickness, as an antidote in cases of poisoning by chloroform vapors, and in certain cases of heart trouble.

The ethyl compounds have been chiefly taken as representatives of the ethereal salts of inorganic acids, and the student must bear in mind that similar bodies may be formed with other alcohol radicals. The organic acids also give rise to a large number of ethereal salts.

**41. Methyl Salts.**—*Methyl formate* $HCO_2CH_3$ is prepared by heating together in a retort equal parts by weight of potassium methyl sulphate and sodium formate, according to the equation:

$$HCO_2Na + KCH_3SO_4 = HCO_2CH_3 + KNaSO_4$$

This compound is isomeric with acetic acid $CH_3 \cdot CO_2H$. It is a very volatile liquid, lighter than water, and boils at 36°. *Methyl acetate* $CH_3CO_2CH_3$ occurs in crude wood spirit. It is prepared by distilling 2 parts of methyl alcohol with 1 part of glacial acetic acid and 1 part of sulphuric acid. It is a fragrant liquid which boils at 56°; it is freely soluble in water, and is lighter than it. It is readily decomposed by the alkalies, and is isomeric with proprionic acid. *Methyl oxalate* $(CO_2)_2(CH_3)_2$ forms colorless crystals, melting at 51°. It is prepared by heating anhydrous oxalic acid with methyl alcohol.

**42. Ethyl Salts.**—*Ethyl formate* $HCO_2C_2H_5$, also called *formic ether*, is isomeric with methyl acetate and propionic acid. It is prepared by distilling a mixture of 10 parts of sulphuric acid, 7 parts of dry sodium formate, and 6 parts of absolute alcohol. The distillate is freed from acid by shaking with a little lime, and redistilled. Formic ether is a fragrant liquid, and is employed in the manufacture of artificial rum and arrack. It is soluble in water, but decomposes into formic acid and alcohol when the solution is kept for some time. *Ethyl acetate* $CH_3 \cdot CO_2C_2H_5$, or *acetic ether*, is prepared by distilling a mixture of alcohol, sulphuric acid, and potassium acetate:

$$\begin{aligned} &C_2H_5 \cdot OH + H_2SO_4 + CH_3CO_2K \\ &= CH_3 \cdot CO_2C_2H_5 + KHSO_4 + H_2O \end{aligned}$$

Ethyl acetate passes over, together with a quantity of alcohol that escapes the reaction. It is purified by shaking with a solution of sodium chloride, and the ether that floats at the top is decanted, dried over calcium chloride, and rectified. Acetic ether is a colorless liquid with an odor resembling that of cider; its specific gravity is .91, and it boils at 72°. It is sparingly soluble in water, but mixes readily in all proportions with alcohol as well as ether. It is used for flavoring. Caustic alkalies, especially in alcoholic solutions, easily saponify it, yielding acetate and alcohol; for example:

$$CH_3CO_2C_2H_5 + KOH = C_2H_5 \cdot OH + KC_2H_3O_2$$

Ammonia converts it into alcohol and acetamide:

$$CH_3CO_2C_2H_5 + NH_3 = C_2H_5 \cdot OH + C_2H_3ONH_2$$

Chlorine converts it into *perchloracetic ether* $CCl_3 \cdot CO_2 \cdot C_2Cl_5$, a compound that smells very much like chloral. If iodine and aluminum act together on acetic ether, the latter is decomposed into ethyl iodide and aluminum acetate. Acetic ether undergoes a remarkable reaction with sodium, which dissolves in it, forming sodium ethylate and sodium aceto-acetate:

$$2CH_3CO_2C_2H_5 + Na_2$$
$$= NaOC_2H_5 + CH_3 \cdot CO \cdot CHNa \cdot CO_2C_2H_5 + H_2$$

**43. Aceto-Acetic Ether.**—Aceto-acetic ether, or *ethyl aceto-acetate* $CH_3 \cdot CO \cdot CH_2 \cdot CO_2C_2H_5$, may be obtained by the action of dilute hydrochloric acid on the above mentioned sodium aceto-acetate, as will be seen from the equation:

$$CH_3 \cdot CO \cdot CHNa \cdot CO_2C_2H_5 + HCl$$
$$= CH_3 \cdot CO \cdot CH_2 \cdot CO_2C_2H_5 + NaCl$$

Ethyl aceto-acetate is a colorless liquid with an odor resembling that of hay. It is only sparingly soluble in water, but dissolves in alcohol; its alcoholic solution gives a violet color with $Fe_2Cl_6$ and a green crystalline precipitate $Cu(C_6H_9O_3)_2$ with a strong solution of copper acetate. Ethyl aceto-acetate has become an important factor in synthetic chemistry, since through its means a large number of complex acids and ketones have been synthesized. This is due to the two following facts:

1. When ethyl aceto-acetate is heated with the alkalies, it yields either a ketone (acetone) or an acid (acetic acid), according to the concentration of the alkaline solution. Thus, with *dilute* aqueous or alcoholic solution of potash, the reaction is as follows:

$$(1) \qquad CH_3 \cdot CO \cdot CH_2 \cdot CO_2C_2H_5 + 2KOH$$
$$= CH_3 \cdot CO \cdot CH_3 + K_2CO_3 + C_2H_5OH$$

while the reaction obtained with a concentrated alcoholic solution of potash is

$$(2) \qquad CH_3 \cdot CO \cdot CH_2 \cdot CO_2C_2H_5 + 2KOH$$
$$= 2CH_3 \cdot CO_2K + C_2H_5OH$$

The decomposition, as shown through the first equation, is known as *ketonic decomposition*, while the latter is known as *acidic decomposition.*

2. When ethyl sodium aceto-acetate is treated with an alkyl iodide, the sodium is replaced by the alkyl group; for instance, *ethyl ethyl-aceto-acetate* may be obtained synthetically, as follows:

$$CH_3COCHNa \cdot CO_2C_2H_5 + C_2H_5I$$
$$= \underset{\text{ethyl ethyl-aceto-acetate}}{CH_3COCHC_2H_5CO_2C_2H_5} + NaI$$

By treating this with sodium, *ethyl sodium ethyl-aceto-acetate* $CH_3 \cdot CO \cdot CNaC_2H_5CO_2C_2H_5$ may be prepared and this may again be readily converted into *ethyl diethyl-aceto-acetate* $CH_3 \cdot CO \cdot C(C_2H_5)_2CO_2C_2H_5$. Other alkyl radicals may, of course, be just as readily substituted. The substituted aceto-acetates may be represented by the general formula $CH_3COCRR'CO_2C_2H_5$, and such a compound can be made to yield the substituted ketone $CH_3CO \cdot CHRR'$ or the substituted acid $CHRR'CO_2H$ (together with acetic acid), according as it undergoes either ketonic or acidic decomposition.

**44. Ethyl Salts of the Acetic Series.**—*Ethyl butyrate* $C_3H_7 \cdot CO_2 \cdot C_2H_5$, sometimes called *butyric ether*, is prepared by distilling butyric acid together with alcohol and sulphuric acid. It is largely produced in the arts, and is sold, owing to its strong odor of pineapples, under the name of *essence of pineapples*, or *oil of ananas* in its alcoholic solution. From this alcoholic solution it may be precipitated by the addition of water. The mixture of butyric acid and its homologues, obtained when butter is decomposed by steam, is used in its preparation on the large scale. *Ethyl pelargonate*, or *pelargonic ether* $C_8H_{17} \cdot CO_2C_2H_5$, is prepared in a similar way from oil of rue, and is used for flavoring purposes under the name of *oil of quince*. *Ethyl caprate* $C_9H_{19}CO_2C_2H_5$, or *capric ether*, is a colorless, fragrant, oily liquid that is obtained by distilling wine lees. It is used to impart to inferior wines a superior flavor. *Amyl acetate* $CH_3CO_2C_5H_{11}$ is prepared by distilling fusel oil with acetic and sulphuric acids. Its alcoholic solution is sold as *essence of pears*.

**45. Ethyl Salts of the Higher Acids of the Acetic Series.**—The ethyl salts of acids of the acetic series containing more than 10 atoms of carbon are, as a rule, prepared by dissolving the acid in alcohol and passing hydrochloric-acid gas into the solution. It is assumed that this converts the alcohol into ethyl chloride, which acts on the acid to form the ethyl salt that is deposited in crystals from the alcoholic solution. *Cetyl palmitate* $C_{15}H_{31} \cdot CO_2 \cdot C_{16}H_{33}$ constitutes the chief part of the crystalline fat, *spermaceti*, found in the peculiar cavities in the head of the sperm whale, and it is resolved, when heated for some time with solid potash, into potassium palmitate and cetyl alcohol. *Ceryl cerotate* $C_{25}H_{53} \cdot CO_2 \cdot C_{27}H_{55}$ composes Chinese wax, the produce of an insect of the cochineal tribe. It is decomposed by fused potash into potassium cerotate and ceryl alcohol. *Melissyl palmitate*, or *myricin*, $C_{15}H_{31} \cdot CO_2 \cdot C_{30}H_{61}$ occurs in beeswax. *Melissyl mellisate* $C_{29}H_{59} \cdot CO_2 \cdot C_{30}H_{61}$ is contained in hay, from which it may be extracted by alcohol.

**46.** *Ethyl benzoate*, or *benzoic ether* $C_6H_5 \cdot CO_2 \cdot C_2H_5$, is prepared as stated in Art. **45**; that is, benzoic acid is dissolved in alcohol and hydrochloric acid passed into the solution; the whole is then distilled, and water is added to the distillate, when ethyl benzoate separates as a fragrant liquid of specific gravity 1.05. It boils at 211°. *Benzyl benzoate* $C_6H_5 \cdot CO_2 \cdot C_7H_7$ is present in the balsams of Peru and Tolu. *Methyl salicylate* $C_6H_4OH \cdot CO_2 \cdot CH_3$, also known as *salicylic ether*, is prepared by passing gaseous hydrogen chloride into a solution of salicylic acid in methyl alcohol. It is the chief constituent of the oil of Gaultheria, known as *essence of wintergreen.* When purified, this compound forms a colorless oil, having a pleasant odor. It boils at 223.7°, and has a specific gravity of 1.197. Ferric chloride colors it violet. If methyl salicylate is treated with a strong solution of soda, in the cold, it yields crystals of $C_6H_4 \cdot ONa \cdot CO_2CH_3$, which, when heated in a sealed tube with methyl iodide, form an oily liquid having the composition $C_6H_4OCH_3 \cdot CO_2 \cdot CH_3$, and which is known as *methyl methyl-salicylate;* and if this compound is saponified with potash, it yields the potassium salt of methyl-salicylic acid $C_6H_4OCH_3 \cdot CO_2H$, a crystalline acid, isomeric with methyl salicylate, but distinguished from the latter by not giving a violet color with ferric chloride. *Phenyl salicylate* $C_6H_4OH \cdot CO_2C_6H_5$, also known as *salol*, is prepared by the action of phosphorus oxychloride $POCl_3$ on a mixture of salicylic acid and phenol. It forms colorless crystals that melt at 43°. It is, like salicylic acid, remarkable for its antiseptic properties.

**47. Oxalic Ether.**—*Oxalic ether* $(CO_2 \cdot C_2H_5)_2$, or *neutral ethyl oxalate*, is prepared by distilling potassium oxalate, alcohol, and concentrated sulphuric acid. Pure oxalic ether is a colorless oily liquid of pleasant odor; its specific gravity is 1.09, and it boils at 186°. It is only very sparingly soluble in cold water, and, if boiled with it, is decomposed into alcohol and oxalic acid. Caustic alkalies decompose it readily into a metallic oxalate and alcohol, and if it is mixed with only half the quantity of potash required for its complete decomposition, it yields pearly scales of *potassium oxal-ethylate* $(CO_2)_2KC_2H_5$, as is seen from the following equation:

$$(CO_2C_2H_5)_2 + KOH = (CO_2)_2KC_2H_5 + C_2H_5 \cdot OH$$

When oxalic ether is treated with excess of dry chlorine gas in sunlight, a white, colorless, crystalline body is obtained that is fusible, insoluble in water, and instantaneously decomposed by alcohol. It consists of perchlor-ethylic oxalate $(CO_2C_2Cl_5)_2$, which may be represented as oxalic ether in which the whole of the hydrogen has been replaced by chlorine.

**48. Ethyl Malonate.**—Ethyl malonate $CH_2(CO_2 \cdot C_2H_5)_2$, also known as *malonic ether*, is obtained by leading hydrochloric-acid gas into a solution of calcium malonate in absolute alcohol, according to the equation:

$$CH_2(CO_2)_2Ca + 2C_2H_5 \cdot OH + 2HCl$$
$$= CH_2(CO_2 \cdot C_2H_5)_2 + CaCl_2 + 2H_2O$$

It is a bitter aromatic liquid, of specific gravity 1.068, that boils at 195° and possesses a remarkable similarity to ethyl aceto-acetate. Thus, the hydrogen of the methylene group is here, as in ethyl aceto-acetate, replaceable by sodium, and the resulting sodium malonic ether readily exchanges its metal for an alkyl radical when treated with an alkyl iodide, and thus is a very useful reagent for the synthesis of fatty acids; for when those alkyl-substituted malonic acids are heated they lose $CO_2$ and yield the corresponding alkyl-substituted fatty acids.

## ETHEREAL SALTS DERIVED FROM GLYCOL

**49.** The number of ethereal salts that may be derived is considerable, because either one or both of the hydroxyl groups of this compound may be replaced, and two different radicals may be introduced. As numerous as these salts are, they have not yet acquired any technical importance in the arts, and will therefore not be treated here.

## ETHEREAL SALTS DERIVED FROM GLYCEROL

**50.** A still larger number of ethereal salts have been derived from glycerol $C_3H_5(OH)_3$, which contains, as is seen from its formula, three hydroxyl groups, each of which may be replaced by a different radical. These salts are generally known as *glycerides*, but are also sometimes called the *salts of propenyl* $C_3H_5$. They have, as a whole, a certain practical interest, because they include the animal and vegetable fats. They may be divided into the two following classes: (1) glycerol esters of the mineral acids, and (2) glycerol fatty acid esters. The above mentioned name "glycerides" is mostly applied to the second class of esters.

**51. Nitroglycerin.**—The most important glycerol ester of the mineral acids is *nitroglycerin* $C_3H_5(NO_3)_3$, also known as *glyceryl trinitrate*, which was discovered by Sobrero in 1847. It is produced by the action of a mixture of sulphuric and nitric acids on glycerol. The latter is added, drop by drop, to a well cooled mixture of concentrated nitric and sulphuric acids, as long as it dissolves; the solution is then poured into water, and the separated heavy oil, which is the nitroglycerin, is removed, washed with water, and dried by means of calcium chloride.

Nitroglycerin is a heavy, oily, and nearly colorless liquid of specific gravity 1.6. It becomes a solid at 8°. It volatilizes very energetically at 160°. It possesses the characteristic sweet taste of glycerine, but is dangerously poisonous when taken internally. It is insoluble in water, and nearly so in alcohol, but dissolves in ether and methyl alcohol. It is very violent in its explosion. If a drop of it is placed upon an anvil and given a sharp blow, it will explode with a very loud report, and if a paper moistened with a drop of nitroglycerin is struck, it will be blown into the smallest fragments. On the application of a flame or red-hot iron, nitroglycerin is comparatively harmless, as it burns very quietly; and when heated over a flame in the open air, it explodes but feebly. In a closed vessel, however, it explodes at about 180° with very great violence. Mixed with *kieselguhr*, it forms *dynamite*. Kieselguhr is a particularly porous, silicious earth that is found near Overlohe, in Hanover, Germany. With nitrocellulose it forms so called smokeless powder. Alkalies convert nitroglycerin into glycerol and nitric acid.

**52. Glycerol Nitrite.**—Glycerol nitrite $C_3H_5(ONO)_3$ is formed by the action of $N_2O_3$ on glycerine. *Glycerol sulphuric acid* $C_3H_5(OH)_2SO_4H$, also known as *sulpho-glyceric acid*, is formed with considerable evolution of heat by mixing 1 part of glycerine with 1 part of sulphuric acid. *Glycerol phosphoric acid* $C_3H_5(OH)_2PO_4H_2$ is formed by the action of metaphosphoric acid on glycerine, but has only been obtained in solution. It occurs combined with the fatty acids and choline as lecithin in the yolks of eggs, in the brain, in the bile, and in the nerve tissues. It is a stiff, syrupy liquid that decomposes into glycerine and phosphoric acid when it is heated with water.

**53. Compounds of Glycerol and Fatty Acids.** Among the large number of ethereal salts formed by glycerol with the fatty acids, only a few of the most important can here be mentioned:

1. *Formic Acid Esters.*—*Monoformin* $C_3H_5(OH)_2 \cdot CO_2H$ is formed by heating oxalic acid and glycerol. *Diformin* $C_3H_5(OH)(CO_2H)_2$ boils at about 164°.
2. *Acetic esters*, or *acetin*, result when acetic acid and glycerine are heated together: *Monacetin* $C_3H_5(OH)_2(C_2H_3O_2)$, at 100°; at 200°, *diacetin* $C_3H_5(OH)(C_2H_3O_2)_2$; at 250°, *triacetin* $C_3H_5(C_2H_3O_2)_3$. The latter is present in cod-liver oil, and it boils at 258°. All the acetins are oily liquids.
3. *Tributyrin* $C_3H_5(C_4H_7O_2)_3$ occurs in butter.
4. *Glycerides of the higher fatty acids* occur in the animal and vegetable fatty oils, fats, and tallow. They can be artificially prepared by heating the fatty acids with glycerine. They are sparingly soluble in alcohol, but dissolve readily in ether. The most important of these are: *Trimyristin*, or *myristin*, $C_3H_5(C_{14}H_{27}O_2)_3$ occurs in spermaceti, in muscat butter, and in oil nuts, from which it is mostly obtained. It crystallizes from ether in shining needles that melt at 55°. *Tripalmitin* $C_3H_5(C_{16}H_{31}O_2)_3$ is found in most fats; it is usually obtained from palm oil, or from Chinese wax, by pressing and crystallizing from alcohol. *Tristearin* $C_3H_5(C_{18}H_{35}O_2)_3$ occurs in tallow. It can be obtained by

heating glycerine and stearic acid to about 300°. It crystallizes from ether in shining leaflets, and melts at 71.5°. *Triolein*, or *olein*, $C_3H_5(C_{18}H_{33}O_2)_3$ is found in oils, like olive oil, from which it is obtained by cooling the olive oil to 0°, pressing out the liquid part, dissolving this in a little alcohol, again freezing to separate the rest of the stearin, and distilling off the alcohol. Olein is less easily decomposed by alkalies than are palmitin and stearin, and is left unaltered when olive oil is treated with a cold concentrated solution of sodium hydrate, which converts the palmitin and stearin into soap and glycerine.

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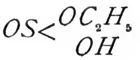
### SULPHONIC ACIDS

**54.** The ethereal salts of sulphurous acid are metameric with the class of compounds known as the *sulphonic acids;* that is to say, both ethyl hydrogen sulphite and ethyl sulphonic acid have the same empirical formula $C_2H_6SO_3$. The difference between sulphonic acids and the sulphites is that, when the sulphonic acids are treated with reducing agents, they yield the corresponding thio-alcohols; thus ethyl sulphonic acid $C_2H_5SO_3H$ yields mercaptan (ethyl thio-alcohol) $C_2H_5SH$. This reaction indicates that the sulphur in ethyl sulphonic acid is combined directly to the carbon of the ethyl group, for there is no doubt that $S$ in mercaptan is so combined. The constitution of ethyl sulphonic acid is, therefore, probably,

$$O_2<\begin{matrix}SC_2H_5\\HO\end{matrix}$$

while that of ethyl hydrogen sulphite is



$$OS<\begin{matrix}OC_2H_5\\OH\end{matrix}$$

When sodium sulphite is heated with ethyl iodide, sodium ethyl sulphonate and sodium iodide are produced:

$$Na_2SO_3+C_2H_5I = C_2H_5SO_2ONa+NaI$$

If sodium sulphite were a salt of $SO(OH)_2$, viz., $SO(ONa)_2$, this reaction would be expected to produce ethyl sodium sulphite $SO(ONa)(OC_2H_5)$. Since this is, however, not the case, $Na_2SO_3$ must have the constitution $SO_2(ONa)Na$.

The sulphonic acids bear the same relationship to sulphuric acid as the carboxylic acids bear to carbonic acid; that is, they contain an alcohol radical or a hydrocarbon radical in place of one of the $OH$ groups. They are monobasic acids, since they still retain one $OH$ group. By partial reduction, they generally yield *sulphinic acids*, which bear the same relation to the $SO(OH)_2$ form of sulphurous acid as the sulphonic acids bear to sulphuric acid. The sulphonic acids of open-chain radicals are of comparatively little technical importance.

Ethylene combines directly with $SO_3$ to produce the crystalline compound *carbyl sulphate* $C_2H_4S_2O_6$, which is the anhydride of ethionic acid, into which it passes when dissolved in cold water. Ethionic acid $CH_2(OSO_3H)\cdot CH_2(SO_3H)$ is a mixed ethereal salt and sulphonic acid derived from glycol. When boiled with water the ethereal-salt portion undergoes hydrolysis, sulphuric acid and *isothionic acid*, or *hydroxy ethyl-sulphonic acid*, $CH_2(OH)\cdot CH_2(SO_3H)$ being produced.

**55.** It is characteristic of closed-chain compounds (or, at least, of such as contain a benzene nucleus) that they readily yield sulphonic acids when heated with strong sulphuric acid. These are very useful for preparing other compounds, e. g., phenols, and on account of their solubility are used as dyestuffs.

When benzene is gently heated with sulphuric acid, *benzene sulphonic acid* $C_6H_5\cdot SO_2OH$ is formed; if fuming sulphuric acid is used, the three (chiefly 1 : 3) *benzene disulphonic acids* $C_6H_4(SO_2OH)_2$ result. Naphthalene may be similarly sulphonated to produce isomeric naphthalene mono- and di-sulphonic acids. Sulphonic acids of most benzene hydrocarbon derivatives are easily obtainable, some of which will receive mention later.

## NITRO COMPOUNDS

**56.** The ethereal salts of nitrous acid are metameric with the nitro-substituted hydrocarbons; ethyl nitrite $C_2H_5O \cdot N : O$ is metameric with nitroethane $C_2H_5 \cdot NO_2$. The nitro compounds may be regarded as derived from nitric acid in the same way that the sulphonic acids are derived from sulphuric acid. The *nitroparaffins* are produced by the action of silver nitrite on alkyl iodides, as is seen from the following equation:

$$C_2H_5I + AgNO_2 = C_2H_5 \cdot NO_2 + AgI$$

The *nitro-hydrocarbons of the benzene series* are produced by the direct action of nitric acid on the hydrocarbons. The nitroparaffins can be primary, secondary, or tertiary, like all other open-chain hydrocarbon-substitution products. The three forms have the same structure as the three forms of alcohols, $NO_2$ being substituted for the $OH$ group.

**57. Nitromethane and Nitroethane.**—Nitromethane $CH_3(NO_2)$ may be obtained by the action of silver nitrite on methyl iodide, or by the action of potassium nitrite on potassium monochloracetate, as is seen from the following equation:

$$CH_2ClCO_2K + KNO_2 + H_2O = KCl + CH_3NO_2 + KHCO_3$$

It is a liquid that boils at 99° to 101°. *Nitroethane* $C_2H_5NO_2$ is obtained, together with a certain quantity of ethyl nitrite, when ethyl iodide is treated with silver nitrite:

$$C_2H_5I + AgNO_2 = C_2H_5NO_2 + AgI$$

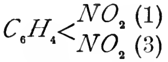
It is a liquid having a peculiar ethereal odor, and boiling at 113°; it burns with a luminous flame, and gives a blood-red color with ferric chloride. *Trichlor-nitromethane* $CCl_3NO_2$, also known as *chloropicrin* or *nitrochloroform*, is produced by the action of nitric acid on chlorinated carbon compounds, as, for instance, chloral; and, also, when chlorine or bleaching powder acts on nitro derivatives, such as fulminating mercury, picric acid, nitromethane, etc.

In the preparation of nitrochloroform, 10 parts of freshly prepared bleaching powder are mixed to a paste with cold water, and placed in a retort. To this is added a saturated solution of picric acid heated to 30°. Reaction then generally takes place without further heating, and the nitrochloroform distils over with the vapor of the water. Nitrochloroform is a colorless, heavy liquid, boiling at 112°, and having a specific gravity of 1.692 at 0°. It possesses a tear-exciting odor, and explodes when rapidly heated.

**58. Nitrobenzene.**—Nitrobenzene $C_6H_5NO_2$ is prepared by pouring benzene in small portions into a mixture of strong nitric and sulphuric acids and adding water. The nitrobenzene separates as an oily, yellow liquid that possesses a strong odor of bitter almonds. It boils at 205° and solidifies at 3°. It is known commercially as *essence of mirbane*, and is used in the manufacture of perfume. By the action of certain reducing agents, such as hydrogen sulphide, ammonium sulphide, iron filings and acetic acid, etc., nitrobenzene is converted into aniline or phenylamine:

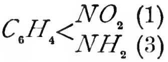
$$C_6H_5NO_2 + 3H_2 = \underset{\text{aniline}}{C_6H_5NH_2} + 2H_2O$$

*Dinitrobenzene* $C_6H_4(NO_2)_2$.—The three isomerides, the 1 : 3 dinitrobenzene, the 1 : 2, and the 1 : 4 dinitrobenzenes are formed when benzene is treated with a large excess of a mixture of nitric and sulphuric acids. The nitro compounds separate on the addition of water, and are purified by crystallization in alcohol. Since they may be regarded as being formed from the further nitration of nitrobenzene, it is only in accordance with the general rule of substitution in aromatic compounds that 1 : 3 dinitrobenzene should be the chief product; this variety crystallizes in pale yellow needles, and melts at 90°. Reducing agents convert it successively into nitrophenyl amine and phenylene diamine:



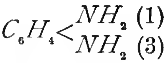
$$C_6H_4<\begin{matrix}NO_2\ (1)\\ NO_2\ (3)\end{matrix}$$

1:3 dinitrobenzene



$$C_6H_4<\begin{matrix}NO_2\ (1)\\ NH_2\ (3)\end{matrix}$$

nitrophenyl amine



$$C_6H_4<\begin{matrix}NH_2\ (1)\\ NH_2\ (3)\end{matrix}$$

phenylene diamine

The 1 : 2 and 1 : 4 dinitrobenzenes are colorless, and melt at 118° and 173°, respectively.

**59. Nitrotoluenes.**—*Para-* and *ortho-nitrotoluene*, i. e., 1:4 $C_6H_4(NO_2)\cdot CH_3$ and 1:2 $C_6H_4(NO_2)\cdot CH_3$, are obtained by treating toluene with fuming nitric acid, and they may be readily separated. Para-nitrotoluene crystallizes in almost colorless needles that melt at 54° and boil at 237°, while the ortho, or 1:2, nitrotoluene is a liquid that boils at 223°. *Meta-nitrotoluene*, or 1:3 $C_6H_4(NO_2)CH_3$, has a melting point of 16°, and boils at 230°. *Dinitrotoluene* $C_6H_3(NO_2)_2CH_3$ is formed by treating either toluene or ortho- or para-nitrotoluene with an excess of a mixture of nitric and sulphuric acids. It crystallizes in long, slender needles that melt at 70°. *Trinitrotoluene* $C_6H_2(NO_2)_3CH_3$, obtained by prolonged heating of a solution of toluene in an excess of a mixture of sulphuric and nitric acids, forms nearly colorless needles; it is slightly soluble in alcohol, and melts at 82°.

If *naphthalene* is boiled in glacial acetic acid with strong nitric acid $\alpha$-nitronaphthalene $C_{10}H_7NO_2$ is obtained; it crystallizes in yellow needles or prisms that melt at 61° and boil at 304°. It is used in the manufacture of dyes, and for destroying the fluorescence of paraffin oils when these are used in the adulteration of vegetable oils. It is soluble in alcohol, but insoluble in water.

Other nitro derivatives will receive attention under the classes of bodies from which they are derived.

## METALLO-ORGANIC COMPOUNDS

**60.** The name *metallo-organic compounds* is applied to compounds of alcohol radicals with metals. Those containing the more basic metals, such as zinc, are usually formed by the direct action of the metals on the alcoholic iodide; while those containing the less basic metals, i. e., tin, lead, etc., are formed by the action of organo-zinc compounds on metallic chlorides. As zinc ethide $Zn(C_2H_5)_2$ is widely used in preparing these compounds, it will be described first.

**61. Zinc Ethide.**—Zinc ethide $Zn(C_2H_5)_2$, also known as *zinc ethyl*, was discovered, together with zinc methide, in

1849, by Frankland. It is prepared by the action of zinc on ethyl iodide, as is seen from the subjoined equation:

$$Zn_2 + 2C_2H_5I = Zn(C_2H_5)_2 + ZnI_2$$

When the reaction is terminated, the product is distilled, and that portion collected that passes above 115°. All these operations are conducted in an atmosphere of carbon dioxide; the process will be minutely described, and the apparatus required is shown in Figs. 2, 3, and 4.

About 50 grams of freshly granulated, chemically pure, and carefully dried zinc are placed in the Florence flask *e* (Fig. 2), which is connected with a Kipp gas generator *a* for the production of carbon dioxide, from which the gas is started through two drying bottles *b* and *c*, containing concentrated sulphuric acid, into the Florence flask *e*. A second perforation in the cork of the Florence flask *e* is for the reception of the tube *f*, which passes through a Liebig condenser *f′* and terminates in a little mercury contained in the beaker *d*. The condenser is cooled by a continuous flow of water in the usual way. When the whole apparatus has been filled with

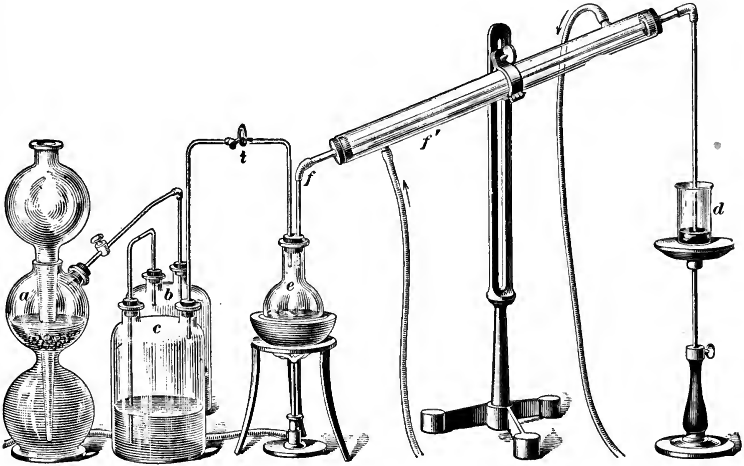


FIG. 2

carbon dioxide, the Florence flask *e* is opened, and 25 grams of ethyl iodide, which have previously been thoroughly dried, are dropped in and the cork is quickly replaced. The carbonic-acid gas is again passed through the whole apparatus for some time, and then cut off by turning the stop-cock of the generator. The flask *e* is then gently heated until the ethyl iodide boils briskly, the vapor being condensed in the tube *f* and runs back into the flask *e*. In about 5 to 6 hours the conversion is complete, and the ethyl iodide ceases to distil. The stop-cock of the generator is now turned on again, and a further stream of carbon dioxide is allowed to pass slowly through the apparatus; the position of the condenser is reversed, as shown in Fig. 3, and the tube *f′* is connected, by means of a perforated cork *k*, with the test tube *o*; the longer limb of a narrow siphon *i*, made of a piece of stout glass tubing, passes through this cork, while its shorter limb connects it with a small test tube *p*, the cork of which is also pierced by a short piece of glass tubing *l*. For the reception and preservation of the zinc ethyl, a number of glass tubes, having a shape as shown in Fig. 4, are prepared. The long narrow neck *r* is passed down the glass tubing *l* to the

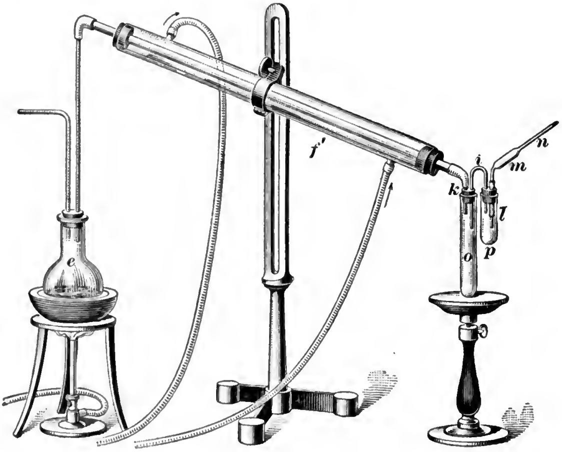


FIG. 3

bottom of *p*, the other end *n* of the tube being connected with an apparatus for passing carbon dioxide similar to *a*. The whole apparatus being filled with this gas, the pinch-cock *t* is slipped over the rubber connection, thus shutting off the supply of carbon dioxide from the generator *a*, and the flask *e* heated on a sand bath, so that the zinc ethyl may distil over; a slow stream of carbon dioxide is constantly passed into *p*, the excess escaping through *l*. When enough zinc ethyl has collected in the tube *o*, a blowpipe flame is applied to narrow tube *n*, which is drawn and sealed; the siphon tube *i* is then gradually pushed down, so that its longer limb may be sufficiently immersed in the zinc ethyl, and the pinch-cock *t* is removed, and the stop-cock of the generator *a* turned on again, when the pressure of the carbon dioxide forces over a part of the zinc ethyl into the small test tube *p*. By heating the tube *m* with a spirit lamp, so as to expel part of the gas, and allowing it to cool, it will become partly filled with zinc ethyl, and may be withdrawn and quickly sealed by means of a blowpipe. The spontaneous inflammability of zinc ethyl and its easy decomposition by water or moisture make the process of its preparation rather difficult and one that requires a great deal of care.

FIG. 4

The process described above may be somewhat accelerated if the zinc is polarized by copper in the copper-zinc couple. To effect this, cupric oxide is reduced by heating it in a tube in a current of hydrogen or coal gas, and 10 grams of it mixed with 90 grams of zinc filings in a 300-cubic-centimeter bottle, which is then heated over a Bunsen burner with continual shaking until it forms gray granular masses. After cooling, 87 grams of ethyl iodide are added, and the mixture is heated to about 90° with a reversed condenser until no more liquid distils back, which is said to require only about 15 to 20 minutes; the rest of the operation is carried on exactly as previously described.

Zinc ethyl is a colorless, mobile, and highly refractive liquid that has a peculiar, penetrating, and very disagreeable odor. Its specific gravity is 1.18, and it boils at 118°: it takes fire spontaneously on contact with air; it burns with a greenish flame that evolves white fumes of zinc oxide, and, if a porcelain plate is pressed against this flame, a deposit of metallic zinc is formed that is surrounded by a yellow ring of oxide that soon changes to white on cooling. Water decomposes it violently, with the formation of zinc hydroxide and the evolution of ethane, as is seen from the following equation:

$$Zn(C_2H_5)_2 + 2H_2O = Zn(HO)_2 + 2C_2H_6$$

When gradually mixed with dry oxygen, it passes through two stages of oxidation, yielding first zinc ethyl-ethoxide $Zn\left\{\begin{matrix}C_2H_5\\OC_2H_5\end{matrix}\right.$, and, finally, zinc ethoxide $Zn(OC_2H_5)_2$, which latter compound is a white powder. With iodine and other halogens, the reaction also takes place in two stages, but consists in the successive substitution of the halogen for the ethyl; thus:

$$Zn(C_2H_5)_2 + I_2 = C_2H_5I + ZnC_2H_5I$$

and

$$ZnC_2H_5I + I_2 = C_2H_5I + ZnI_2$$

**62. Zinc Methide.**—Zinc methide $Zn(CH_3)_2$, also known as *zinc methyl*, is prepared in a similar manner. It is a mobile, refractive, and spontaneously inflammable liquid that boils at 46°. It resembles zinc ethide in most of its reactions.

**63. Methides and Ethides of Boron and Silicon.** *Boron methide* $B(CH_3)_3$ may be prepared by the action of zinc methide on ethyl borate, as is seen from the following equation:

$$2(C_2H_5)_3BO_3 + 3Zn(CH_3)_2 = 2B(CH_3)_3 + 3Zn(O\cdot C_2H_5)_2$$

It is a gas that condenses to a liquid at a low temperature, and possesses an extremely penetrating and disagreeable odor. *Boron ethide* $B(C_2H_5)_3$, also sometimes called *triborethyl*, can be prepared like the corresponding methyl compound, or by the action of boron chloride on zinc ethide:

$$2BCl_3 + 3Zn(C_2H_5)_2 = 2B(C_2H_5)_3 + 3ZnCl_2$$

It is a spontaneously inflammable liquid that burns with a green flame, and possesses an irritating odor. It is insoluble in water, but is slowly converted by it into $B(C_2H_5)_2OH$. It has a specific gravity of .69, and boils at 95°. *Silicon methide* $Si(CH_3)_4$ is prepared by the action of $SiCl_4$ on zinc methide. It is a liquid that boils at 30° and burns in the air, producing a white smoke of silica. It is not decomposed by water. *Silicon ethide* $Si(C_2H_5)_4$ is prepared by the action of $SiCl_4$ on zinc ethide. It is a colorless mobile liquid, not decomposed by water, combustible, burning with a brilliant white flame, thereby producing silicic acid. It is indifferent to the action of reagents, and, as it acts in all points like a hydrocarbon, it is often called *silicon nonane*, after the ninth member of the paraffin series $C_9H_{20}$, in which one carbon atom has been replaced by a silicon atom. When acted on by chlorine, it yields $SiC_8H_{19}Cl$, and when this is dissolved in alcohol and heated with potassium acetate, the acetate $SiC_8H_{19} \cdot C_2H_3O_2$ is obtained, which may be further converted into silicon-nonyl alcohol $SiC_8H_{19} \cdot OH$ by boiling it with an alcoholic solution of potash. Silicon-nonyl alcohol, also known as *silicon-nonyl hydrate*, is a colorless liquid, insoluble in water, and boiling at 190°.

**64. Ethyl Phosphines.**—Primary, secondary, and tertiary ethyl phosphines are known. *Monoethyl phosphine* $(C_2H_5)H_2P$ and *diethyl phosphine* $(C_2H_5)_2HP$ are produced when ethyl iodide is made to react on $PH_4I$ in the presence of an excess of zinc oxide:

$$2C_2H_5I + 2PH_4I + ZnO = 2[(C_2H_5)H_2P \cdot HI] + ZnI_2 + H_2O$$
$$2C_2H_5I + PH_4I + ZnO = (C_2H_5)_2HPHI + ZnI_2 + H_2O$$

As both reactions are accomplished simultaneously, both phosphines are obtained at the same time. They are separated by the action of water on the two hydriodides that are formed. That of the monoethyl phosphine is decomposed by water, while that of diethyl phosphine is only decomposed by the alkalies. It is, therefore, sufficient to add water to the product of the reaction in order to liberate the monoethyl phosphine; and when this compound has been entirely expelled by heat, potassium hydrate is added to the residue, which will cause the liberation of the diethyl phosphine.

Monoethyl phosphine is a colorless liquid, boiling at 25°; it is lighter than water, in which it is insoluble, and possesses the most disagreeable odor. It takes fire when brought in contact with either chlorine or nitric acid. Diethyl phosphine is also a liquid that is lighter than water; it boils at 85°. It has a very strong affinity for oxygen, and very often takes fire spontaneously when in contact with air.

*Triethyl phosphine* $P(C_2H_5)_3$ may be obtained by the action of phosphorus trichloride on zinc ethyl; the operation must be conducted out of contact with the air, and the zinc ethyl must be diluted with anhydrous ether; the reaction may be expressed by the following equation:

$$2PCl_3 + 3Zn(C_2H_5)_2 = 2P(C_2H_5)_3 + 3ZnCl_2$$

It is a colorless liquid with a strong odor, boiling at 127°, and having a specific gravity of .81. It combines directly with oxygen, for which it has a very strong affinity, forming *triethyl-phosphine oxide* $PO(C_2H_5)_3$, which is a crystalline compound very soluble in alcohol and water. It combines directly with methyl iodide, forming $P(C_2H_5)_3CH_3 \cdot I$; and with sulphur, with the evolution of heat, it forms $P(C_2H_5)_3S$, which crystallizes in needles from its hot aqueous solution. It has, further, a great affinity for carbon disulphide, and combines with it very energetically, forming a red crystalline compound that is soluble in alcohol. The presence of $CS_2$ in coal gas may then easily be detected by leading some of the gas into triethyl phosphine, which at once obtains a distinctly red color when the former compound contaminates the coal gas.

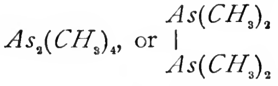
**65. The Methyl and Phenyl Phosphines.**—The methyl phosphines, viz., *monomethyl phosphine*, *dimethyl* *phosphine*, and *trimethyl phosphine*, are similar to the ethyl phosphines, and are also similarly prepared.

*Phenyl phosphine* $PH_2 \cdot C_6H_5$, also known as *phosphaniline*, is prepared by passing dry hydriodic-acid gas into phosphenyl chloride $C_6H_5PCl_2$, when the compound $C_6H_5PI_2 \cdot HI$ is formed; this is decomposed by alcohol with the formation of phenyl phosphine. This compound is a liquid, with a pungent, disagreeable odor; it boils at 160°, and is heavier than water. It readily oxidizes in the air, forming phosphenyl oxide $C_6H_5PH_2O$, which forms a crystalline, easily soluble mass. Phenyl phosphine is insoluble in aqueous acids, but unites with dry hydrogen iodide with the formation of *phenyl-phosphonium iodide* $C_6H_5PH_3I$. *Diphenyl phosphine* $PH(C_6H_5)_2$, which boils at 280°, *triphenyl phosphine* $P(C_6H_5)_3$, which boils at 75°, and *triphenyl-phosphonium iodide* $P(C_6H_5)_3HI$ are also known. *Diethyl-phenyl phosphine* $C_6H_5P(C_2H_5)_2$, which is formed by the action of zinc ethyl on phosphenyl chloride and the treatment of the product with caustic soda, is a colorless liquid with a strong odor. It boils at 222°, and has a specific gravity of .9571 at 13°. It is insoluble in water, but soluble in acids. *Phosphenyl chloride* $PC_6H_5Cl$ is obtained when mercury diphenyl $(C_6H_5)_2Hg$ is heated with $PCl_3$, or by leading a mixture of benzene and phosphorus trichloride through a red-hot tube. It is a liquid of piercing odor, has a specific gravity of 1.319, and boils at 220°. It combines with chlorine to form the tetrachloride $PC_6H_5Cl_4$. It is decomposed by water into hydrochloric and phenyl hypophosphorus (phosphenylous) acids $C_6H_5PHO(OH)$.

**66. Triethyl Arsine.**—Triethyl arsine $As(C_2H_5)_3$ is prepared by the distillation of an alloy of sodium and arsenic with ethyl iodide. At the same time, there is formed another body, containing $As_2(C_2H_5)_4$, analogous to dimethyl arsine. Both compounds are liquids of powerful odor; they may be separated by means of distillation in an atmosphere of carbon dioxide, the triethyl arsine passing over last. It may also be prepared by distilling $AsCl_3$ with zinc ethyl.

It is a colorless, very disagreeable-smelling liquid that boils at 140°, and is soluble in water, alcohol, and ether. *Trimethyl arsine* $As(CH_3)_3$ is formed, together with *dimethyl arsine* $As(CH_3)_2$, when an alloy of arsenic and sodium is submitted to the action of methyl iodide; or it may be obtained by acting with $AsCl_3$ on zinc methide. It is a strong-smelling liquid that boils at 75°.

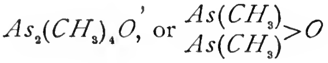
**67. Cacodyl and Its Compounds.**—Dimethyl arsine $As(CH_3)_2$ was discovered in 1760 by Cadet, and later was more thoroughly investigated by Bunsen and Berzelius; the latter proposed the name *cacodyl* (from the Greek κακώδης, *kakodes*, "stinking," owing to its extremely disagreeable odor). A little consideration will show that, as arsenic is either trivalent or pentavalent, this cacodyl is a compound radical $[As'''(CH_3)_2]'$, and it deserves special interest because it is capable of behaving like an elementary substance. Its molecular formula, as the formula $As(CH_3)_2$ represents only one volume of vapor, should, therefore, be



$$As_2(CH_3)_4, \text{ or } \begin{matrix} As(CH_3)_2 \\ | \\ As(CH_3)_2 \end{matrix}$$

and its correct name *tetramethyl diarsine* or *dicacodyl*, or *free cacodyl.*

The oldest cacodyl compound, the one discovered by Cadet, and originally known as *fuming liquor of Cadet*, and which through Bunsen's investigation, was found to be *dicacodyl oxide*



$$As_2(CH_3)_4O, \text{ or } \begin{matrix} As(CH_3) \\ As(CH_3) \end{matrix}\!\!>O$$

is the product of the distillation of potassium acetate and arsenious oxide, as is seen from the following equation:

$$2As_2O_3+8CH_3CO_2K = 2As_2(CH_3)_4O+4CO_2+4K_2CO_3$$

The collected distillate is an oily liquid, having an extremely offensive odor, resembling that of garlic, and producing dense white fumes in the air. The strong tendency of this compound to take fire spontaneously in the air and the poisonous character of its vapor make it a difficult compound to handle and experiment with. It has a specific gravity of 1.46, and boils at 150°. Dicacodyl oxide combines with acids to form salts. It dissolves in alcohol, and by treating this solution with an alcoholic solution of mercuric chloride, a crystalline precipitate, having the composition $As_2(CH_3)_4OHgCl_2$, is obtained, which, by distilling with concentrated hydrochloric acid in an atmosphere of $CO_2$, is converted into *cacodyl chloride* $As(CH_3)_2Cl$. This compound is a colorless oily liquid that not only produces in the air dense white fumes that are extremely poisonous, but even takes fire spontaneously. It is heavier than water, insoluble in that liquid and in ether, but readily soluble in alcohol. When heated in contact with zinc, in an atmosphere of carbon dioxide to about 100°, a compound of zinc chloride with cacodyl is formed; and if this compound is treated with water, *dicacodyl* $As_2(CH_3)_4$ is obtained as a heavy, oily, colorless, and transparent liquid that boils at 170°, and crystallizes at −6° in large transparent crystals. It is spontaneously inflammable in air, and when its vapor is passed through a tube that is heated to 400°, it is decomposed, as is shown in the following equation:

$$As_2(CH_3)_4 = 2CH_4 + C_2H_4 + 2As$$

With a limited supply of air, dicacodyl throws off white fumes, passing into the oxide and ultimately into *cacodylic acid* $As(CH_3)_2O \cdot OH$, a compound that may be considered as arsenic acid $AsO(OH)_3$ in which two hydroxyl groups have been replaced by two methyl groups. The simplest way to prepare this acid, however, is to oxidize dicacodyl oxide with mercuric oxide in the presence of water; the reaction may be expressed by the following equation:

$$As_2(CH_3)_4O + 2HgO + H_2O = 2As(CH_3)_2O \cdot OH + Hg_2$$

This acid is a rather stable compound that is soluble in water, and from which it crystallizes. It melts at 200° with decomposition. Hydriodic acid reduces it to *cacodyl iodide* $As(CH_3)_2I$, and hydrogen sulphide to *cacodyl sulphide*. By $PCl_5$ it is converted into dimethyl-arsine trichloride

$(CH_3)_2AsCl_3$, which regenerates cacodylic acid with water. *Cacodyl cyanide* $As(CH_3)_2CN$ is obtained when cacodyl chloride is heated with mercuric cyanide, as is seen from the equation:

$$2As(CH_3)_2Cl+Hg(CN)_2 = 2As(CH_3)_2CN+HgCl_2$$

It forms colorless, four-sided, lustrous, prismatic crystals that melt at 33° into a colorless liquid that boils at 140°. It is but slightly soluble in water, and takes fire only when strongly heated. The vapor evolved by its evaporation is extremely poisonous; by the evaporation of a few drops, the atmosphere of a room is contaminated to such an extent as to cause instantaneous numbness of the limbs, vertigo, and unconsciousness, and the quick death of small animals.

Cacodyl iodide is a thin, yellowish, heavy liquid, with a very offensive odor. Cacodyl bromide and fluoride have also been prepared. *Cacodyl trichloride*, or *dimethyl-arsine trichloride* $(CH_3)_2AsCl_3$, is prepared by distilling dicacodyl oxide with strong hydrochloric acid. It is a colorless liquid that, although not exactly fuming in air, emits a vapor that, like those of most cacodyl compounds, is extremely poisonous. It is insoluble in water and ether, but soluble in alcohol. It boils at about 100°, when it gives off a colorless, instantaneously inflammable vapor of methyl chloride; and a heavy, irritating liquid called *methyl-arsine dichloride* $AsCH_3Cl_2$ distils over, which boils at 133° and is soluble in water without decomposition. By evaporating the aqueous solution of methyl-arsine dichloride with sodium carbonate and extracting the residue with alcohol, *methyl-arsine oxide* $AsCH_3O$ may be crystallized from this alcoholic solution. Mercuric oxide, in the presence of water, converts this oxide into *methyl-arsenic acid* $AsCH_3O(OH)_2$.

When dicacodyl is acted on by methyl iodide, it yields cacodyl iodide and *tetramethyl-arsonium iodide* $As(CH_3)_4I$, as is seen from the following equation:

$$As_2(CH_3)_4+2CH_3I = As(CH_3)_2I+As(CH_3)_4I$$

This last compound, when decomposed by moist silver oxide, yields the corresponding hydrate $As(CH_3)_4OH$, which is strongly alkaline, and may be crystallized. *Pentamethyl arsine* $As(CH_3)_5$, corresponding with $AsCl_5$, has also been prepared. The ethyl compounds of arsenic are similar to the methyl compounds.

**68. Antimony Compounds.**—Antimony also forms compounds with the alcohol radicals. They are produced either: (1) by the action of alkyl iodides on potassium or sodium antimonides, or (2) by the interaction of zinc alkyls and antimony trichloride. *Trimethyl stibine* $Sb(CH_3)_3$, also known as *antimony methyl*, is obtained by heating methyl iodide with potassium antimonide. Its specific gravity at 15° is 1.523, and it boils at 81°. *Triethyl stibine* $Sb(C_2H_5)_3$, also known as *stibethyl*, is obtained by distilling ethyl iodide with an alloy of antimony and potassium. It boils at 159°. Both compounds are liquids that take fire in the air, and both are insoluble in water. With oxygen, sulphur, and the halogens, they combine energetically, and decompose the concentrated haloid acids, liberating their hydrogen, as is seen from the following equation:

$$Sb(C_2H_5)_3 + 2HCl = Sb(C_2H_5)_3Cl_2 + H_2$$

*Triethyl-stibine oxide* $Sb(C_2H_5)_3O$ is soluble in water, which is also true of *triethyl-stibine sulphide* $Sb(C_2H_5)_3S$, consisting of shining crystals. Its solution behaves somewhat like a calcium sulphide; it precipitates sulphides from solutions of the heavy metals, with the formation of salts of triethyl stibine.

**69. Bismuth Compounds.**—*Bismuth trimethyl* $Bi(CH_3)_3$ and *bismuth triethyl* $Bi(C_2H_5)_3$ are liquids. They can be distilled in vacuo but explode when heated at atmospheric pressure. Bismuth trimethyl is changed by hydrochloric acid to $BiCl_3$ and methane. Bismuth triethyl is spontaneously inflammable; it unites with iodine to form *bismuth-diethyl iodide* $Bi(C_2H_5)_2I$, and unites with mercuric chloride to form *bismuth-ethyl chloride* $Bi(C_2H_5)Cl_2$, as is seen from the subjoined equation:

$$Bi(C_2H_5)_3 + 2HgCl_2 = Bi(C_2H_5)Cl_2 + 2Hg(C_2H_5)Cl$$

From the alcoholic solution of the iodide, the alkalies precipitate *bismuth-ethyl oxide* $Bi(C_2H_5)O$, an amorphous yellow powder that takes fire readily in the air. The nitrate $Bi(C_2H_5)<\begin{matrix}O\cdot NO_2\\ O\cdot NO_2\end{matrix}$ is obtained when silver nitrate is added to the iodide.

**70. Lead Compounds.**—The compounds of lead with alcohol radicals are produced (1) by acting on lead chloride with zinc ethide, and (2) by the interaction of alkyl iodides and a lead and sodium alloy. *Lead tetramethyl* $Pb(CH_3)_4$ has a specific gravity of 2.03, and boils at 110°. It has a faint odor, is unaffected by air, and is not soluble in water. When heated with hydrochloric acid, *lead-trimethyl chloride* $Pb(CH_3)_3Cl$ is obtained, as is seen from the following equation:

$$Pb(CH_3)_4 + HCl = Pb(CH_3)_3Cl + CH_4$$

It is a crystalline compound that may be sublimed. *Lead tetraethyl* $Pb(C_2H_5)_4$ and *lead triethyl* $Pb_2(C_2H_5)_6$ are oily liquids that cannot be distilled without decomposition. The iodide $Pb(C_2H_5)_3I$ is produced when iodine acts on lead tetraethyl. On heating with moist silver oxide, *lead-triethyl hydrate* $Pb(C_2H_5)_3OH$ distils over, which has a very alkaline reaction and forms crystalline salts with the acids. The sulphate $[Pb(C_2H_5)_3]_2SO_4$ dissolves in water with difficulty.

**71. Mercury Compounds.**—The mercury compounds of this class may be obtained by different methods; namely:

1. By the interaction of sodium amalgam and alkyl iodides in the presence of acetic ester; the part that the latter compound takes in this reaction has not yet been explained:

$$2C_2H_5I + Hg\cdot Na_2 = (C_2H_5)_2Hg + 2NaI$$

2. By the action of potassium cyanide on mercury alkyl iodides.

3. By the action of zinc alkyls on mercury alkyl iodides; for example:

$$2C_2H_5HgI + Zn(C_2H_5)_2 = 2(C_2H_5)_2Hg + ZnI_2$$

4. By the action of zinc alkyls on mercuric chloride; for example:

$$HgCl_2 + Zn(C_2H_5)_2 = (C_2H_5)_2Hg + ZnCl_2$$

The mercury compounds of this class are colorless, heavy liquids, with a faint but peculiar and characteristic odor. Their vapors are extremely poisonous. Neither water nor exposure to the air changes these compounds, but subjected to heat they ignite readily. *Mercury methide* $Hg(CH_3)_2$ is one of the heaviest liquids known, its specific gravity being 3.069; it is so heavy that glass floats in it. It boils at 95°, and burns with a bright flame; its vapor is very poisonous. When acted on by strong hydrochloric acid, it yields *mercury-methyl chloride* $HgCH_3Cl$, which is a crystalline compound, sparingly soluble in water. *Mercury ethide* $Hg(C_2H_5)_2$ is prepared as shown above; it has a specific gravity of 2.44, and boils at 159°; when heated to 200°, it is decomposed into metallic mercury and butane. It yields ethane $C_2H_6$ when treated with concentrated sulphuric acid. Mercury-ethyl chloride $HgC_2H_5Cl$ is prepared by acting on $Hg(C_2H_5)_2$ with mercuric chloride dissolved in alcohol:

$$Hg(C_2H_5)_2 + HgCl_2 = 2HgC_2H_5Cl$$

It is insoluble in water, but crystallizes from alcohol. When mercury-ethyl chloride is acted on with moist silver oxide, it is converted into mercury-ethyl hydrate $HgC_2H_5OH$. This latter compound is a thick, alkaline liquid that blisters the skin when brought in contact with it. It is soluble in water and forms salts with the acids. *Mercury-methyl iodide* $HgCH_3I$ forms shining needles that melt at 143° and are insoluble in water. Silver nitrate converts it into *methyl-mercury nitrate* $CH_3Hg\cdot O\cdot NO_2$. *Mercury-ethyl iodide* $HgC_2H_5I$ is only slightly soluble in water and alcohol, but crystallizes from a hot caustic-soda solution; it is decomposed by sunlight into mercuric iodide and $C_4H_{10}$. *Mercury-allyl iodide* $C_3H_5HgI$ melts at 135°, and is converted by $HI$ into propylene and mercuric iodide. Like mercury-ethyl chloride, it is converted into mercury-ethyl hydroxide by the action of silver oxide. *Mercury-ethyl sulphide* $(HgC_2H_5)_2S$ is a yellow precipitate formed by ammonium sulphide in an alcoholic solution of mercury-ethyl chloride. It can be crystallized from ether. *Mercury diphenyl* $(C_6H_5)_2Hg$ is formed when sodium amalgam acts on bromobenzene. It is a fusible crystalline solid that melts at 120°. It is insoluble in water, sparingly soluble in alcohol and ether, and readily soluble in benzene. When heated in a sealed tube with $HgCl_2$ and alcohol, it yields *mercury-phenyl chloride* $HgC_6H_5Cl$, and by decomposing this with moist silver oxide, *mercury-phenyl hydroxide* $HgC_6H_5 \cdot OH$ is obtained as a crystalline, strongly alkaline base.

**72. Tin Compounds.**—The reactions resorted to in order to combine tin with alkyls are the same as were employed with arsenic, antimony, and other elements: (1) The action of zinc alkyls on stannic chloride, when $Sn(CH_3)_4$ and $Sn(C_2H_5)_4$ are produced. (2) The action of alkyl iodides on a tin-sodium alloy. When the alloy contains a considerable amount of sodium, $Sn(C_2H_5)_3$ is produced, but when a comparatively small amount of sodium is present, the chief product is $Sn(C_2H_5)_2I_2$. Sodium removes iodine from both of the primarily formed iodides, with the formation of $Sn_2(C_2H_5)_4$ and $Sn_2(C_2H_5)_6$. These can be separated by means of alcohol, in which the latter compound is insoluble. *Tin tetramethyl* $Sn(CH_3)_4$, corresponding with $SnCl_4$, boils at 78°. *Tin tetraethyl*, or *stannic ethide* $Sn(C_2H_5)_4$, has a specific gravity of 1.19, and boils at 181°. It is a remarkably stable compound. Both are colorless, ethereal-smelling liquids, and are insoluble in water. By the action of the halogens the alkyls are successively eliminated. Hydrochloric acid acts similarly:

$$Sn(C_2H_5)_4 + I_2 = Sn(C_2H_5)_3I + C_2H_5I, \text{ etc.}$$
$$Sn(C_2H_5)_4 + HCl = Sn(C_2H_5)_3Cl + C_2H_6, \text{ etc.}$$

*Tin-triethyl iodide* $Sn(C_2H_5)_3I$ boils at 231°, and has a specific gravity of 1.833. *Tin-triethyl chloride* $Sn(C_2H_5)_3Cl$ boils at about 209°, and has a specific gravity of 1.428. Both of these compounds are soluble in alcohol. When either is acted on by silver oxide or caustic potash, *tin-triethyl hydroxide* $Sn(C_2H_5)_3OH$ is produced, a crystalline compound that melts at 66° and boils at 272°. It is sparingly soluble in water, but dissolves readily in alcohol as well as in ether. It is a strongly alkaline compound that yields crystalline salts with the acids; for instance, $Sn(C_2H_5)_3{\cdot}O{\cdot}NO_2$, formed with nitric acid, and $[Sn(C_2H_5)_3]_2SO_4$, formed with sulphuric acid. When tin-triethyl hydroxide is heated for some time to almost its boiling temperature, it decomposes into water and *tin-triethyl oxide* $\begin{matrix}Sn(C_2H_5)_3\\Sn(C_2H_5)_3\end{matrix}{>}O$. This is an oily liquid that, in the presence of water, at once regenerates the hydroxide. *Tin triethyl* $Sn_2(C_2H_5)_6$ is an oily liquid of powerful odor, resembling that of mustard-seed oil. It boils at 270°, decomposing into $Sn(C_2H_5)_4$ and $Sn$. It combines with oxygen, forming tin-triethyl oxide, and, with iodine, yielding *tin-triethyl iodide* $Sn(C_2H_5)_3I$. *Tin diethyl* $Sn_2(C_2H_5)_4$, or $Sn(C_2H_5)_2$, is a thick, oily liquid that decomposes into $Sn(C_2H_5)_4$ and tin when heated. It combines with oxygen and the halogens. *Tin-diethyl chloride* $Sn(C_2H_5)_2Cl_2$ melts at 85° and boils at 245°. *Tin-diethyl iodide* $Sn(C_2H_5)_2I_2$ fuses at 44.5° and boils at 245°. Ammonium hydroxide and the alkalies precipitate, from aqueous solutions of both the halogen compounds, *tin-diethyl oxide* $Sn(C_2H_5)_2O$ as a white insoluble powder. It is soluble in an excess of the alkalies, and forms crystalline salts with the acids, as, for instance, with nitric acid, $Sn(C_2H_5)_2{<}\begin{matrix}O{\cdot}NO_2\\O{\cdot}NO_2\end{matrix}$.

**73. Compounds of Aluminum.**—The alkyl derivatives of the metals of the aluminum group are produced by the action of the mercury alkyls on those metals. *Aluminum trimethyl* $Al(CH_3)_3$ boils at 130°. *Aluminum triethyl* $Al(C_2H_5)_3$ boils at 194°. Both compounds are colorless liquids that are spontaneously inflammable; they are violently decomposed by water into aluminum hydrate, methane, and ethane, respectively. Alkyl derivatives of gallium and indium have not been prepared. *Thallium-diethyl chloride*

$Tl(C_2H_5)_2Cl$ has been prepared by the action of zinc ethide on thallium chloride. If thallium-diethyl chloride is acted on by silver salts, thallium-diethyl salts are obtained, as, for instance, $Tl(C_2H_5)_2ONO_2$. By decomposing thallium-diethyl sulphate with barium hydrate, *thallium-diethyl hydroxide* $Tl(C_2H_5)_2OH$ is obtained. This salt has a strongly alkaline reaction, and is readily soluble in water, whence it crystallizes in shining needles.

## AMMONIA DERIVATIVES

**74.** The ammonia derivatives are usually subdivided into (1) amines, or ammonia bases; (2) amides; (3) amido acids.

*Amines* result from the substitution of alcohol radicals for hydrogen in ammonia; for example, $NH_2 \cdot CH_3$, $NH(CH_3)_2$, $N(CH_3)_3$, etc. This class of compounds also includes the ammonium bases originated by the substitution of alcohol radicals for hydrogen in ammonium hydrate $NH_4OH$. All these compounds are naturally basic.

*Amides* in general correspond with the amines, but the hydrogen of the ammonia in the former compounds is replaced by acid radicals; $NH_2(CH_3CO)$, $NH(CH_3CO)_2$, etc. are examples of this class. Some chemists, however, consider amides as derivatives of organic acids, in which one or more $OH$ groups of the acid group $COOH$ have been replaced by $(NH_2)'$, $(NH)''$, or $N'''$, respectively. Amides are, as a rule, only slightly basic compounds, the acid radical having more or less neutralized the strongly basic character of ammonia.

*Amido acids* are derived from organic acids by the substitution of the group $(NH_2)'$ for an atom of hydrogen in the hydrocarbon radical of the acid; the compound $CH_2(NH_2) \cdot COOH$, for instance, is derived from acetic acid $CH_3COOH$. They are both basic and acid in character.

A compound containing the group $NH_2$ is known as an *amide* compound; one containing the group $NH$, as an *imide* compound; and one that contains an atom of $N'''$, attached to a carbon atom only, as a *nitrile* compound.

## AMINES OR AMMONIA BASES AND AMMONIUM BASES

**75. Nature of Amines.**—Amines are known as primary, secondary, tertiary, or quaternary amines, corresponding with the number of hydrogen atoms that have been replaced; it is self-evident that a quaternary amine can be derived only by the replacement of the 4 hydrogen atoms in $NH_4 \cdot OH$. The different amines may be graphically represented as follows, $R$ being the alcohol radical:

| $NH_2R'$ | $NHR_2'$ or $NHR''$ | $NR'''$ or $NR_3'$ | $NR_4'OH$ |
|---|---|---|---|
| primary or amido bases | secondary or imido bases | tertiary or nitrile bases | quaternary bases |

Amines are further distinguished as *monamines*, *diamines*, and *triamines*, according to the number of nitrogen atoms they contain; thus, $NH_2R$ is a primary monamine, $N_2H_4R''$ is a primary diamine, and $N_3H_6R'''$ is a primary triamine; $NHR_2'$ or $NHR''$ is a secondary monamine, $N_2H_2R_2''$ or $N_2H_2R''R_2'$ is a secondary diamine, $N_3H_3R_2'''$, $N_3H_3R'''R_3'$, and $N_3H_3R'R''R'''$ are secondary triamines; $NR_3'$ and $NR'''$ are tertiary monamines, $N_2R_3''$ or $N_2R''R_4'$ is a tertiary diamine, and $N_3R_3'''$ and $N_3R'''R_6'$ are tertiary triamines.

The most general method of the production of primary amines consists in reducing the corresponding nitro compound with nascent hydrogen, and, as nitro compounds are much more readily obtained from closed-chain than from open-chain hydrocarbons, this method finds most frequent application in the preparation of the aromatic primary compounds; the following equation may serve as a typical example:

$$C_6H_5NO_2 + 3H_2 = C_6H_5NH_2 + 2H_2O$$

The fatty amines may be prepared by heating the alkyl halides with ammonia in alcohol. The cyanides of hydrocarbon radicals are convertible into primary amines by treatment with nascent hydrogen:

$$C_2H_5 \cdot CN + 2H_2 = C_2H_5 \cdot CH_2 \cdot NH_2$$

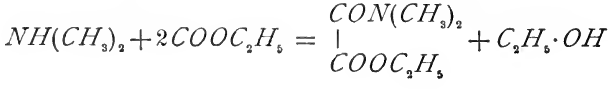
The amines, as a whole, strongly resemble ammonia. The lower members of this group of compounds are gases that are easily soluble in water and possess a strong ammoniacal odor, but are distinguished from ammonia by their ready combustibility. The higher members are more or less oily liquids. Amines expel ammonia from ammonium salts when heated with them, and, in a like manner, the monamines are expelled by diamines, and these in turn by the triamines, from which fact it might be inferred that the basic power of amines increases with the number of alcohol radicals they contain; in this, however, as in many similar cases, the expulsion of one base or acid by another is a question of relative volatility as well as of strength of combination.

**76. General Preparation of Amines.**—*Methyl amine* $NH_2CH_3$, *dimethyl amine* $NH(CH_3)_2$, and *trimethyl amine* $N(CH_3)_3$, in the form of their hydriodides, and *tetramethyl-ammonium iodide* $N(CH_3)_4I$ are all obtained when a strong solution of ammonia in alcohol is heated with methyl iodide for some hours in a closed tube at 100°. The reactions that occur may be represented by the subjoined equations:

$$\begin{aligned} NH_3 + CH_3I &= NH_2CH_3 \cdot HI \\ 2NH_3 + 2CH_3I &= NH(CH_3)_2 \cdot HI + NH_4I \\ 3NH_3 + 3CH_3I &= N(CH_3)_3 \cdot HI + 2NH_4I \\ 4NH_3 + 4CH_3I &= N(CH_3)_4I + 3NH_4I \end{aligned}$$

The hydriodides of the first three amines crystallize on cooling, leaving the tetramethyl-ammonium iodide in solution. The hydriodides are distilled with $KOH$ into a receiver cooled in ice, when a mixture of $N(CH_3)_3$, $NH(CH_3)_2$, and a little $NH_2CH_3$ is condensed, much of the last escaping as a gas with the $NH_3$ from the $NH_4I$. The mixed amines are then digested with ethyl oxalate, when the trimethyl amine is not affected, and can thus be readily distilled off. The methyl amine is converted into methyl oxamide, and the dimethyl amine into ethyl dimethyl oxamate, as is seen from the following equations:

$$2NH_2CH_3 + 2COOC_2H_5 = 2CONHCH_3 + 2C_2H_5OH$$



$$NH(CH_3)_2 + 2COOC_2H_5 = \begin{array}{l} CON(CH_3)_2 \\ | \\ COOC_2H_5 \end{array} + C_2H_5 \cdot OH$$

Water at 0° dissolves the last-named compound, and leaves the methyl oxamide undissolved. On distillation with $KOH$, the methyl oxamide yields potassium oxalate and methyl amine, as is shown in the following equation:

$$2CONHCH_3 + 2KOH = K_2C_2O_4 + 2NH_2CH_3$$

and the ethyl-dimethyl oxamate yields potassium oxalate, dimethyl amine, and alcohol; thus:

$$\begin{gathered} C_2O_2[N(CH_3)_2]OC_2H_5 + 2KOH \\ = K_2C_2O_4 + NH(CH_3)_2 + C_2H_5 \cdot OH \end{gathered}$$

Any tetramethyl-ammonium iodide that may have remained with the crystalline iodides, not being decomposed by $KOH$, will be left behind in the retort after distillation.

**77. Methyl Amine.**—Methyl amine $NH_2CH_3$ occurs in bone oil, in the distillate from wood, and in the fruit of *Mercurialis perennis*, a plant belonging to the order of *Euphorbiaceæ*. It is a colorless gas, with an ammoniacal odor, that condenses to a light liquid at a temperature a few degrees below zero. Its combustibility in the air distinguishes it from ammonia. At 12°, one volume of water dissolves 1,150 volumes of the gas. The aqueous solution manifests all the properties of aqueous ammonia, but does not, however, dissolve the oxides of cobalt, nickel, and cadmium.

**78. Dimethyl Amine.**—Dimethyl amine $NH(CH_3)_2$ is a gas that occurs in wood spirit and in guano. It dissolves readily in water, and is condensed in the cold to a liquid that begins to boil at 7.2°.

**79. Trimethyl Amine.**—Trimethyl amine $N(CH_3)_3$ occurs in many plants, as in the flowers of hawthorn, pear, and wild cherry, in arnica, etc. It also occurs in the roe of herring, and is prepared from herring brine in large quantities. It is prepared on a large scale by distilling the vinasse obtained in the refining of beet sugar, which corresponds with the molasses from cane sugar, but is not fit for food. Trimethyl amine is a liquid that boils at 3.5°. The penetrating fish-like odor is characteristic of it. It is inflammable and mixes readily with water. Like ammonia, it forms salts by direct combination with acids.

**80. Tetramethyl-Ammonium Hydroxide.**—Tetramethyl-ammonium hydroxide $N(CH_3)_4OH$ is prepared by decomposing the iodide with $Ag_2O + H_2O$, as is seen from the following equation:

$$2N(CH_3)_4I + Ag_2O + H_2O = 2N(CH_3)_4OH + 2AgI$$

It consists of deliquescent needles, with a strong alkaline reaction. It forms a number of salts, many of which are poisonous.

**81. Ethyl Amines.**—These compounds may be prepared by the action of ammonia on ethyl iodide, and are separated from one another in a similar way to that described in Art. **76.** *Ethyl amine* $NH_2 \cdot C_2H_5$ is a light, mobile, colorless liquid that is inflammable and boils at 18.7°. Its specific gravity is .696; it has a very strong odor resembling that of ammonia. It mixes with water, alcohol, and ether. Its aqueous solution is caustic and precipitates most of the metallic salts in the same way as a solution of ammonia, and, like the latter, redissolves cupric hydrate, forming a blue liquid. *Dichlorethyl amine* $NCl_2 \cdot C_2H_5$ is obtained by the action of chlorine on an aqueous solution of ethyl amine. It is a golden-yellow liquid of a very pungent odor, resembling that of chlorpicrin. Its specific gravity is 1.24, and it boils at 88°. It is insoluble in water, and is converted by zinc ethyl into triethyl amine; thus:

$$NCl_2C_2H_5 + Zn(C_2H_5)_2 = N(C_2H_5)_3 + ZnCl_2$$

The corresponding iodide is a dark-blue liquid that is easily decomposed by heat. *Diethyl amine* $NH(C_2H_5)_2$ is an ammoniacal liquid, boiling at 56° and readily soluble in water. When *diethyl-amine hydrochloride* $NH(C_2H_5)_2HCl$ is distilled with potassium nitrite and a little water, *ethyl nitroso-amine* is obtained; this compound contains the group $\cdot NO$ in place of the hydrogen atom attached to the nitrogen, its composition being $(C_2H_5)_2N\cdot NO$. It is a yellow, aromatic liquid, insoluble in water, of specific gravity .95, and boils at 177°. This compound is readily reconverted into diethyl amine by nascent hydrogen; thus:

$$2(C_2H_5)_2N\cdot NO + 4H = 2NH(C_2H_5)_2 + H_2O + N_2O$$

When it is dissolved in hydrochloric acid, and hydrochloric-acid gas is passed into the solution, it yields nitrosyl chloride and diethyl-amine hydrochloride:

$$(C_2H_5)_2N\cdot NO + 2HCl = N(C_2H_5)_2H_2Cl + NOCl$$

*Triethyl amine* $N(C_2H_5)_3$ may be prepared by heating a mixture of diethyl amine and ethyl amine with ethyl bromide in a sealed glass tube, when a beautiful fibrous mass of triethyl-ammonium bromide is formed, from which the triethyl amine may be obtained by distillation with potash. Triethyl amine is a colorless, pleasant-smelling liquid. It boils at 89°, and is only very sparingly soluble in water. It possesses a strongly alkaline reaction, and resembles ammonia in many of its reactions with the salts; it is, however, distinguished from this compound by the fact that it dissolves alumina, and that it does not dissolve silver oxide, which is, as we know, quite readily soluble in ammonia.

**82. Tetrethyl-Ammonium Compounds.**—When triethyl amine and ethyl iodide are brought together, a violent reaction, that raises the mixture to a boiling heat, takes place, with the formation of *tetrethyl-ammonium iodide* $N(C_2H_5)_4I$, which is obtained as a white crystalline mass. Tetrethyl-ammonium iodide is soluble in hot water, from which it crystallizes, on cooling, in beautiful large crystals. Its iodine may be removed by treating a solution of it with silver salts. If, for instance, silver sulphate or nitrate is employed, the sulphate or nitrate of tetrethyl ammonium, together with silver iodide, is produced, and, when freshly prepared silver oxide is used, *tetrethyl-ammonium hydroxide* $N(C_2H_5)_4OH$ is formed, which, on filtering off the silver precipitate, is obtained as a clear, colorless liquid. It has a strongly alkaline reaction and an intensely bitter taste. In its chemical behavior, tetrethyl-ammonium hydroxide is very similar to potassium hydroxide; like this compound, it destroys the skin and saponifies fatty substances, with the formation of true soaps, but it produces, in chromic salts, a precipitate of chromic hydroxide that does not dissolve in an excess of the reagent, while the precipitate formed by $KOH$ is soluble in an excess of the reagent. On evaporating a solution of tetrethyl-ammonium hydroxide in a vacuum, long, slender, needle-shaped crystals are deposited that consist of the hydroxide with a certain amount of water of crystallization. After some time, the crystals disappear, and a semisolid mass of the anhydrous salt is left. An aqueous concentrated solution of this anhydrous compound can be boiled without decomposition, but if the dry substance is heated, it decomposes readily into triethyl amine, water, and ethene; thus:

$$N(C_2H_5)_4OH = H_2O + N(C_2H_5)_3 + C_2H_4$$

The other salts of tetrethyl ammonium are obtained by treating the hydroxide with acids; several of them form well developed and beautiful crystals. The platino-chloride $[N(C_2H_5)_4Cl]_2PtCl_4$ crystallizes in orange-yellow octahedrons, that are slightly soluble in water, but nearly insoluble in alcohol, as well as in ether.

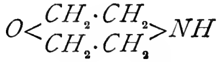
**83.** Other alcohol radicals, such as propyl, butyl, amyl, etc., likewise produce amines and ammonia bases. It is not necessary that all the atoms in $NH_3$ are replaced by the same alcohol radical; in fact, we distinguish between *simple amines*, that is, those containing similar alcohol radicals, and *mixed amines*, containing different alcohols, just as we distinguish between simple and mixed ethers; methyl-ethyl amine $NH(CH_3)(C_2H_5)$ and methyl-ethyl-amyl amine $N(CH_2)(C_2H_5)(C_5H_{11})$ are examples of mixed amines.

There are various methods of ascertaining whether an amine is primary, secondary, or tertiary. The simplest way to distinguish a primary amine from a secondary, and a secondary from a tertiary amine, consists in treating the amine in question alternately with methyl iodide and caustic potash, until all the hydrogen atoms in the ammonia present are replaced by methyl groups. Whether the latter have entered, and what their number may be, is most conveniently determined by the analysis of the platinum double chloride of the base previous to, and after, the action of the methyl iodide. If two methyl groups have entered the compound, it is obvious that the amine was primary; if one methyl group has entered, then the base was secondary; and should the base be found to have remained unchanged, then it must be assumed that it is tertiary in its character.

**84. Diamines.**—The divalent like the monovalent alkyls can replace two hydrogen atoms in two ammonia molecules and produce primary, secondary, and tertiary *diamines*, as we have seen in Art. **75.** The open-chain diamines most commonly met with are those derived from ethylene, and if we assume that ethylene diamine $C_2H_4(NH_2)_2$ is derived from glycol $C_2H_4(OH)_2$, in which the two hydroxyl groups have been replaced by the two amidogen groups $(NH_2)_2$, it will be seen that *alcohol amines*, such as $C_2H_4(NH_2)(OH)$, can also exist. Such alcohol amines are primary amines, and are generally termed *hydramines*. The hydramine $C_2H_4(NH_2)OH$ is also known as *hydroxyethyl amine*. This compound is formed by the action of ammonia on ethylene chlorhydrate.

$$C_2H_4(OH)Cl + 2NH_3 = C_2H_4(NH_2)(OH) + NH_4Cl$$

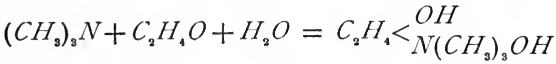
The secondary monamine, *dihydroxyethyl amine* $(C_2H_4OH)_2NH$, is formed at the same time, and when this compound is dehydrated, a compound is formed that, owing to its close relationship to morphine, is known as *morpholine*, and has the formula



$$(C_2H_4)_2O\cdot NH, \text{ or } O<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>NH$$

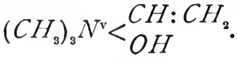
$$\textit{Choline}\ N(C_2H_4OH)(CH_3)_3\cdot OH, \text{ or } C_2H_4<\begin{matrix}OH\\ N(CH_3)_3OH,\end{matrix}$$

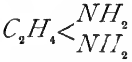
also known as *hydroxyethyl-trimethyl-ammonium hydroxide*, or *bilineurine*, or *sincaline*, is widely distributed in the animal organism, especially in the brain and in the yolk of eggs, in which it is present as *lecithin*, a compound of choline with glycero-phosphoric acid and fatty acids. It is present in hops, hence it occurs in beer. It is obtained, too, from sinapin (the alkaloid of *Sinapis alba*), when it is boiled with alkalies (hence the name *sincaline*). It was prepared synthetically by Würtz by heating ethene oxide or ethene chlorhydrin with trimethyl amine in aqueous solution:



$$(CH_3)_3N + C_2H_4O + H_2O = C_2H_4<{}^{OH}_{N(CH_3)_3OH}$$

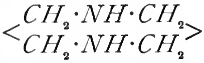
Choline deliquesces in the air. It is strongly alkaline, crystallizes with difficulty, and absorbs $CO_2$. It is not poisonous by itself, but when oxidized with nitric acid, it yields *muscarine*, or *hydroxy-choline* $NC_2H_3(OH)_2(CH_3)_3$, which constitutes the poisonous matter in the fungus *Agaricus muscarius* (commonly known as "toadstool").

When treated with hydriodic acid, choline yields the iodine derivatives $N(C_2H_4I)(CH_3)_3I$, which, with $Ag_2O + H_2O$, yields *neurine*, or *trimethyl-vinyl-ammonium hydroxide* $C_5H_{13}NO$, or  $(CH_3)_3N^v<{}^{CH:CH_2}_{OH}$. It resembles choline, but has not been crystallized. It is very poisonous. It occurs with the ptomaines—alkaloids of decay, partly poisonous and partly non-toxic.

*Ethylene diamine*  $C_2H_4<{}^{NH_2}_{NH_2}$ is formed by the action of ethylene bromide on an alcoholic solution of ammonia at 100°.

It may also be prepared by the action of tin and hydrochloric acid on dicyanogen:

$$C_2N_2 + 4H_2 = C_2H_8N_2$$

Ethylene diamine is a solid that melts at 8.5°, becoming a colorless liquid that boils at 116.5°. It has a strong alkaline reaction and an ammoniacal odor. Nitrous acid converts it into ethylene oxide. *Diethylene diamine*  $<{}^{CH_2 \cdot NH \cdot CH_2}_{CH_2 \cdot NH \cdot CH_2}>$ boils at 146°. *Triethylene diamine* $N_2(C_2H_4)_3$ boils at 210°.

# ORGANIC CHEMISTRY

(PART 6)

## DERIVATIVES OF HYDROCARBONS

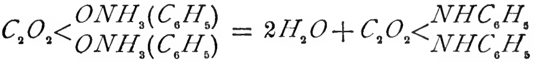
### AMIDO DERIVATIVES OF THE BENZENE HYDROCARBONS

**85.** The ammonia bases derived from aromatic hydrocarbons must be divided into two distinct classes of compounds; one in which the amido, imido, or nitrile group enters the side chain of the hydrocarbon, and the other in which the group is attached to the closed-chain nucleus. The bases of the first class behave in every respect like the fatty amines, but those of the second class show slight differences, due to the fact that a closed-chain nucleus is always somewhat more acidic than an open-chain nucleus. For the same reason, the nuclear aromatic amines show some relationship to the amides and amido acids. Hence, some chemists term the aromatic amines "amido compounds."

**86. Phenyl Amine, or Aniline.**—The simplest ammonia base of the aromatic alcohols that has obtained great commercial importance is *phenyl amine* $C_6H_5 \cdot NH_2$, also known as *amido-benzene* and *aniline*. This important compound was discovered in 1826 by Unverdorben, who obtained it by the dry distillation of indigo, and gave it the name of "crystallina"; in 1836 Runge found it in coal tar and named it "cyanol." In 1841 Fritzsche prepared it by distilling indigo with potash, and gave it the name of "aniline," while in 1842, Zinin obtained it by the reduction of nitrobenzene, and called it "benzidam." It was, at last, accurately investigated by A. W. Hofmann in 1843. It occurs in coal tar and also in bone oil. Since 1864, aniline has been prepared on a large scale by reducing nitrobenzene $C_6H_5NO_2$ with metallic iron in conjunction with hydrochloric or acetic acid. To prepare aniline in this way, 1 part of nitrobenzene is heated with $1\frac{1}{2}$ parts of iron filings and 1 part of glacial acetic acid; the solid product of the reaction is mixed with lime and distilled with superheated steam. On a small scale, as for experimental purposes, more satisfactory results are obtained by using tin and hydrochloric acid as reducing agents. The product obtained by either process may be purified by converting it into oxalate by saturating it with oxalic acid, crystallizing this salt several times from alcohol, and decomposing it with potash.

Aniline is a colorless, mobile, and highly refractive liquid that quickly changes its color on exposure to air, becoming first yellow, and then brown, and is finally converted, by the air, into a sticky resinous mass. It possesses a weak, but characteristic, and peculiar odor. It has a specific gravity of 1.03, and may be solidified by cold and then fused at $-8°$; it boils at 184°. It is poisonous, and burns with a smoky flame. It appears almost insoluble in water, but the water takes up about $\frac{1}{30}$ of its weight of aniline, and aniline takes up about $\frac{1}{20}$ of its weight of water; it mixes freely with alcohol and ether, and is otherwise a good solvent for many difficultly soluble substances, as, for instance, indigo and sulphur. It does not restore the blue color to reddened litmus paper, but possesses, nevertheless, the character of a base, for it forms well defined salts with the acids. If a nitrate and sulphuric acid are added to aniline, a red color is produced. If a few drops of aniline are poured into sulphuric acid and a little potassium dichromate is added to it, a beautiful blue color is obtained that changes to violet on the addition of water. A solution of chloride of lime added to aniline brings forth a brilliant violet tint. When a solution of an aniline salt is heated with cupric chlorate, an intense black color is developed. All these reactions, and many others, are applied in the arts in the preparation of coloring matter of great brilliancy. Among the most important of these are rosaniline, and pararosaniline, which will be treated further on.

**87. Salts of Aniline.**—The salts of this compound are prepared by saturating it with the acids. *Aniline hydrochloride* $C_6H_5 \cdot NH_2HCl$, which is commercially known as *aniline salts*, forms colorless needles that are quite freely soluble in water and alcohol. They fuse and can be distilled without decomposition. Platinic chloride precipitates from a solution of aniline hydrochloride fine yellow needles of chloroplatinate. *Aniline oxalate* $(C_6H_5NH_2)_2C_2H_2O_4$ crystallizes from water in large, hard, and well developed prisms. When exposed to heat, it loses the elements of water, and is converted into oxanilide:



$$C_2O_2 < \begin{matrix} ONH_3(C_6H_5) \\ ONH_3(C_6H_5) \end{matrix} = 2H_2O + C_2O_2 < \begin{matrix} NHC_6H_5 \\ NHC_6H_5 \end{matrix}$$

aniline oxalate oxanilide

**88. Aniline Substitution-Products.** — Aniline substitution-products are obtained by the reduction of the corresponding nitro compounds; thus 1 : 2 chloronitrobenzene $C_6H_4Cl \cdot NO_2$ yields 1 : 2 chloraniline $C_6H_4ClNH_2$. By the action of chlorine or bromine water on aniline, the trichloranilines and tribromanilines are derived; the latter form the white precipitate that bromine water gives with aniline.

*Nitranilines* or *nitrophenyl amines* $C_6H_4 \cdot NO_2 \cdot NH_2$ are obtained by the partial reduction of the corresponding dinitrobenzene by means of ammonium sulphide. The three nitranilines crystallize in yellow needles or prisms. They are only slightly soluble in water, but dissolve readily in alcohol. The presence of the acidic nitro group greatly interferes with the basic character of the aniline; dinitraniline, for instance, is neutral, while trinitraniline exhibits acid properties.

*Aniline-sulphonic acid* $C_6H_4(NH_2)SO_3H$, or 1 : 2 *amidobenzene-sulphonic acid*, or *sulphanilic acid*, is obtained by heating either aniline sulphate to about 200° or aniline together with fuming sulphuric acid. It crystallizes in rhombic plates that are only difficultly soluble in water and crumble to pieces under the influence of the atmosphere. Aniline-sulphonic acid is the parent substance of various dyes.

**89. Alkyl Derivatives of Aniline.**—By substituting alcohol radicals for either one or both hydrogen atoms of the amidogen group, secondary and tertiary amines may be obtained. Among the great variety of amines that may thus be obtained, only methyl aniline and dimethyl aniline will be considered here. They are produced together in the arts by heating, to 229°, methyl alcohol with aniline hydrochloride in a closed vessel. The product contains the hydrochlorides of the methyl anilines.

*Methyl aniline* $C_6H_5\cdot NH(CH_3)$ is a colorless liquid that becomes brown on exposure to air; it is lighter than water, having a specific gravity of .976, and has an odor like aniline, which is, however, stronger and more aromatic. By the action of nitrous acid on methyl aniline, or better, by the addition of methyl-aniline hydrochloride to a solution of potassium nitrite, a thick oily compound—*nitrosomethyl aniline*—is obtained; thus:

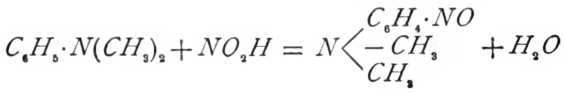
$$C_6H_5\cdot NH(CH_3) + NO_2H = \underset{\text{nitrosomethyl aniline}}{C_6H_5N\cdot(NO)(CH_3)} + H_2O$$

It may be regarded as methyl aniline in which the hydrogen atom of the $NH$ group has been replaced by the nitrosyl group $(NO)'$. All the aromatic amines undergo similar reactions.

*Dimethyl aniline* $C_6H_5\cdot N(CH_3)_2$ is prepared on a manufacturing scale by the action of methyl chloride on a heated mixture of aniline and caustic soda, as is seen from the following equation:

$$\begin{aligned} &2CH_3Cl + C_6H_5NH_2 + 2NaOH \\ &= C_6H_5N(CH_3)_2 + 2NaCl + 2H_2O \end{aligned}$$

It is an oily liquid that boils at 192° and solidifies in the cold. It is, like methyl aniline, lighter than water, its specific gravity being .945. When it is exposed to the action of nitrous acid, *nitrosodimethyl aniline* $C_6H_4N(NO)(CH_3)_2$ is obtained, as is seen from the following equation:



$$C_6H_5\cdot N(CH_3)_2 + NO_2H = N\left\langle\begin{matrix} C_6H_4\cdot NO \\ -CH_3 \\ CH_3 \end{matrix}\right. + H_2O$$

A number of important dyes and coloring matters, as, for instance, *malachite green*, are prepared from dimethyl aniline. Many other alcoholic derivatives of aniline have been prepared. *Diphenyl amine* $NH(C_6H_5)_2$, also known as *phenyl aniline*, is a secondary monamine that may be considered as derived from ammonia by the substitution of two phenyl groups for two atoms of hydrogen. It is prepared by heating aniline hydrochloride with aniline to 250° in a closed vessel from which the $NH_3$ is allowed to escape from time to time.

$$C_6H_5 \cdot NH_2 \cdot HCl + C_6H_5 \cdot NH_2 = NH(C_6H_5)_2 + NH_3HCl$$

The excess of aniline employed decomposes the ammonium chloride, so that a mixture of aniline hydrochloride and diphenyl amine is left; on adding water, the diphenyl amine is left undissolved and is obtained by filtration. Diphenyl amine forms crystals that fuse at 54° and boil at 310°. It does not dissolve in water, as has been already mentioned, but it is freely soluble in alcohol, ether, benzene, and petroleum. It has an agreeable odor. It is a weak base, its salt being readily decomposed by water. When heated with a mixture of sulphuric and oxalic acids, it yields a beautiful blue color that is known as *diphenyl-amine blue*. When diphenyl amine is acted on by nitric acid, three atoms of hydrogen in the phenyl group are replaced by $NO_2$, producing *hexanitro-diphenyl amine* $NH[C_6H_2(NO_2)_3]_2$, in which the remaining ammonia hydrogen may be replaced by $NH_4$, yielding a compound that has the composition $N(NH_4)[C_6H_2(NO_2)_3]_2$, and is known commercially as *aurantia*. It is a beautiful orange-colored dye. When a trace of nitric acid is added to a solution of diphenyl amine in strong sulphuric acid, an intense blue color is developed. This is used as a very delicate test for nitric acid.

**90. Acid Derivatives of Aniline.**—These compounds, known as *anilides*, may be considered as amides in which the hydrogen atoms are either partly or entirely replaced by phenyl. They may be formed:

1. By the action of acid chlorides on aniline, as is seen from the following equation:

$$\underset{\text{aniline}}{C_6H_5NH_2} + \underset{\text{acetic chloride}}{C_2H_3OCl} = \underset{\text{acetanilide}}{C_6H_5NHC_2H_3O} + HCl$$

2. By heating aniline salts with organic acids; thus:

$$C_6H_5NH_2 + C_2H_3O \cdot OH = C_6H_5NH \cdot C_2H_3O + H_2O$$

*Formanilide* $C_6H_5HN(CHO)$ is prepared by heating aniline and formic acid. It crystallizes in prisms that melt at 46°, and is easily soluble in water as well as in ether and alcohol. *Acetanilide* $C_6H_5HNC_2H_3O$ is prepared either by boiling aniline with glacial acetic acid for several days, or by the action of acetic anhydride on aniline in the presence of a caustic-soda solution. It crystallizes in white, shining prisms that melt at about 112° and volatilize at 295°, without undergoing decomposition. It is sparingly soluble in cold water, but readily dissolves in hot water, alcohol, and ether. This and *methyl-acetanilide* $C_6H_5(CH_3)NC_2H_3O$, which melts at 103°, are used as a remedy against headache, and the latter is known pharmaceutically as *exalgin.*

**91. Amido Toluenes.**—The three *toluidines* $C_6H_4CH_3 \cdot NH_2$ result from the reduction of the three corresponding nitro toluenes. They are metameric with methyl aniline. They are also present in coal tar. *Orthotoluidine* is a colorless liquid; its specific gravity is 1.003, it boils at 199°, and changes to pink when exposed to the air. It is colored violet by a solution of chloride of lime, and blue by sulphuric and nitrous acids and ferric chloride. *Metatoluidine* is a colorless liquid, has a specific gravity of .998, and boils at 202°. *Paratoluidine* is a solid, heavier than water. It crystallizes from its dilute alcoholic solution in large plates; it fuses at 45°, and boils at 198°. It is almost insoluble in water, but freely soluble in alcohol and in ether. It is not colored by chloride of lime. Toluidine exists nearly always in commercial aniline. It is important and necessary for the preparation of certain aniline colors.

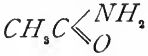
**92. Amido Benzenes.**—*Benzyl amine* $C_6H_5 \cdot CH_2NH_2$, which is metameric with toluidine, is obtained, together with *dibenzyl amine* $(C_6H_5CH_2)_2NH$ and *tribenzyl amine* $(C_6H_5CH_2)_3N$, when benzyl chloride is heated with alcoholic ammonia:

$$C_6H_5 \cdot CH_2Cl + NH_3 = C_6H_5CH_2NH_2, HCl$$

By distilling the hydrochloride thus obtained with potash, benzyl amine is obtained as a colorless, limpid liquid that boils at 185° and is miscible with water, alcohol, and ether. Tribenzyl amine crystallizes in beautiful, colorless needles or plates that fuse at 91°. It does not dissolve in water, is slightly soluble in cold alcohol, and very readily soluble in hot alcohol and ether. *Xylidine* $C_6H_3(CH_3)_2NH_2$ occurs in six modifications, all of which are known. Amido-orthoxylene $C_6H_3(CH_3 : CH_3 : NH_2)$, or 1 : 2 : 4 amido-xylene, is a solid, melting at 49°, while the other five varieties are liquids, with a boiling point that lies between 212° and 226°. *Naphthyl amine* $C_{10}H_7 \cdot NH_2$ is obtained by reducing nitronaphthalene $C_{10}H_7(NO_2)$. The naphthyl amine thus obtained is $\alpha$-naphthyl amine; it crystallizes in fine, colorless needles, fusing at 50°, and boiling at 300°. It has an extremely disagreeable fetid odor. It dissolves sparingly in water, but readily in alcohol; though its reaction is not alkaline, it neutralizes the acids, with which it forms well defined and crystallizable salts that give, with ferric chloride, a blue precipitate, changing to purple oxynaphthyl amine $C_{10}H_9NO$. $\beta$-naphthyl amine crystallizes in pearly needles, is fusible at 112°, and boils at 294°. It gives no color with ferric chloride.

**93. Diamido Benzenes.**—*Diamido benzenes* $C_6H_4(NH_2)_2$, also known as *phenylene diamines* $N_2H_4(C_6H_4)$, are di-substituted benzenes; they exist in three modifications, and are prepared by reducing the three modifications of dinitrobenzene. They are di-acid bases forming well defined salts. Metaphenylene diamine is the most easily prepared. It crystallizes in tables, melts at 63°, and boils at 287°. Nitrous acid converts it into Bismarck brown, the presence of the slightest trace of this acid being shown by the yellow coloration it gives with the diamine. Paraphenylene diamine crystallizes in plates. *Toluylene diamine* $C_6H_3(CH_3)(NH_2)_2$ (1 : 2 : 4) is, as metadiamine, easily obtained by the reduction of dinitrotoluene $C_6H_3(CH_3)(NO_2)_2$. It is used in the preparation of certain red dyestuffs. The *xylene diamines* $C_6H_2(CH_3)_2(NH_2)_2$ are homologous with the above. The *diamido naphthalenes* $C_{10}H_6(NH_2)_2$, also known as *naphthylene diamines*, corresponding with phenylene diamine, are obtained by the reduction of dinitronaphthalenes.

### AMIDES

**94.** These compounds may be considered as composed on the model of ammonia by the substitution of an acid radical for hydrogen. Acetamide  $CH_3C\left\langle\begin{matrix}NH_2\\O\end{matrix}\right.$ consists of the acetyl radical $CH_3CO$, which has replaced one of the hydrogen atoms of ammonia $NH_3$. These compounds may be either primary, secondary, or tertiary, according to the number of hydrogen atoms that have been replaced. For example:

| | | |
|---|---|---|
| $NH_2 \cdot C_2H_3O$ | $NH \cdot (C_2H_3O)_2$ | $N(C_2H_3O)_3$ |
| primary acetamide | secondary acetamide | tertiary acetamide |

Of these compounds, the primary amides are the most important; they are solid crystalline compounds, sparingly soluble or insoluble in water, but soluble in alcohol and ether. They can be distilled without decomposition. They differ from the amines by being easily saponifiable, by breaking up into their components, i. e., acid and ammonia, when strongly heated with water or boiled with the alkalies. Further, amides may be either monamides, or diamides, or triamides, according to the number of ammonia molecules that take part in their formation. Amides may be prepared from ammonia, in a similar manner to the amines, by the action of the chloride of an acid radical, as seen from the following equation:

$$CH_3CO\cdot Cl + 2NH_3 = CH_3CO\cdot NH_2 + NH_3HCl$$

or by the action of an ethereal salt, when the hydrogen is exchanged for the acid radical:

$$CH_3CO\cdot OC_2H_5 + NH_3 = CH_3CO\cdot NH_2 + C_2H_5OH$$

Another method of preparing amides consists in dehydrating, by heat or otherwise, the ammonia salts of the acids, whereupon the hydrogen of the ammonia and the $OH$ group of the acid will form water, leaving the group $NH_2$ combined to the acid radical. The following equation may serve as a characteristic example:

$$\underset{\substack{\text{ammonium}\\\text{acetate}}}{CH_3CO_2NH_4} = \underset{\text{acetamide}}{CH_3CO\cdot NH_2} + H_2O$$

Nitrous acid converts the primary amides into the corresponding acid:

$$CH_3CO\cdot NH_2 + HNO_2 = CH_3COOH + N_2 + H_2O$$

Dehydrating agents convert the primary amides into nitriles (cyanides) of hydrocarbon radicals:

$$CH_3CO\cdot NH_2 = CH_3\cdot C\vdots N + H_2O$$

**95. Formamide.**—Formamide $HCO\cdot NH_2$, the amide of formic acid, is obtained by the dry distillation of ammonium formate, or by heating ethyl formate and ammonia to 100° in a sealed tube. It is a liquid that is readily soluble in water and alcohol; it boils with partial decomposition at 193°, and breaks up into $CO$ and $NH_3$ when quickly heated to about 200°. It yields hydrocyanic acid when heated with $P_2O_5$:

$$3HCO\cdot NH_2 + P_2O_5 = 3HCN + 2H_3PO_4$$

*Methyl formamide* $HCO\cdot NHCH_3$ is prepared by distilling methyl amine formate. *Ethyl formamide* $HCO\cdot NHC_2H_5$ is obtained by the action of ethyl amine on ethyl formate.

*Ethylene diformamide* $(HCO)_2N_2H_2(C_2H_4)$ is obtained by heating ethyl diamine and chloral:

$$N_2H_4(C_2H_4) + 2CCl_3CHO = (HCO)_2N_2H_2(C_2H_4) + 2CHCl_3$$

It is a liquid that, when heated with acids or alkalies, is decomposed into ethylene diamine and formic acid.

**96. Acetamide.**—Acetamide $C_2H_3O \cdot NH_2$, the amide of acetic acid, may be prepared by distilling a mixture of dry sodium acetate and sal ammoniac. It crystallizes in long needles, fuses at 82° and boils at 222°. It dissolves readily in water and alcohol, but sparingly in ether. When heated with acids or alkalies, it is decomposed into acetic acid and ammonia. It has a disagreeable odor. Solution of acetamide dissolves silver oxide and precipitates *silver acetamide* $C_2H_3O \cdot NHAg$. When boiled with mercuric oxide, it yields, on cooling, crystals of *mercuric acetamide* $(C_2H_3O \cdot NH)_2Hg$. *Chloracetamides* can be prepared from the three chloracetic acids, as acetamide may be prepared from acetic acid. They are as follows:

| | |
|---|---|
| Monochloracetamide | $CH_2ClCO \cdot NH_2$ |
| Dichloracetamide | $CHCl_2CO \cdot NH_2$ |
| Trichloracetamide | $CCl_3CO \cdot NH_2$ |

They are crystalline solids; their fusing points lie between 96° and 136°, and their boiling points between 224° and 240°. *Diacetamide* $(CH_3CO)_2NH$ is a crystalline compound that fuses at 78° and boils at 223°. *Triacetamide* $(CH_3CO)_3N$ melts between 78° and 79°.

**97. Amides of Benzene, Etc.**—*Benzamide* $C_6H_5CO \cdot NH_2$ is prepared by the action of ammonia on benzoyl chloride:

$$C_6H_5CO \cdot Cl + 2NH_3 = NH_4Cl + C_6H_5CONH_2$$

It may also be obtained by the action of ammonia on ethyl benzoate

$$C_6H_5 \cdot CO \cdot OC_2H_5 + NH_3 = C_2H_5OH + C_6H_5 \cdot CO \cdot NH_2$$

It is a brilliant, colorless, crystalline body that fuses at 130°, and volatilizes, undecomposed, between 286° and 290°.

It is sparingly soluble in cold water, but dissolves freely in hot water, alcohol, and ether. Its reactions are, for the most part, similar to those of acetamide; it forms a crystalline compound with $HCl$. Its aqueous solution dissolves mercuric oxide, forming *benzene mercuramide* $C_6H_5CO \cdot NHg$.

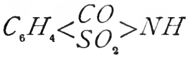
*Glycolamide* $CH_2(OH)CO \cdot NH_2$ is prepared by heating glycolide in ammonia:

$$(CH_2 \cdot CO)_2O_2 + 2NH_3 = 2CH_2(OH)CO \cdot NH_2$$

It crystallizes in needles that melt at 120°. It is soluble in water and possesses a sweet taste. Acids and alkalies convert it into ammonia and glycolic acid.

*Lactamide* $C_2H_4(OH)CONH_2$ is obtained in crystalline form when an alcoholic solution of lactide is treated with ammonia, and the liquid concentrated by evaporation. It melts at 74°, and is soluble in water and alcohol.

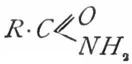
**98. Sulphonamides.**—Sulphonamides are the amides of sulphonic acid; for example, $C_6H_5 \cdot SO_2NH_2$ is *benzene sulphonamide*. One of the most important compounds of this class is 1 : 2 *benzoic sulphonamide* $C_6H_4(CO_2H) \cdot SO_2NH_2$, which is the parent substance of *saccharine*, the well known sugar substitute. Saccharine is 1 : 2 benzoic sulpho-imide



$$C_6H_4 < \begin{matrix} CO \\ SO_2 \end{matrix} > NH$$

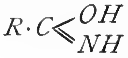
By treating toluene $C_6H_5(CH_3)$ with sulphuric acid, it yields ortho- and para-toluene sulphonic acids $C_6H_4(CH_3)SO_2OH$; these are oxidized to the corresponding benzoic sulphonic acids $C_6H_4(CO_2H) \cdot SO_2OH$, which, by treatment with $PCl_5$, become the dichloride $C_6H_4(COCl)SO_2Cl$. Ammonia converts the 1 : 4 derivative into $C_6H_4(CONH_2) \cdot SO_2NH_2$, which is insoluble in water, and the 1 : 2 derivative into $C_6H_4(CO_2NH_4) \cdot SO_2NH_2$, which is soluble; when an acid is added to a solution of the latter, saccharine is precipitated. Saccharine melts at 224°; it is only sparingly soluble in water, but readily in the alkalies, since the $H$ in the $NH$ group is replaceable by metals to form soluble salts. Saccharine is said to be 280 times sweeter than cane sugar.

**99. Constitution of Primary Amides.**—The constitution of the primary amides may be represented by two formulas:



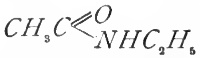
$$R\cdot C\Big<{}^{O}_{NH_2}$$

and



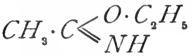
$$R\cdot C\Big<{}^{OH}_{NH}$$

and, although the two amides corresponding to both formulas apparently do not exist, many derivatives of amides are known to exist in both forms; for instance, *ethyl acetamide* has the constitution



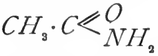
$$CH_3C\Big<{}^{O}_{NHC_2H_5}$$

and the compound known as *acetimido ether* has the constitution represented by the formula



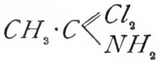
$$CH_3\cdot C\Big<{}^{O\cdot C_2H_5}_{NH}$$

The constitution of acetamide is generally represented as



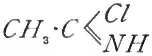
$$CH_3\cdot C\Big<{}^{O}_{NH_2}$$

but by acting on it with $PCl_5$, *acetamido chloride* is obtained, the constitution of which is



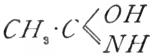
$$CH_3\cdot C\Big<{}^{Cl_2}_{NH_2}$$

This compound readily loses $HCl$, and is thus converted into acetimido chloride



$$CH_3\cdot C\Big<{}^{Cl}_{NH}$$

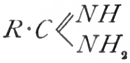
which certainly is a derivative of an amide, whose constitution corresponds with the formula



$$CH_3\cdot C\Big<{}^{OH}_{NH}$$

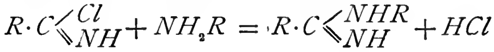
in which an atom of $Cl$ has replaced the group $OH$.

The compounds known as *amidines*



$$R\cdot C\Big<{}^{NH}_{NH_2}$$

may be regarded as derived from either formula, although the fact that they are obtained by treating imido chlorides with ammonia (or primary amines) seems to indicate that they are derived from the second formula:



$$R\cdot C{<}\begin{matrix}Cl\\NH\end{matrix}+NH_2R=R\cdot C{<}\begin{matrix}NHR\\NH\end{matrix}+HCl$$

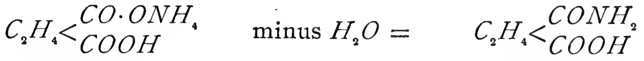
The *amidoximes*

$$R{<}\begin{matrix}NOH\\NH_2\end{matrix}$$

may be regarded as derived from the amidines; they are the products of the action of hydroxyl amines on the cyanides (nitriles); thus, hydrogen cyanide and hydroxyl amine yield isuret (methenyl amidoxime), isomeric with urea:

$$HCN+NH_2OH = HC(N\cdot OH)\cdot NH_2$$

**100. Amides and Amic Acids.**—There exist two distinct classes of amides originating from dibasic organic acids; namely, one that is formed by the substitution of $NH_2$ for the hydroxyl radical in both carboxyl groups, and bears the name *amides;* and the other in which only one hydroxyl group is removed by substitution, called *amic acids.* Oxalic acid $COOH\cdot COOH$, for example, yields $CONH_2\cdot CONH_2$, known as *oxamide*, and $COOH\cdot CONH_2$, known as oxamic acid. The amic acids may be regarded as being derived from the acid ammonium salts by the abstraction of a molecule of water; for example,



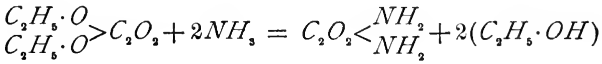
$$C_2H_4{<}\begin{matrix}CO\cdot ONH_4\\COOH\end{matrix}\quad \text{minus } H_2O = \quad C_2H_4{<}\begin{matrix}CONH_2\\COOH\end{matrix}$$

acid ammonium succinate succinamic acid

$$COONH_4\cdot COOH \quad \text{minus } H_2O = \quad CONH_2\cdot COOH$$

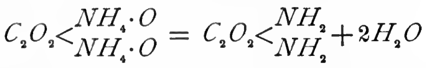
acid ammonium oxalate oxamic acid

**101. Oxamide.**—Oxamide $(CONH_2)_2$ is precipitated when ethyl oxalate is shaken with aqueous ammonia:



$$\begin{matrix}C_2H_5\cdot O\\C_2H_5\cdot O\end{matrix}{>}C_2O_2+2NH_3 = C_2O_2{<}\begin{matrix}NH_2\\NH_2\end{matrix}+2(C_2H_5\cdot OH)$$

It may also be formed by the dry distillation of ammonium oxalate:



$$C_2O_2{<}\begin{matrix}NH_4\cdot O\\NH_4\cdot O\end{matrix} = C_2O_2{<}\begin{matrix}NH_2\\NH_2\end{matrix}+2H_2O$$

It is a white crystalline powder, and is insoluble in cold water and alcohol, but somewhat soluble in boiling water, from which it is, however, redeposited on cooling. It may be crystallized in needles from a hot saturated solution of calcium chloride. Oxamide is partly sublimed when heated, the greater part, however, being decomposed. When heated to 200° with water, it is converted into ammonium oxalate. If its vapor is passed through a red-hot glass tube, the oxamide is completely decomposed into carbon monoxide, carbon dioxide, ammonia, hydrocyanic acid, and urea, as is seen from the following equation:

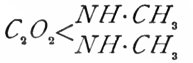
$$2(CONH_2)_2 = CO+CO_2+NH_3+CNH+CN_2H_4O$$

When boiled with dilute mineral acids, oxamide is decomposed into oxalic acid and an ammonia salt:

$$(CONH_2)_2+H_2SO_4+2H_2O = (COOH)_2+(NH_4)_2SO_4$$

Boiled with alkalies, it yields oxalates and ammonia.

The substituted oxamides containing alcohol radicals are produced by the action of the primary amines on ethyl oxalate; for example:



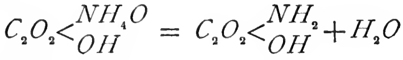
$$C_2O_2{<}\begin{matrix}NH\cdot CH_3\\NH\cdot CH_3\end{matrix}$$

dimethyl oxamide

$$C_2O_2{<}\begin{matrix}NHC_2H_5\\NHC_2H_5\end{matrix}$$

diethyl oxamide

*Oxamic acid* $C_2O_2{<}\begin{matrix}NH_2\\OH\end{matrix}$, or $CONH_2\cdot COOH$, is readily prepared by heating acid ammonium oxalate to between 220° and 238°:



$$C_2O_2{<}\begin{matrix}NH_4O\\OH\end{matrix} = C_2O_2{<}\begin{matrix}NH_2\\OH\end{matrix}+H_2O$$

acid ammonium oxalate

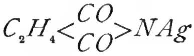
oxamic acid

It is a yellowish-white crystalline powder, sparingly soluble in cold water, and nearly insoluble in alcohol and ether.

It fuses at 173°, and decomposes, yielding oxamide, formic acid, and water.

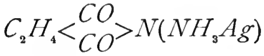
**102. Succinamide.**—Succinamide $C_2H_4(CONH_2)_2$ is obtained by the action of ammonia on ethyl succinate. It is insoluble in cold water and alcohol, but soluble in hot water, from which it crystallizes in needles. When heated to 200°, it yields ammonia and succinimide.

*Succinimide* $C_2H_4(CO)_2NH$, or $C_2H_4<\genfrac{}{}{0pt}{}{CO}{CO}>NH$, is formed by heating succinic anhydride $C_4H_4O_3$ in a current of ammonia. It crystallizes in rhombic plates, melts at 126°, and boils at 280°. It is readily soluble in water and alcohol. A hot alcoholic solution of succinimide, mixed first with ammonia and then with silver nitrate, yields, on cooling, large crystals of *silver succinimide*



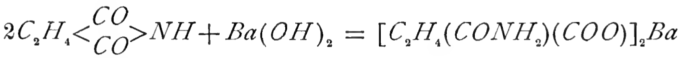
$$C_2H_4<\genfrac{}{}{0pt}{}{CO}{CO}>NAg$$

and when this salt is dissolved in ammonia, it yields, by spontaneous evaporation, *silver ammonium succinimide*



$$C_2H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N(NH_3Ag)$$

which is first obtained as a syrupy mass, but soon solidifies to a mass of hard brittle crystals. *Succinamic acid* $C_2H_4<\genfrac{}{}{0pt}{}{CONH_2}{COOH_2}$ is prepared from the barium salt obtained by heating succinimide with baryta water:

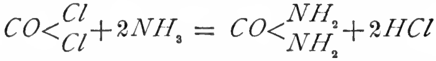


$$2C_2H_4<\genfrac{}{}{0pt}{}{CO}{CO}>NH + Ba(OH)_2 = [C_2H_4(CONH_2)(COO)]_2Ba$$

This acid is a crystalline body that is readily decomposed by the action of the alkalies into succinic acid and ammonia.

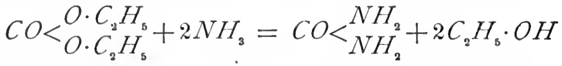
**103. Carbamide or Urea.**—Carbamide or urea $CO<\genfrac{}{}{0pt}{}{NH_2}{NH_2}$ may be regarded as the diamide of carbonic acid $CO(OH)_2$. It was discovered by Von Rouelle in urine in 1773, and was first synthesized by Wöhler in 1828, who obtained it by heating an aqueous solution of ammonium isocyanate $CONNH_4 = CO(NH_2)_2$. It was the first instance of the successful synthesis of an organic body. It occurs in various animal fluids, chiefly in the urine of mammals, but it is also present in minute quantities in the urine of birds and reptiles. A full-grown man voids, on an average, about 30 grams of urea daily. It is formed artificially by many different reactions:

1. By the action of carbonyl chloride on ammonia:



$$CO<\begin{matrix}Cl\\Cl\end{matrix}+2NH_3 = CO<\begin{matrix}NH_2\\NH_2\end{matrix}+2HCl$$

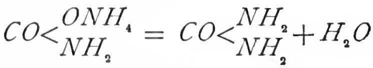
2. By the action of ammonia on ethyl carbonate:



$$CO<\begin{matrix}O\cdot C_2H_5\\O\cdot C_2H_5\end{matrix}+2NH_3 = CO<\begin{matrix}NH_2\\NH_2\end{matrix}+2C_2H_5\cdot OH$$

ethyl carbonate urea alcohol

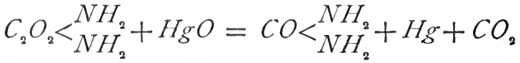
3. When ammonium carbamate is heated to about 135° under pressure in a sealed tube:



$$CO<\begin{matrix}ONH_4\\NH_2\end{matrix} = CO<\begin{matrix}NH_2\\NH_2\end{matrix}+H_2O$$

ammonium carbamate

4. When oxamide is heated with mercuric oxide:



$$C_2O_2<\begin{matrix}NH_2\\NH_2\end{matrix}+HgO = CO<\begin{matrix}NH_2\\NH_2\end{matrix}+Hg+CO_2$$

oxamide

Urea may be obtained from urine by the following process: A quantity of urine is filtered to separate it from any mucus that might be present, and is then evaporated on a water bath to about one-eighth of its original bulk, cooled, and mixed with an equal volume of cold, pure nitric acid; the mixture is allowed to stand in a cool place for about 24 hours, when a mass of brown crystals will have been formed. These are collected on a filter, washed with ice-cold water until the washings are nearly colorless, dissolved in boiling water, and mixed with precipitated $BaCO_3$, rubbed to a paste with water as long as the addition of $BaCO_3$ causes effervescence. The excess of $BaCO_3$ is filtered off, the filtrate evaporated on a steam bath, when a mixture of urea and barium nitrate is obtained, from which the urea may be extracted by strong alcohol and crystallized by evaporation.

The artificial preparation of urea is readily accomplished in the following manner: Potassium isocyanate is prepared by heating, in an iron dish, 28 parts of well dried potassium ferrocyanide with 14 parts manganese dioxide, to dull redness, and stirring until it ceases to smolder. The mass is allowed to cool and then coarsely powdered, treated with cold water, and filtered. To the filtrate, which is a solution of potassium isocyanate, are added 20 parts of crystallized ammonium sulphate, which is then evaporated to dryness on a water bath, and the residue treated with alcohol to extract the urea.

Urea crystallizes in long rhombic prisms or needles that have a cooling taste like niter. Urea dissolves in 1 part of cold water and 5 parts of alcohol, but is nearly insoluble in ether. It melts at 132°, and above this temperature breaks up into ammonia, biuret, and cyanuric acid. When urea is heated with water above 100°, or when boiled with alkalies or acids, it decomposes into carbon dioxide and ammonia. A similar decomposition occurs in urine. Nitrous acid decomposes urea in the same manner that it decomposes all other amides:

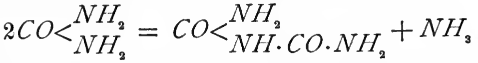
$$CO<\begin{matrix}NH_2\\NH_2\end{matrix}+N_2O_3=CO_2+2N_2+2H_2O$$

An alkaline hypobromite decomposes urea into nitrogen, carbon dioxide, and water:

$$CO<\begin{matrix}NH_2\\NH_2\end{matrix}+3NaOBr=CO_2+N_2+2H_2O+3NaBr$$

Urea forms crystalline compounds with acids, bases, and salts. *Urea nitrate* $CH_4N_2O\cdot HNO_3$ crystallizes in little shining leaves that are only very sparingly soluble in nitric acid. Urea oxalate $CO(NH_2)_2C_2H_2O_4,2Aq$ crystallizes also in leaf-shaped crystals that are, however, soluble in water. On evaporating a solution containing both urea and sodium chloride, the compound $CH_4N_2O \cdot NaCl, 2Aq$ separates in shining crystals.

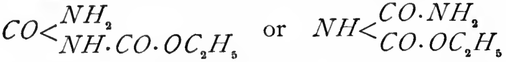
**104. Biuret or Allophanamide.**—Biuret or allophanamide $NH(CONH_2)_2$ is obtained, as has been previously stated, when urea is heated above 150°:



$$2CO<\begin{array}{l}NH_2\\NH_2\end{array} = CO<\begin{array}{l}NH_2\\NH \cdot CO \cdot NH_2\end{array} + NH_3$$

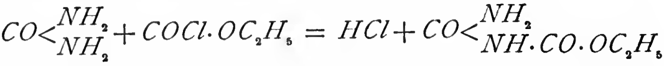
Biuret is readily soluble in alcohol and water, and crystallizes with one molecule of water.

*Ethyl allophanate* $NH_2 \cdot CO \cdot NH \cdot COO \cdot C_2H_5$ or



$$CO<\begin{array}{l}NH_2\\NH \cdot CO \cdot OC_2H_5\end{array} \quad \text{or} \quad NH<\begin{array}{l}CO \cdot NH_2\\CO \cdot OC_2H_5\end{array}$$

is obtained when urea is acted on by ethyl chlorcarbonate:



$$CO<\begin{array}{l}NH_2\\NH_2\end{array} + COCl \cdot OC_2H_5 = HCl + CO<\begin{array}{l}NH_2\\NH \cdot CO \cdot OC_2H_5\end{array}$$

It crystallizes in shining prismatic crystals that are soluble in water and alcohol. Treated with barium hydrate, ethyl allophanate yields the barium salt of allophanic acid $C_2H_4N_2O_3$; but this acid cannot be obtained in the free state, because if an attempt is made to separate it from the barium salt, the acid is immediately resolved into urea and carbon dioxide.

*Thiocarbamide*, or *sulpho-urea* $CS(NH_2)_2$, is the amide of thiocarbonic acid $CS(OH)_2$. It is obtained from ammonium thiocyanate $CS : N \cdot NH_4$, just as urea is obtained from isocyanate. It crystallizes easily from hot water in thick rhombic prisms that dissolve easily in water and alcohol, but with difficulty in ether; they possess a bitter taste, and closely resemble urea in its chemical reactions; it melts at 169°.

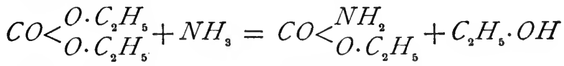
**105. Carbamic Acid.**—Carbamic acid $CO(NH_2)OH$ does not exist in the free state, but it seems that its ammonium salt (ammonium carbamate) is contained in commercial ammonium carbonate, and is formed by the direct union of two molecules of ammonia with carbon dioxide:

$$2NH_3 + CO_2 = CO(NH_2)ONH_4$$

It is a white mass that breaks up at 60° into $2NH_3$ and $CO_2$, which, however, combine again on cooling. When ammonium carbamate is heated in a sealed tube, to 130° to 140°, it yields ammonium carbonate and urea:

$$2CO(NH_2)ONH_4 = CO(ONH_4)_2 + CO(NH_2)_2$$

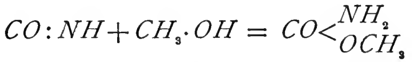
The esters of carbamic acid are called *urethanes;* they may be obtained by the action of ammonia on carbonic esters at ordinary temperature; for instance,



$$CO{<}^{O\cdot C_2H_5}_{O\cdot C_2H_5} + NH_3 = CO{<}^{NH_2}_{O\cdot C_2H_5} + C_2H_5\cdot OH$$

ethyl carbonate — ethyl carbamate or urethane

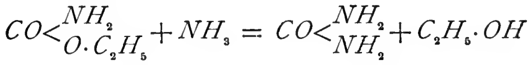
or by the direct union of cyanic acid with the alcohols; for example,



$$CO{:}NH + CH_3\cdot OH = CO{<}^{NH_2}_{OCH_3}$$

cyanic acid — methyl alcohol — methyl urethane

The urethanes are crystalline volatile bodies, soluble in alcohol, ether, and water. Alkalies decompose them into $CO_2$, ammonia, and the alcohols. They yield urea when heated with ammonia:



$$CO{<}^{NH_2}_{O\cdot C_2H_5} + NH_3 = CO{<}^{NH_2}_{NH_2} + C_2H_5\cdot OH$$

Conversely, on heating urea with alcohols, the urethanes are regenerated. *Methyl carbamate*, or *methyl urethane* $CO{<}^{NH_2}_{OCH_3}$, crystallizes in plates that melt at 52° and boil at 177°. *Ethyl carbamate*, or *ethyl urethane* $CO{<}^{NH_2}_{OC_2H_5}$, consists of large plates that melt at 53° and boil at 195°. *Allyl carbamate* $CO{<}^{NH_2}_{OC_3H_5}$ is a solid that melts at 21° and boils at 204°.

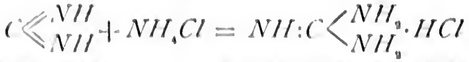
**106. Thiocarbamic Acid.**—Thiocarbamic acid $CO{<}^{NH_2}_{SH}$ is not known to exist in the free state. Its ammonium salt is prepared by leading $COS$ into alcoholic ammonia. It is a colorless, crystalline mass that, however, owing to the formation of ammonium sulphide when exposed to the air, soon acquires a yellow color. When heated to 130°, it is decomposed into urea and hydrogen sulphide. *Dithiocarbamic acid* $CS{<}^{NH_2}_{SH}$ is obtained as a red, oily liquid by the decomposition of its ammonium salt with dilute sulphuric acid. Dithiocarbamic acid is easily decomposed into sulpho-cyanic acid $CN{\cdot}SH$ and $H_2S$. Water decomposes it into cyanic acid and $2H_2S$. Its ammonium salt, *ammonium thiocarbamate* $NH_2{\cdot}CS{\cdot}SNH_4$ is formed when ammonia in alcoholic solution acts on carbon disulphide:

$$2NH_3 + CS_2 = CS{<}^{NH_2}_{SNH_4}$$

It crystallizes in yellow prisms or needles.

**107. Guanidines.**—These compounds are amidines of carbonic acid. Guanidine, the parent substance, is also known as *imido-urea*, since it may be considered as containing an imido group in the place of the oxygen of urea; thus, $CO(NH_2)_2$ is urea and $C(NH)(NH_2)_2$ is guanidine. Guanidine was first obtained by the oxidation of guanine (a substance closely related to uric acid and found in guano) with hydrochloric acid and potassium chlorate. Since then it has been prepared by the following reactions:

1. When an alcoholic solution of cyanamide is heated to 100° with ammonium chloride:



$$C{\ll}^{NH}_{NH} + NH_4Cl = NH{:}C{<}^{NH_2}_{NH_2}{\cdot}HCl$$

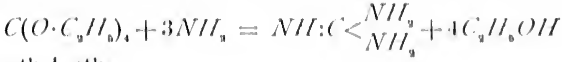
cyanamide hydrochloride of guanidine

2. By heating chloropicrin with aqueous ammonia to 150°:

$$CCl_3(NO_2) + 3NH_3 = NH{:}C{<}^{NH_2}_{NH_2} + 3HCl + NO_2H$$

chloropicrin guanidine

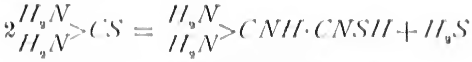
3. By heating ethyl orthocarbonate with aqueous ammonia to 150°:



$$C(O\cdot C_2H_5)_4 + 3NH_3 = NH{:}C{<}^{NH_2}_{NH_2} + 4C_2H_5OH$$

ethyl ortho-carbonate

4. It is most readily prepared from thiocyanate, which is made by the prolonged heating of ammonium thiocyanate to 180° to 190°, and the further transposition of the thio-urea that forms at first:



$$2\,{}^{H_2N}_{H_2N}{>}CS = {}^{H_2N}_{H_2N}{>}CNH\cdot CNSH + H_2S$$

thio-urea guanidine thiocyanate

The guanidine thiocyanate thus obtained is dissolved in a little water, mixed with half its weight of potassium carbonate, and evaporated to dryness, whereupon a mixture of guanidine carbonate and potassium thiocyanate is obtained. This is boiled with alcohol, which dissolves the thiocyanate and leaves *guanidine carbonate* $(N_3H_5C)_2\cdot H_2CO_3$, which may be recrystallized from water. The guanidine carbonate is converted into *guanidine sulphate* $(N_3H_5C)_2H_2SO_4$ and decomposed by baryta water; the filtrate from the $BaSO_4$ is evaporated over sulphuric acid, when guanidine is obtained as a deliquescent crystalline substance. It is very freely soluble in water and alcohol, has a strong alkaline reaction, and absorbs $CO_2$ from the air. With acids it forms crystallizable salts.

*Guanidine nitrate* $CN_3H_5HNO_3$ is precipitated when nitric acid is added to an aqueous solution of guanidine. It crystallizes in plates from water, in which it is only sparingly soluble. *Hydrochloride of guanidine* $CN_3H_5HCl$ yields a platinum salt $(CN_3H_5HCl)_2PtCl_4$ that crystallizes in yellow needles and is only sparingly soluble in alcohol.

## AMIDO ACIDS

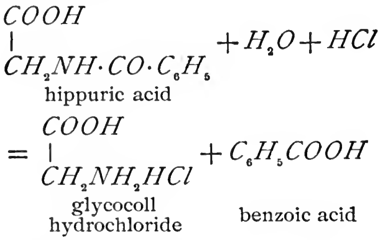
**108.** Amido acids may be prepared from chloro-substituted acids by treatment with ammonia; thus, if, for instance, monochloracetic acid is treated with ammonia, *amido-acetic acid* is obtained, as is seen from the following equation:

$$\underset{\text{monochlor-acetic acid}}{CH_2Cl\cdot CO_2H} + 2NH_3 = \underset{\text{amido-acetic acid}}{CH_2(NH_2)\cdot CO_2H} + NH_3\cdot HCl$$

They are metameric with the amides, but differ from these compounds by possessing a greater resistance against hydrolyzing agents; that is, the amido group is more firmly attached and less easily evolved as $NH_3$. Nitrous acid replaces the $NH_2$ group by an $OH$ group, as in the case of amines and amides, a hydroxy acid resulting, as may be seen from the following example:

$$\begin{aligned} &CH_2(NH_2)\cdot CO_2H + NO\cdot OH \\ &= CH_2(OH)CO_2H + N_2 + H_2O \end{aligned}$$

**109. Glycocoll.**—Glycocoll, or *amido-acetic acid* $CH_2(NH_2)\cdot CO_2H$, is also known as *glycocine* or *glycine;* it was discovered by Braconnot in 1820, who obtained it by decomposing glue with boiling sulphuric acid. It owes its name to this method of formation and to its sweet taste, being derived from the Greek γλυκύς, *glukus*, "sweet," and κόλλα, *kolla*, "glue." It may be obtained as a decomposition product when hippuric acid is boiled with concentrated hydrochloric acid:



$$\underset{\text{hippuric acid}}{\begin{matrix}COOH\\ |\\ CH_2NH\cdot CO\cdot C_6H_5\end{matrix}} + H_2O + HCl = \underset{\text{glycocoll hydrochloride}}{\begin{matrix}COOH\\ |\\ CH_2NH_2HCl\end{matrix}} + \underset{\text{benzoic acid}}{C_6H_5COOH}$$

or by the action of ammonia on bromacetic or chloracetic acid:

$$C_2H_3ClO_2 + 2NH_3 = NH_4Cl + CH_2(NH_2)CO_2H$$

Glycocoll is a solid body, crystallizing from water in large rhombic prisms that are soluble in 4 parts of cold water. It is insoluble in alcohol and ether. It has a sweet taste and melts with decomposition. Its solution has a feeble acid reaction. Heated with baryta, it is decomposed into methyl amine and carbon dioxide; nitrous acid converts it into glycollic acid. Ferric chloride imparts an intense red coloration to glycocoll solutions; this coloration disappears when acids are added, but it is restored by ammonia.

An aqueous solution of glycocoll will dissolve many metallic oxides, forming salts; of these, the copper salt $[CH_2(NH_2)CO_2]_2Cu, H_2O$ is very characteristic. It crystallizes in dark-blue needles. The silver salt $CH_2(NH_2)CO_2Ag$ crystallizes on standing over sulphuric acid. The combinations of glycocoll with salts, as, for instance, $CH_2(NH_2)CO_2H \cdot NO_3K$ and $CH_2(NH_2)CO_2H \cdot NO_3Ag$, are mostly crystalline bodies. Glycocoll yields the following compounds with hydrochloric acid: $CH_2(NH_2)CO_2H \cdot HCl$ and $2[CH_2(NH_2)CO_2H] \cdot HCl$. The first is obtained with an excess of hydrochloric acid, and crystallizes in long needles. The nitrate $CH_2(NH_2)CO_2H \cdot HNO_3$ forms long prisms.

**110. Methyl glycocoll** $CH_2(NHCH_3) \cdot CO_2H$ or

$$CH_2 <\begin{matrix} NH \cdot CH_3 \\ CO_2H \end{matrix}$$

is also known as *sarcosine;* it was first discovered by Liebig in 1847. It may be obtained by the reaction of methyl amine and monochloracetic acid, by an interchange analogous to that which yields glycocoll:

$$\underset{\substack{\text{monochloracetic} \\ \text{acid}}}{C_2H_3ClO_2} + \underset{\text{methyl amine}}{2NH_2(CH_3)}$$

$$= \underset{\text{sarcosine}}{CH_2(NHCH_3) \cdot CO_2H} + \underset{\substack{\text{methyl-amine} \\ \text{hydrochloride}}}{NH_2(CH_3)HCl}$$

It is also formed in the decomposition of creatine and caffeine by baryta water. Sarcosine crystallizes in rhomboidal prisms; it dissolves readily in water, but only with difficulty in alcohol. It begins to melt between 210° and 215°, undergoing decomposition. It is neutral, but forms salts with acids that have an acid reaction. Ignited with soda-lime, it evolves methyl amine.

*Trimethyl glycocoll*, or *betaine*, $CH_2[N(CH_3)_2]\cdot CO_2CH_3$ or  $CH_2<\begin{matrix}N(CH_3)_3\\CO\text{———}\end{matrix}>O$, occurs already formed in the sugar beet (*Beta vulgaris*); hence, it is present in the molasses from the beet, and makes the latter valuable for obtaining trimethyl amine. It is also found in the leaves and stalks of *Lycium barbarum*, in cotton seed, malt, and in wheat sprouts. It crystallizes with 1 molecule of water of crystallization. Betaine may be formed synthetically by the action of trimethyl amine on chloracetic acid:

$$CH_2Cl\cdot CO_2H + N(CH_3)_3 = CH_2[N(CH_3)_2]\cdot CO_2CH_3 + HCl$$

Betaine hydrochloride is also obtained by the careful oxidation of choline hydrochloride

$$\begin{aligned}&N(C_2H_4OH)(CH_3)_3Cl + O_2\\&= CH_2[N(CH_3)_2]\cdot CO_2CH_3, HCl + H_2O\end{aligned}$$

Betaine is soluble in water and alcohol, and forms salts with the acids.

**111. Hippuric Acid** $CH_2(NHC_6H_5CO)\cdot CO_2H$.—This is also known as *benzoyl glycocoll* or *benzamido-acetic acid*, and occurs in considerable quantities in the urine of horses and cows, from which it may be prepared by boiling it with milk of lime and precipitating the concentrated filtrate with hydrochloric acid. For purification, the crude acid thus obtained is washed with chlorine water; or, the solution of the crude acid in soda lye is boiled with sodium hypochlorite, until it becomes colorless, and the solution, after cooling, is again precipitated with hydrochloric acid. Hippuric acid may be prepared synthetically by heating benzoyl chloride with silver glycocoll:

$$\begin{aligned}&CH_2(NH_2)\cdot CO_2Ag + C_6H_5COCl\\&= CH_2(NHC_6H_5CO)\cdot CO_2H + AgCl\end{aligned}$$

or by heating benzamide with chloracetic acid:

$$CH_2Cl\cdot CO_2H + C_6H_5CO\cdot NH_2$$
$$= CH_2(NHC_6H_5CO)\cdot CO_2H + HCl$$

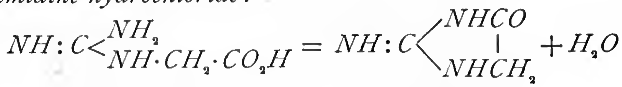
When properly purified, hippuric acid crystallizes in long, colorless prisms; it is slightly soluble in cold water, and freely soluble in hot water and alcohol; it is, however, insoluble in ether, which distinguishes it from benzoic acid. Like benzoic acid, it dissolves readily in ammonia, and is precipitated in feathery crystals by hydrochloric acid; but these are not dissolved by the addition of ether. When heated in a retort, hippuric acid decomposes and yields a sublimate of benzoic acid. At the same time, a certain quantity of an oily body, having a disagreeable odor, distils; this is phenyl cyanide $C_6H_5\cdot CN$.

If, in the preparation of hippuric acid from urine, the latter is in the slightest degree putrid, the hippuric acid is entirely destroyed during the boiling, ammonia is disengaged in considerable quantities, and the liquid will only yield benzoic acid, which does not exist in the unchanged secretion. In cases where benzoic acid is taken internally, it is changed in the system to hippuric acid, and leaves the system as such in the urine, in which it may be readily detected. Hippuric acid dissolves so abundantly in an aqueous solution of sodium phosphate that this solution loses entirely its alkaline character, and becomes acid. This reaction may explain the acid character of fresh urine of man and of herbivorous animals. Most metallic oxides readily dissolve in hippuric acid, forming *hippurates;* those of potassium, sodium, and ammonium are exceedingly soluble and, consequently, very difficult to crystallize; their solutions form a cream-colored precipitate with ferric salts, and a white, curdy precipitate with silver nitrate and mercurous nitrate.

Glycocoll may be considered as the parent substance of two physiologically important compounds, namely, *creatine* and *creatinine*. When solutions of cyanamide and glycocoll are mixed, a compound that has the formula

$$CH_2[C(NH)(NH_2)(NH)]\cdot CO_2H$$

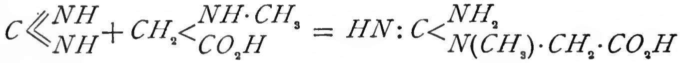
is obtained; this compound is known as *glyco-cyamine* or *guanido-acetic acid*, and when glyco-cyamine hydrochloride is heated at 160°, it loses water and is converted into *glyco-cyamidine hydrochloride:*



$$NH:C<\begin{matrix}NH_2\\NH\cdot CH_2\cdot CO_2H\end{matrix}=NH:C\Big<\begin{matrix}NHCO\\ \quad|\\NHCH_2\end{matrix}+H_2O$$

glyco-cyamine glyco-cyamidine

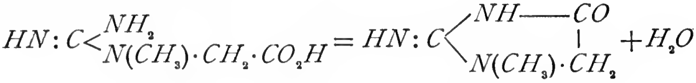
If, now, instead of glycocoll, methyl glycocoll (sarcosine) is employed and mixed with cyanamide, we obtain creatine; thus:



$$C\ll\begin{matrix}NH\\NH\end{matrix}+CH_2<\begin{matrix}NH\cdot CH_3\\CO_2H\end{matrix}=HN:C<\begin{matrix}NH_2\\N(CH_3)\cdot CH_2\cdot CO_2H\end{matrix}$$

cyanamide methyl glycocoll creatine

Creatinine (or methyl glyco-cyamidine) results from creatine in precisely the same way as glyco-cyamidine from glyco-cyamine:

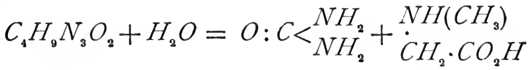


$$HN:C<\begin{matrix}NH_2\\N(CH_3)\cdot CH_2\cdot CO_2H\end{matrix}=HN:C\Big<\begin{matrix}NH\text{——}CO\\ \qquad\quad|\\N(CH_3)\cdot CH_2\end{matrix}+H_2O$$

creatine creatinine

**112. Creatine and Creatinine.**—Creatine, or methyl glyco-cyamine $C_4H_9N_3O_2$, which is also sometimes called *methyl guanidine-acetic acid*, was first discovered in 1834 by Chevreul in meat extract. Liebig in 1847 subjected it to an exhaustive investigation. It is found especially in the juice of muscles. It may be prepared by treating a solution of meat extract with basic acetate of lead, filtering, removing the excess of lead acetate by hydrogen sulphide, and evaporating the solution at a gentle heat until it crystallizes. The crystals are separated from the mother liquor, and alcohol, added to the latter, precipitates a fresh quantity of creatine. Creatine crystallizes with 1 molecule of water in glistening prisms, which, when heated to 100°, sustain a loss of water and become opaque. Its reaction is neutral, it has a faintly bitter taste, and dissolves rather readily in boiling water, but very sparingly in alcohol and ether. *Creatine nitrate* $C_4H_9N_3O_2\cdot HNO_3$ crystallizes in prisms.

When solutions of the salts of creatine are heated above 30°, they are converted into salts of creatinine, a stronger base containing $H_2$ and $O$ less than creatine. When creatine is boiled with baryta water, it is converted into sarcosine, ammonia being disengaged and barium carbonate precipitated at the same time. It is generally considered that the ammonia and carbon dioxide are produced in this case at the expense of the urea, which is formed directly by the decomposition of creatine:



$$\underset{\text{creatine}}{C_4H_9N_3O_2} + H_2O = \underset{\text{urea}}{O:C<\begin{matrix}NH_2\\ NH_2\end{matrix}} + \underset{\text{sarcosine}}{\begin{matrix}NH(CH_3)\\ \cdot\\ CH_2\cdot CO_2H\end{matrix}}$$

Creatinine $C_4H_7N_3O$, or *methyl glyco-cyamidine*, occurs almost constantly in urine (about .25 per cent.) and is readily obtained from creatine by heating it in a water bath and passing a current of pure hydrochloric-acid gas over it so long as any water is formed. The creatinine hydrochloride thus obtained is dissolved in water, decomposed by lead hydrate, the solution filtered and slowly evaporated, whereupon it deposits prismatic crystals of $C_4H_7N_3O, 2Aq$ that lose water on exposure to air and become opaque. It is much more soluble than creatine in alcohol and water. It is a strong base that can expel ammonia from ammonium salts, and yields crystallized salts with acids. Its compound with zinc chloride $(C_4H_7N_3O)_2ZnCl_2$ is particularly characteristic. Zinc chloride precipitates it from creatinine solutions as a crystalline powder that only dissolves with difficulty in water. When creatinine is boiled with baryta water, it yields ammonia and methyl hydantoin, according to the equation:

$$C_4H_7N_3O + H_2O = NH_3 + C_4H_6N_2O_2$$

This compound is the methylated derivative of *hydantoin*, or *glycolyl-urea* $O:C<\begin{matrix}NH\cdot CO\\ NH\cdot CH_2\end{matrix}$ and is eventually decomposed into sarcosine, $CO_2$, and $NH_3$.

**113. Amido-Propionic Acid.**—Amido-propionic acid $CH_3\cdot CH(NH_2)\cdot CO_2H$, also known as *alanine*, is derived from *a*-chlor- and *a*-brom-proprionic acids, by means of ammonia. It forms hard needles of a sweetish taste, which dissolve in about 5 parts of water, and are difficultly soluble in alcohol and insoluble in ether. When exposed to heat the acid begins to char at about 237°, and melts at 255°, and then sublimes with decomposition. Nitrous acid converts it into ethylidene lactic acid. *Butalanine*, which occurs in the pancreas of the ox, is *a*-amido-isovaleric acid, and has the formula $(CH_3)_2 : CH\cdot CH(NH_2)\cdot CO_2H$.

**114. Leucine.**—Leucine, or *a-amido-caproic acid*, $C_6H_{13}NO_2$ or $CH_3\cdot(CH_2)_3\cdot CH(NH_2)\cdot CO_2H$, was discovered in 1818 by Proust in old cheese; its occurrence is physiologically important. It is present in the pancreas, in the spleen, in the lymph glands, and, in typhoid, it occurs in the liver. It is a product of the decay of albuminoids. It is also formed when horn, gelatinous tissues, or albuminous matters are boiled with dilute sulphuric acid, or fused with potassium hydrate. In the reactions, *tyrosine*, and sometimes glycocoll, is formed. Leucine crystallizes in pearly scales that have a fatty feel, melt at 170°, and sublime, undecomposed, when very carefully heated; rapid heating breaks leucine up into amyl amine and $CO_2$:

$$C_5H_{10}(NH_2)\cdot CO_2H = NH_2\cdot C_5H_{11} + CO_2$$

It is soluble in 48 parts of water at 12°, and in 800 parts of alcohol. It is neutral in its reactions, but forms compounds with acids as well as with bases. Hydriodic acid converts it into caproic acid and ammonia:

$$C_5H_{10}(NH_2)\cdot CO_2H + 2HI = C_5H_{11}\cdot CO_2H + NH_3 + I_2$$

Treatment with nitrous acid converts leucine into leucic or hydroxy-caproic acid:

$$C_5H_{10}(NH_2)\cdot CO_2H + HNO_2 = C_5H_{10}(HO)\cdot CO_2H + N_2 + H_2O$$

Leucine may be prepared synthetically by the action of ammonia on bromocaproic acid:

$$NH_3 + C_5H_{10}Br\cdot CO_2H = C_5H_{10}(NH_2)CO_2H + HBr$$

or by digesting valeraldehyde ammonia with hydrocyanic and hydrochloric acids:

$$C_5H_{10}O\cdot NH_3 + HCN + HCl + H_2O$$
$$= C_5H_{10}(NH_2)CO_2H + NH_4Cl$$

**115. Tyrosine.**—Tyrosine, or *hydroxy-phenyl-amido-propionic acid*, $C_9H_{11}NO_3$ or $CH_2(C_6H_4OH)CH(NH_2)CO_2H$, is formed together with leucine when albuminoids or gelatinoid substances are either boiled with dilute sulphuric acid or fused with potassium hydrate. It may be prepared by boiling, for 16 hours, 1 part of horn shavings with 2 parts of sulphuric acid diluted with 4 times its volume of water. The liquid is then neutralized with milk of lime, filtered, the filtrate evaporated to half its volume, acidified with sulphuric acid, and then treated with an excess of lead carbonate. The solution containing the tyrosine as lead salt is decomposed by hydrogen sulphide, filtered, and evaporated. The tyrosine crystallizes out, while the mother liquor contains leucine in solution. Tyrosine is insoluble in ether, slightly soluble in alcohol and cold water, dissolves in 150 parts of hot water, and crystallizes therefrom in long, slender needles. It forms definite compounds with both acids and bases. Tyrosine may be recognized by the following reaction. When its aqueous solution is boiled with a solution of mercuric nitrate, a voluminous yellow precipitate is formed that assumes a deep copper-red color by boiling with nitric acid containing a small quantity of nitrous oxide.

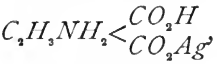
**116. Asparagine.**—Asparagine, or *amido-succinamic acid*, $C_4H_8N_2O_3$ or $C_2H_3NH_2(CO\cdot NH_2)COOH$, occurs naturally in asparagus, beets, the roots of marshmallow, licorice wood, and in the buds of cereals, peas, vetches, and beans before they flower. It may be prepared from marshmallow roots by chopping them, macerating them in the cold with milk of lime, precipitating the filtered liquid with barium carbonate, and evaporating the clear solution over the water bath to a syrup. The asparagine then crystallizes, on cooling, in shining transparent prisms that have a faint cooling taste, and are moderately soluble in hot water, but insoluble in alcohol and ether. The crystals contain 1 molecule of water. Asparagine is capable of acting as a weak acid and as a weak base. In contact with ferments, asparagine is converted into ammonium succinate. When acted on by nitrous acid, it is converted into malic acid:

$$\begin{aligned} &C_2H_3NH_2(CO\cdot NH_2)CO\cdot OH + 2HNO_2 \\ &= C_2H_3OH(CO\cdot OH)(CO\cdot OH) + N_4 + 2H_2O \end{aligned}$$

This reaction led at first to the conclusion that asparagine was an amide of malic acid, with which, however, it is only isomeric. Ordinary asparagine is levorotary, but an isomeride has been found in the mother liquor from crude asparagine, which is dextrorotary to the same extent, and is much sweeter than ordinary asparagine. A solution of the two in equal proportions is optically inactive, but the asparagines are deposited from it in crystals, which are, respectively, right-handed and left-handed. The isomeric derivatives from each kind retain the optical properties of their source. When asparagine is boiled with acids or alkalies, it is converted into *amido-succinic* or *aspartic acid:*

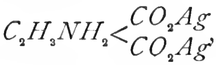
$$\begin{aligned} &C_2H_3NH_2(CO\cdot NH_2)(CO\cdot OH) + H_2O \\ &= C_2H_3NH_2(CO\cdot OH)(CO\cdot OH) + NH_3 \end{aligned}$$

Aspartic acid occurs in beet molasses, and is obtained by various reactions from albuminous substances. It crystallizes in small rhombic prisms, is moderately soluble in cold water and alcohol, but more soluble in hot water, from which it crystallizes. Its acid solution is dextrorotary, while its alkaline solution is levorotary. Like other amido acids, it unites both with acids and with alkalies; with the latter it forms both acid and neutral salts; for instance,



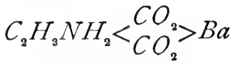
$$C_2H_3NH_2{<}\begin{matrix}CO_2H\\CO_2Ag\end{matrix},$$

acid salt



$$C_2H_3NH_2{<}\begin{matrix}CO_2Ag\\CO_2Ag\end{matrix},$$

neutral salt



$$C_2H_3NH_2{<}\begin{matrix}CO_2\\CO_2\end{matrix}{>}Ba$$

neutral salt

By the action of nitrous acid, aspartic acid is converted into malic acid. An optically inactive variety of aspartic acid is also known; this is obtained by heating fumarimide with water:

$$\underset{\text{fumarimide}}{C_4H_2O_2{\cdot}NH} + 2H_2O = \underset{\substack{\text{aspartic acid}\\ \text{(inactive)}}}{C_4H_7NO_4}$$

It crystallizes in large monoclinic prisms, and is a little more soluble in water than the active acid; nitrous acid converts it into inactive malic acid.

**117. Amidobenzoic Acids.**—Amidobenzoic acids have the formula $C_6H_4(NH_2){\cdot}CO_2H$; of these the 1 : 2 acid known as *anthranilic acid* is the most important; being an oxidation product of indigo. It is prepared by reducing 1 : 2 nitrobenzoic acid; it sublimes in needles, melts at 144°, and dissolves in hot water.

**118. Amidosulphonic Acids.**—Amidosulphonic acids also exist. *Taurine*, or *amido-ethyl-sulphonic acid* $C_2H_4(NH_2)SO_3H$, was discovered in the bile of oxen by Gmelin in 1824, and may be prepared by boiling ox gall with dilute hydrochloric acid, evaporating to dryness on the steam bath, and treating the residue with absolute alcohol, which leaves the taurine undissolved. This is dissolved in water, from which the taurine crystallizes in large prisms that are moderately soluble in water and entirely insoluble in alcohol. It melts and decomposes at about 240°. Taurine contains the groups $NH_2$ and $SO_3H$, and is, therefore, both a base and a sulphonic acid. But as the two groups neutralize each other, the compound has a neutral reaction. It can form salts with the alkalies. Boiling acids and alkalies do not affect it, but when fused with potassium hydrate it is decomposed, forming the acetate and sulphite of potassium, as is seen from the following equation:

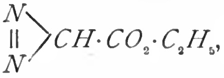
$$C_2H_4(NH_2)SO_3H + 3KOH$$
$$= CH_3{\cdot}COOK + K_2SO_3 + NH_3 + H_2O + H_2$$

Nitrous acid converts it into isothionic acid:

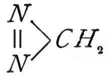
$$C_2H_4(NH_2)SO_3H + HNO_2 = C_2H_4OH{\cdot}SO_3H + H_2O + N_2$$

## DIAZO AND AZO COMPOUNDS

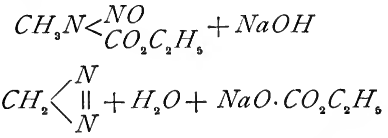
**119. Diazo Compounds.**—Diazo compounds may be defined as compounds that contain two doubly linked nitrogen atoms, each of which is linked to a monovalent atom or radical; their type may be represented as $R\cdot N:N\cdot R'$, where $R$ and $R'$ are either monovalent atoms or radicals. Diazo compounds are formed by the action of nitrous oxides on ammonia bases, and the reaction that takes place is called a *diazo reaction.* The amines of open-chain hydrocarbons seem to have little tendency to undergo this reaction, and it has always been found that diazo compounds of the type $R\cdot N:N\cdot R'$ are only known when $R$ is a positive monovalent radical containing a benzene ring, and $R'$ a negative monovalent radical. Amido acids of the open-chain series appear to form an exception, as they undergo the diazo reaction and form diazo compounds that contain the two doubly linked nitrogen atoms. These compounds are, however, differently constructed; while in the true diazo compounds the extra affinities of the two nitrogen atoms are combined to two different atoms or radicals, in the open-chain diazo compounds, they are both joined to a single carbon atom, and have only been isolated as ethereal salts or as amides.

**120. Diazo Compounds of Fatty Amines.**—The compounds  $\begin{matrix}N\\ \|\\ N\end{matrix}\!>CH\cdot CO_2H$, known as *diazo-acetic acid*, being derived from an open-chain carbon, has not been obtained in the free state, but its ethereal salt, *ethyl diazo-acetate*  $\begin{matrix}N\\ \|\\ N\end{matrix}\!>CH\cdot CO_2\cdot C_2H_5$, has been obtained as a yellow, oily precipitate, when an aqueous solution of hydrochloride of ethyl amido-acetate is treated with sodium nitrite. It boils at 144°, and undergoes decomposition when treated with acids; this decomposition takes an explosive character if the acid is strong. *Diazo-acetamide*  $\begin{matrix}N\\ \|\\ N\end{matrix}\!>CH\cdot ONH_2$ is obtained when ethyl diazo-acetate is slowly and carefully dissolved in strong ammonia. It is a yellow, crystalline body that is soluble in water, and detonates when suddenly heated. *Triazo-acetic acid* is obtained as its sodium salt by heating ethyl diazo-acetate with strong sodium hydrate; from this the mineral acids separate the free acid, which crystallizes in orange-red tablets, having the composition $C_3H_3N_6(COOH)_3,3H_2O$. Its aqueous solution, as well as that of its salts, is colored red by exposure to air and by nitric acid. It is important as the source of hydrazine $H_2N\cdot NH_2$, the sulphate of which may be prepared by heating triazo-acetic acid with dilute sulphuric acid:

$$C_3H_3N_6(COOH)_3+3H_2SO_4+6H_2O$$
$$= 3(N_2H_4,H_2SO_4)+3(COOH)_2$$



*Diazomethane* $\left.\begin{array}{c}N\\ \|\\ N\end{array}\right>CH_2$ is, at the ordinary temperature, a yellow, odorless, but extremely poisonous, gas that strongly attacks the skin, the eyes, and the lungs. It is prepared by the action of alkalies on nitrosomethyl urethane:



$$CH_3N{<}\begin{array}{l}NO\\ CO_2C_2H_5\end{array}+NaOH$$
$$= CH_2\left<\begin{array}{c}N\\ \|\\ N\end{array}\right.+H_2O+NaO\cdot CO_2C_2H_5$$

It is converted by water into methyl alcohol.

**121. Diazo Compounds of Aromatic Amines.**—At a more or less elevated temperature, the amines of closed-chain hydrocarbons, i. e., the aromatic amines, react with nitrous acid exactly similar to the amines of the open-chain hydrocarbon, i. e., the fatty amines; that is, the group $NH_2$ is replaced by the $OH$ group; for instance:

$$C_6H_5\cdot NH_2+HNO_2 = C_6H_5OH+N_2+H_2O$$

If this reaction, however, is executed at a lower temperature, and, especially, if a salt of an amine is used, the result is entirely different, the diazo compound being formed as an intermediate product:

$$\underset{\text{aniline nitrate}}{C_6H_5\cdot NH_2HNO_3} + HNO_2 = \underset{\text{diazobenzene nitrate}}{C_6H_5\cdot N:N\cdot NO_3} + 2H_2O$$

The salts of diazo compounds are, as a rule, prepared in aqueous solutions, since they are only used as intermediate products in the preparation of other compounds, and for the production of azo compounds. The amido compound is dissolved in dilute acid, the solution cooled in ice, and the calculated quantity of sodium nitrite added.

For preparing the crystalline salts, amyl nitrite is the one most advantageously used, and the reaction should be effected in absolute alcohol; the amine and the amyl nitrite are dissolved in the alcohol, and an acid is added to the cooled solution; after a few minutes the diazo salt crystallizes, and may be washed with alcohol and ether:

$$C_6H_5\cdot NH_2HCl + C_5H_{11}NO_2$$
$$= C_6H_5\cdot N:N\cdot Cl + C_5H_{11}\cdot OH + H_2O$$

**122. Diazobenzene Nitrate.**—Diazobenzene nitrate $C_6H_5N_2\cdot NO_3$ is obtained as a crystalline deposit when a current of nitrous vapors is passed into a saturated solution of aniline nitrate:

$$\underset{\text{aniline nitrate}}{C_6H_5\cdot NH_2HNO_3} + HNO_2 = \underset{\text{diazobenzene nitrate}}{C_6H_5N_2\cdot NO_3} + 2H_2O$$

It will be seen from the equation that this compound is formed by the substitution of 1 atom of nitrogen for 3 atoms of hydrogen in aniline nitrate. It forms long, colorless prisms, very soluble in water, slightly soluble in alcohol, and insoluble in ether. It explodes quite violently by heating or by percussion.

Besides this nitrate, there are other compounds of diazobenzene. They all contain the group $\cdot N:N\cdot$, characteristic of the diazo compounds, and are linked on one side to phenyl, and on the other to chlorine, bromine, or an oxidized group. The following formulas show plainly their constitution:

$C_6H_5 \cdot N:N \cdot Cl$ (diazobenzene chloride)
$C_6H_5 \cdot N:N \cdot Br$ (diazobenzene bromide)
$C_6H_5 \cdot N:N \cdot NO_3$ (diazobenzene nitrate)
$C_6H_5 \cdot N:N \cdot SO_4H$ (diazobenzene sulphate)

These compounds present several interesting reactions:

1. When heated with water, they disengage nitrogen and are converted into phenols:

$$C_6H_5 \cdot N:N \cdot NO_3 + H_2O = C_6H_5 \cdot OH + N_2 + HNO_3$$

2. The diazo group may be replaced by $H$, the hydrocarbon being formed, by boiling the compound with alcohol:

$$\begin{aligned} &C_6H_5 \cdot N:N \cdot Cl + C_2H_5 \cdot OH \\ &= C_6H_5H + N_2 + HCl + CH_3 \cdot CHO \end{aligned}$$

3. When warmed with a cuprous salt, diazo compounds give off nitrogen, and are converted into benzene-substitution products:

$$C_6H_5 \cdot N:N \cdot Br = C_6H_5Br + N_2$$

It is thus possible to replace the $NH_2$ group in aromatic compounds by the halogens or cyanogens. This reaction is known as *Sandmeyer's reaction.*

4. With auric and platinic chlorides, diazobenzene chloride forms double salts. When the platinic chloride is submitted to dry distillation, it yields chlorobenzene:

$$(C_6H_5 \cdot N:N \cdot Cl)_2PtCl_4 = 2C_6H_5Cl + 2N_2 + 2Cl_2 + Pt$$

The above reactions show conclusively that diazobenzene compounds must contain the $C_6H_5$ group; that the nitrogen atoms are linked in the manner represented is concluded from the fact that diazobenzene salts yield phenyl-hydrazine salts when reduced:

$$C_6H_5 \cdot N:N \cdot Cl + H_4 = C_6H_5 \cdot NH \cdot NH_2, HCl$$

**123. Diazo-Amido Compounds.**—When it is attempted to prepare a diazobenzene compound in the absence of an acid, a diazo compound is obtained that is more complex than the preceding. Thus, *diazo-amido benzene* $C_6H_5 \cdot N:N \cdot NH \cdot C_6H_5$ is obtained when $N_2O_3$ is passed in a cooled solution of aniline in alcohol. It forms brilliant golden-yellow scales that fuse at about 91°, and if heated to a higher temperature, explode violently.

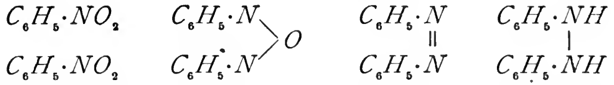
If an alcoholic solution of diazo-amido benzene is left standing for some time, or if it is gently heated with a little aniline hydrochloride, it undergoes an intramolecular transformation, being converted into the corresponding amido-azo compound; thus,

$$\underset{\text{diazo-amido benzene}}{C_6H_5 \cdot N:N \cdot NH \cdot C_6H_5} \quad \text{becomes} \quad \underset{\text{amido-azo benzene}}{C_6H_5 \cdot N:NC_6H_4 \cdot NH_2}$$

This change shows us at once the difference that exists between diazo compounds and azo compounds, which will be treated on in the following articles. Both classes of compounds contain the group $\cdot N:N\cdot$, but in the diazo compounds this group forms the connecting link between an aromatic group and a monovalent atom or group, while in the azo compound it connects two aromatic groups. This may be understood at once from the following formulas:

| *Diazo derivatives.* | *Azo derivatives.* |
|---|---|
| $C_6H_5 \cdot N:N \cdot Cl$<br>diazobenzene chloride | $C_6H_5 \cdot N:N \cdot C_6H_5$<br>azobenzene |
| $C_6H_5 \cdot N:N \cdot NH \cdot C_6H_5$<br>diazo-amido benzene | $C_6H_5 \cdot N:N \cdot C_6H_4 \cdot NH_2$<br>amido-azo benzene |

**124. Azo Compounds.**—When a nitro compound is reduced in acid solution, the corresponding amido derivative is immediately produced; but when an alkaline solution is employed there are formed, in the case of the aromatic nitro compounds, three intermediate products, derived from two molecules of the nitro compound. Thus, nitrobenzene in alkaline solution will yield *azoxybenzene*, *azobenzene*, and *hydrazobenzene*, according to the reducing power of the agent employed.



$$\begin{array}{cccc} C_6H_5\cdot NO_2 & C_6H_5\cdot N\diagdown & C_6H_5\cdot N & C_6H_5\cdot NH \\ & \qquad\qquad > O & \| & | \\ C_6H_5\cdot NO_2 & C_6H_5\cdot N\diagup & C_6H_5\cdot N & C_6H_5\cdot NH \end{array}$$

2 molecules of nitrobenzene — azoxybenzene — azobenzene — hydrazobenzene

*Azoxybenzene* $C_{12}H_{10}N_2O$, which is the product of the incomplete reduction of 2 molecules of nitrobenzene, may be prepared by boiling an alcoholic solution of potassium hydrate with nitrobenzene, or by oxydizing azobenzene by chromic acid in acetic acid. Azoxybenzene forms long, yellow needles that are insoluble in water, but readily dissolve in alcohol and ether. It melts at 36°, and is decomposed by distillation into aniline and azobenzene. By reducing agents it is converted into azobenzene and hydrazobenzene.

*Azobenzene* $C_{12}H_{10}N_2$, or $C_6H_5\cdot N:N\cdot C_6H_5$, is obtained by the action of a reducing agent, such as sodium amalgam, on an alcoholic solution of nitrobenzene:

$$2C_6H_5NO_2 + 8H = C_6H_5\cdot N:N\cdot C_6H_5 + 4H_2O$$

It is easily prepared by dissolving nitrobenzene in alcohol, adding an equal weight of potassium hydrate, and distilling, when the alcohol is oxidized to acetic acid, and the nitrobenzene reduced to azobenzene. As the end of the distillation approaches, the azobenzene comes over as a dark-red oil that, after a short time, solidifies to a crystalline mass. It is but slightly soluble in water, but dissolves readily in alcohol and ether.

Azobenzene is converted into *hydrazobenzene*

$$C_6H_5HN\cdot NHC_6H_5$$

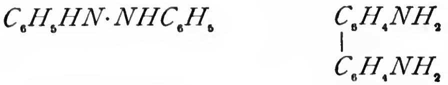
by reducing agents, such as zinc dust, sodium hydrate, and ammonium sulphide, in the presence of alcohol:

$$C_6H_5N:NC_6H_5 + 2H = C_6H_5HN\cdot NHC_6H_5$$

The latter body crystallizes in tables, is fusible at 131°, and almost insoluble in water, but soluble in alcohol and ether. When submitted to dry distillation, hydrazobenzene breaks up into azobenzene and aniline, as is seen from the following equation:

$$\underset{\text{hydrazobenzene}}{2C_6H_5HN{\cdot}NHC_6H_5} = \underset{\text{azobenzene}}{C_6H_5N:NC_6H_5} + \underset{\text{aniline}}{2C_6H_5NH_2}$$

Acids convert hydrazobenzene into a basic isomeride *benzidine* from which a considerable number of valuable dyestuffs are derived:



$$C_6H_5HN{\cdot}NHC_6H_5 \qquad \begin{array}{c} C_6H_4NH_2 \\ | \\ C_6H_4NH_2 \end{array}$$

hydrazobenzene benzidine

**125. Dyestuffs.**—It is the object of the dyer to fix certain coloring matters permanently in the fabric, and, consequently his processes vary with the nature of the latter, and of the color to be applied. In order that uniformity of colors and perfect penetration in the fiber may be obtained, it is essential that the dyestuff be in solution, and that it forms an insoluble compound (the dye) with either the fiber of the material itself or with some other substance (the mordant) previously fixed in the fiber. Most dyestuffs are capable of forming dyes with wool—and, also, though to a smaller extent, with silk—without the medium of a mordant; the dyes thus produced are known as *substantive dyes.* With cotton, however, the medium of a mordant appears to be nearly always necessary, and the dyes thus obtained are known as *adjective dyes.* It will be seen that, since a dyestuff must enter into some form of chemical combination before it can become a dye, it must be a compound that possesses a certain amount of chemical activity, and it has been found that those compounds that are most successfully employed as dyestuffs are either acid or basic in character. This observation has been found to be of considerable practical value, since it has shown that, although a compound may be apparently useless as a dyestuff, it may become useful if it is treated in such a way that the necessary acidity or basicity is imparted to it. From what has been said in various previous articles, it will be readily understood that it is possible to impart acidity to an organic compound by the introduction of certain radicals, as, for instance, $OH$ and $SO_2OH$, or to impart basicity by the introduction of the group $NH_2$. Of course, only certain organic compounds can be converted into dyestuffs by the introduction of such radicals; these compounds are known as *chromogens*, and the groups that lend them their dyeing capacity are called *auxochromes*. An acid auxochrome will yield an acid dyestuff capable of being fixed by a basic mordant (as alumina, for instance), while a basic auxochrome will yield a basic dyestuff that can be fixed by an acid mordant (as, for instance, by tannin). The dyestuff by itself may be a colorless substance, but it must be soluble in water, and the compound that is formed in the fiber must be colored as well as insoluble.

Azobenzene is a colored substance, but as it is chemically inactive as well as insoluble, it is, therefore, not a dyestuff, but it is a chromogen, for by the introduction of the $OH$ or $NH_2$ group, compounds are produced that are either dyestuffs (provided they are soluble in water) or become dyestuffs when rendered soluble by conversion into sulphonic acids.

**126. Amido-Azo Compounds.**—Amido-azo compounds are produced by the interaction of a diazo chloride and an amine (or amido compound); thus *amido-azo benzene* $C_6H_5N:N\cdot C_6H_4(NH_2)$ may be prepared by the action of diazobenzene chloride on aniline:

$$C_6H_5N:NCl + C_6H_5\cdot NH_2 = C_6H_5N:N\cdot C_6H_4(NH_2) + HCl$$

Amido-azo benzene crystallizes from hot alcohol in yellow rhombic needles; its hydrochloride forms violet needles. It forms the chief constituent of the commercial *aniline yellow*.

*Diamido-azo benzene* $C_6H_5\cdot N:N\cdot C_6H_3(NH_2)_2$ is prepared by the action of diazobenzene chloride on metaphenylene diamine, as is seen from the equation:

$$C_6H_5N:NCl + C_6H_4(NH_2)_2$$
$$= C_6H_5\cdot N:N\cdot C_6H_3(NH_2)_2 + HCl$$

It is a yellow crystalline base that dissolves with red color in acids. Its hydrochloride is an orange-yellow dyestuff, known commercially as *chrysoidine.*

*Triamido-azo benzene* $C_6H_4(NH_2)\cdot N:N\cdot C_6H_3(NH_2)_2$ is produced by the action of $N_2O_3$ on metaphenylene diamine. It forms brownish-yellow crystals, readily soluble in hot water; the salts are reddish brown. Its hydrochloride forms the coloring matter *Bismarck brown.*

*Dimethyl-amido-azo benzene* $C_6H_5\cdot N:N\cdot C_6H_4\cdot N(CH_3)_2$ crystallizes in golden-yellow plates. The chloride crystallizes in violet needles. The sodium salt of its monosulphonic acid, *dimethyl-amidoazo-benzene-sulphonic acid* $C_6H_4(SO_3H)\cdot N:N\cdot C_6H_4\cdot N(CH_3)_2$, is also known as *methyl-orange*, *helianthin*, or *orange III;* it is used in the laboratory instead of litmus, as an indicator in alkalimetrical titrations, the yellow solution being colored red by traces of acid.

**127. Hydroxy-Azo Compounds.**—Hydroxy-azo compounds, or short oxy-azo compounds, are prepared by the interaction of a diazo chloride and a phenol. Thus, *hydroxy-azo benzene* $C_6H_5\cdot N:N\cdot C_6H_4(OH)$ is prepared from diazobenzene chloride and phenol, as is seen from the following equation:

$$C_6H_5\cdot N:NCl + C_6H_5OH = C_6H_5\cdot N:N\cdot C_6H_4(OH) + HCl$$

It crystallizes in brick-red rhombic prisms, and is a yellowish-red dye. *Dihydroxy-azo-benzene-sulphonic acid* $C_6H_4(SO_3H)\cdot N:N\cdot C_6H_3(OH)_2$ is prepared from diazo-benzene-sulphonic acid and resorcinol $C_6H_4(OH)_2$. It forms a sodium salt that is known as *resorcin yellow.*

**128. Hydrazine Compounds.**—Just as the amines are derived from ammonia $NH_3$, so the hydrazines are derived from *hydrazine* $H_2N\cdot NH_2$. They may be *primary hydrazines*, represented by the general formula $R\cdot NH\cdot NH_2$, or *secondary hydrazines*, represented by the formula $R_2:N\cdot NH_2$. When $R$ is an alkyl radical, the hydrazines are best prepared by the action of reducing agents on the corresponding nitrosoamines:

$$R_2:N\cdot NO+H_4 = R:N\cdot NH_2+H_2O$$

but when $R$ is an aromatic radical, the hydrazines are most readily prepared by the reduction of the corresponding diazo compound. The alkyl hydrazines are of little importance, and will not be considered here. The most important hydrazine compound is *phenyl hydrazine* $C_6H_5\cdot NH\cdot NH_2$, which is obtained by reducing diazobenzene chloride with sodium sulphite, or stannous chloride and hydrochloric acid:

$$C_6H_5N:NCl+4HCl+2SnCl_2$$
$$= C_6H_5NH\cdot NH_2HCl+2SnCl_4$$

Phenyl-hydrazine hydrochloride is obtained as a precipitate that, after being filtered off and washed with a mixture of alcohol and ether, is dissolved in a little water and decomposed by strong $NaOH$, whereupon the hydrazine falls as an oily layer that is removed and freed from water by distilling with potassium carbonate. Phenyl hydrazine is a colorless oil, solidifying, on cooling, in tabular crystals that melt at 23°. It boils at 241° with partial decomposition. Its specific gravity at 23° is 1.091. Phenyl hydrazine is sparingly soluble in water, but readily in alcohol and ether. It acts as a powerful base, forming salts with the acids, and is a strong reducing agent. It readily absorbs oxygen from the air, becoming brown. It reduces alkaline cupric solutions, *even in the cold*, precipitating yellow cuprous hydroxide, and evolving nitrogen, while aniline and benzene are found in the solution. This is a general reaction for identifying hydrazines, and may also be employed for diazo compounds by boiling their aqueous solutions with hydropotassium sulphite, to reduce them to hydrazines, and adding potash and an alkaline cupric solution. It also reduces mercuric oxide in the cold, forming nitrogen, aniline, benzene, and mercury diphenyl. Phenyl-hydrazine hydrochloride mixed with sodium acetate forms a general test for aldehydes and ketones, with which it forms insoluble, oily, or crystalline compounds, thus precipitating them from their aqueous solutions.

## CYANOGEN AND ITS COMPOUNDS

**129.** In the earlier parts of the eighteenth century, a blue color was accidentally discovered by a manufacturer of colors at Berlin, Germany; it was sold under the name of *Prussian blue.* This color was used for a considerable time, but little attention was paid to its chemical composition, until Maquer, near the end of that century, discovered that, by boiling Prussian blue with an alkali, the former was decomposed, yielding a residue of red oxide of iron and a solution that reproduced the blue when a salt of iron was added to it; from this he inferred that Prussian blue was a compound of oxide of iron with an acid for which the alkali had a stronger affinity. This theory was confirmed in 1782 by the investigations of Scheele, who observed that, when an alkaline solution, prepared for making the blue, was allowed to stand for some time exposed to the atmosphere or to the action of carbon dioxide, the solution lost its power of furnishing the color, but a paper, previously impregnated with oxide of iron, was colored blue by the escaping vapor. Scheele also prepared this acid in a pure state, which, in reference to its origin, was called *prussic acid.*

The investigations of Berthollet in 1787 not only proved the components of prussic acid to be carbon, nitrogen, and oxygen, but also showed that the power of the alkaline liquor to produce Prussian blue depended on the presence of a yellow salt, crystallizing in octahedrons, and containing prussic acid, potash, and oxide of iron, though the latter was so intimately bound up with the other constituents that it could not be separated by those substances that are usually employed to precipitate iron. Porrett, in 1814, decomposed Prussian blue with baryta, and subsequently removed the baryta from the salt thus obtained by means of sulphuric acid, when he obtained a solution of the acid which he named *ferrurctted chyazic acid.* In 1815, Gay-Lussac, having boiled Prussian blue (or *prussiate of iron*, as it was then called) with red oxide of mercury and water, and crystallized the so called prussiate of mercury, exposed it, in the dry state, to the action of heat, and obtained a gas having the composition $CN$, which was called *cyanogen*, from the Greek **κύανος**, *kyanos*, "blue," in allusion to its connection with Prussian blue. It was then seen that the substance that had been called ferruretted chyazic acid contained iron and the elements of cyanogen, whence it was called *ferrocyanic acid*, and its salts were spoken of as *ferrocyanates*. Robiquet first obtained this acid in the crystallized state, having the composition $C_6H_4N_6Fe$; and since it was found that, when brought in contact with metallic oxides, it exchanged the $H_4$ for an equivalent quantity of the metal, according to the equation:

$$H_4C_6N_6Fe + 2M''O = M''_2 \cdot C_6N_6Fe + 2H_2O$$

it was concluded that the $C_6N_6Fe$ composed a distinct group or radical, which was named *ferrocyanogen*, the acid being called *hydroferrocyanic acid*, and the salt *ferrocyanide*. The formula $Fcy$ is given by some writers to the radical $C_6N_6Fe$.

**130. Cyanogen.**—The preparation (by heating cyanide of mercury) and properties of cyanogen have been treated on in a general way in *Inorganic Chemistry*, but it seems advisable to add a few details here. All organic compounds that contain nitrogen give sodium cyanide when ignited with sodium; similarly, potassium cyanide is obtained when charcoal containing nitrogen is heated with potassium carbonate. Cyanogen itself is most readily prepared by heating mercuric cyanide $Hg(CN)_2$. But, in heating mercuric cyanide, a black solid substance, *paracyanogen*, is formed, and remains behind in the retort. It has the same composition as cyanogen, and must, therefore, be considered as its polymeric modification. Cyanogen is a colorless gas with a strong odor; it is readily soluble in alcohol and water, and burns with a purple-colored flame. It is extremely poisonous. In aqueous solution, cyanogen soon undergoes change, and a brown, amorphous body, *azulmic acid* $C_4N_5H_5O$, is deposited. In the solution are found ammonium salts, especially the carbonate, formate, and oxalate, together with urea.

**131. Potassium Ferrocyanide.** — Potassium ferrocyanide $4KCN,Fe(CN)_2,3H_2O$, or $K_4C_6N_6Fe,3H_2O$, or $(KCN)_2 \cdot CN \cdot Fe'' \cdot CN \cdot (KCN)_2,3H_2O$, is prepared on a large scale by calcining animal matter, such as blood, horn, refuse of skins, and leather, in a closed iron vessel with potassium carbonate. The charred mass, which contains potassium cyanide, is exhausted with boiling water, and ferrous sulphate is added to the solution, which is then evaporated to crystallization; or the solution is boiled with metallic iron, which dissolves, with the evolution of hydrogen. The iron may also be added to the mixture of animal matter and potassium carbonate before calcining; after cooling, the mass is pulverized and exhausted with boiling water. The solution contains ferrocyanide. When sufficiently concentrated, it deposits the salt in yellow crystals. They are unaltered by the air, but lose 12.8 per cĕnt. of water at 100°. The anhydrous salt is white. Potassium ferrocyanide dissolves in 2 parts of boiling and 4 parts of cold water, but is insoluble in alcohol. When heated with bodies rich in oxygen, as, for instance, with manganese dioxide, it is converted into potassium cyanate, the iron itself being oxidized to peroxide. Potassium ferrocyanide is not poisonous. When ignited it breaks up, according to the following equation:

$$4KCN,Fe(CN)_2 = 4KCN + FeC_2 + N_2$$

This decomposition is made use of for the purpose of preparing potassium cyanide. As, however, a portion of the cyanogen is lost in this way, potassium carbonate is generally added, when the reaction represented by the subjoined equation takes place:

$$4KCN,Fe(CN)_2 + K_2CO_3 = 5KCN + KCNO + CO_2 + Fe$$

The potassium cyanide $KCN$, prepared in this way, necessarily contains potassium cyanate $KCNO$. Potassium ferrocyanide is the starting point for the preparation of all compounds containing cyanogen. Nearly all the acids decompose potassium ferrocyanide, evolving hydrocyanic acid and producing compounds containing cyanogen and iron, which become blue when exposed to the atmosphere, from the formation of Prussian blue and similar compounds. It is for this reason that the yellow crystals of potassium ferrocyanide become green and blue when exposed to the air of the laboratory. Oxidizing agents convert the ferrocyanide into ferricyanide, as will be seen later. With a large number of metallic salts, the ferrocyanide gives precipitates, so that it is a valuable reagent in analysis. The following are some of these precipitates:

| | |
|---|---|
| Zinc ferrocyanide $Zn_2(CN)_6Fe$ | white |
| Copper ferrocyanide $Cu_2(CN)_6Fe$ | dark brown |
| Lead ferrocyanide $Pb_2(CN)_6Fe$ | white |
| Silver ferrocyanide $Ag_4(CN)_6Fe$ | white |

Potassium ferrocyanide is extensively employed in the manufacture of colors, in dyeing, and in calico printing.

**132. Hydrocyanic Acid.**—Hydrocyanic, or prussic, acid $HC\vdots N$ is a most powerful poison; a few drops, taken internally, generally kill immediately. It occurs free in all parts of the Java tree (*Pangium edule*), in amygdalin, a glucoside of bitter almonds, in the kernels of many stone fruits, such as peaches, cherries, etc., in laurel, and in many other plants. It is prepared by the decomposition of metallic cyanides with hydrochloric acid, as represented in the following equation:

$$\underset{\substack{\text{potassium}\\ \text{cyanide}}}{KCN} + HCl = KCl + \underset{\substack{\text{hydrocyanic}\\ \text{acid}}}{HCN}$$

or by distilling potassium ferrocyanide with dilute sulphuric acid. It can also be obtained by treating chloroform with ammonia, as is seen from the following equation:

$$CHCl_3 + NH_3 = HCN + 3HCl$$

It is produced synthetically by passing a succession of electric sparks through a mixture of equal volumes of nitrogen and acetylene.

Hydrocyanic acid is a volatile liquid, that boils at 26.5° and solidifies at −15°. It has a very characteristic odor, suggesting bitter almonds. It is very readily soluble in all proportions in water, and it is this solution that is popularly known as prussic acid. Pure hydrocyanic acid is very unstable. By standing, a brown substance is deposited. By boiling with alkalies or acids, it is converted into formic acid and ammonia. It scarcely reddens blue litmus paper. On contact with incandescent bodies, it takes fire and burns with a pale violet flame. Hydrocyanic acid may be detected by the following tests:

1. It gives a white precipitate of silver cyanide with silver nitrate, and this precipitate does not darken on exposure to light. When properly dried and heated, silver cyanide gives off cyanogen.

2. If a drop of hydrocyanic acid is added to a mixed solution of ferric and ferrous sulphates, and an excess of potassium hydrate added, a thick, dark-colored precipitate is obtained; and if this is treated with an excess of hydrochloric acid, the ferrous and ferric oxides precipitated are dissolved, and Prussian blue will remain, strongly coloring the liquid.

3. If a drop of hydrocyanic acid is mixed with a drop of ammonium sulphide and then evaporated to dryness, ammonium sulphocyanide is formed, and a blood-red color is produced when the spot is touched with a drop of ferric chloride acidulated with hydrochloric acid.

**133. Potassium Cyanide.**—Potassium cyanide $KCN$ is prepared by heating dried potassium ferrocyanide to redness in stoneware retorts. After cooling, the mass is exhausted with alcohol; this solvent leaves a black deposit, consisting of charcoal and iron, and the solution, evaporated in vacuo, deposits the potassium cyanide as a white crystalline mass. Potassium cyanide has a caustic taste and an after taste of bitter almonds. It is quite soluble in water, but only sparingly soluble in absolute alcohol. Potassium cyanide of commerce is in white opaque lumps, and contains about 90 per cent. of cyanide, the rest being cyanate and carbonate. When exposed to air, it deliquesces, and smells of hydrocyanic acid and ammonia, the former being produced from the cyanide and the latter from the cyanate by the action of the moisture of the air:

$$KCN + H_2O = KOH + HCN$$
$$KCNO + 2H_2O = NH_3 + KHCO_3$$

When the aqueous solution of potassium cyanide is boiled, it disengages ammonia and is converted into potassium formate:

$$KCN + 2H_2O = NH_3 + HCO_2K$$

When potassium cyanide is heated with sulphur, it is converted into potassium sulphocyanate. Iodine dissolves very freely in a solution of potassium cyanide; potassium iodide is formed and cyanogen iodide is deposited in crystals. A solution of potassium cyanide dissolves the cyanides of many other metals, as, for instance, gold, silver, zinc, etc., forming soluble cyanides. This property is utilized in the extraction of gold from its ores; it is also used in electroplating, photography, and in the laboratory. It is one of the most dangerous poisons. Potassium cyanide is sometimes obtained in considerable quantities from the blast furnaces of iron works, being formed from the potassium carbonate in the ashes of the fuel.

**134. Ammonium Cyanide.**—Ammonium cyanide $NH_4CN$ is a colorless, very volatile substance that crystallizes in cubes. It is prepared by distilling a mixture of potassium cyanide and ammonium chloride, or by allowing the vapor of anhydrous hydrocyanic acid and ammoniacal gas to mingle; or, lastly, by passing a mixture of ammonia and carbonic oxide through a red-hot porcelain tube. *Sodium cyanide* $NaCN$ is a very soluble salt, corresponding closely with potassium cyanide. The cyanides of *barium*, *strontium*, and *calcium* are less soluble than the alkali cyanides, and are readily decomposed by carbonic acid. *Zinc cyanide* $Zn(CN)_2$ is precipitated by potassium cyanide from zinc-sulphate solution; it is soluble in potassium cyanide, forming the double cyanide $Zn(CN)_2(KCN)_2$. *Nickel cyanide* $Ni(CN)_2$

is obtained, by the action of $KCN$ on a nickel salt, as a pale-green precipitate that is soluble in an excess of the reagent, forming $Ni(CN)_2(KCN)_2$, from which nickel cyanide may be reprecipitated by hydrochloric acid. Nickel cyanide is remarkable for its insolubility even in boiling hydrochloric acid.

**135. Cobalt Cyanide.**—Cobalt cyanide $Co(CN)_2$ is obtained as a reddish-brown precipitate when potassium cyanide is added to a solution of cobalt nitrate; it is soluble in an excess of the reagent, forming potassium cobalto-cyanide $K_4Co(CN)_6$, which, by the addition of alcohol, may be obtained in small, red, deliquescent crystals. When exposed to air or boiled with water, it undergoes oxidation, the cobaltous compound being converted into a cobaltic compound; thus,

$$4K_4Co''(CN)_6 + O_2 + 2H_2O = 4K_3Co'''(CN)_6 + 4KOH$$

Potassium-cobaltic cyanide is a pale-yellow salt, its solution being nearly colorless, so that the brown solution, formed at first when potassium cyanide is added in excess to a solution of a cobalt salt, gradually becomes pale when exposed to the atmosphere. This solution, when mixed with hydrochloric acid in excess, yields hydro-cobaltic-cyanic acid $H_3Co(CN)_6$, which is soluble, forming a distinction between cobalt and nickel. When both metals are present, the addition of hydrochloric acid to the solution in excess of $KCN$ produces a yellowish-green precipitate of nickel-cobaltic cyanide $Ni_3[Co(CN)_6]_2$, which is decomposed by boiling with potash, the nickel being precipitated as hydrate, and the cobalt passing into solution as potassium-cobaltic cyanide:

$$Ni_3[Co(CN)_6]_2 + 6KOH = 3Ni(OH)_2 + 2K_3Co(CN)_6$$

**136. Ferrous Cyanide.**—Ferrous cyanide $Fe(CN)_2$ is precipitated as a reddish-brown mass when a solution of potassium cyanide is added to a ferrous salt. This precipitate dissolves when boiled with an excess of the reagent, and the solution, when evaporated, deposits yellow crystals of potassium ferrocyanide:

$$Fe(CN)_2 + 4KCN = K_4Fe(CN)_6$$

The constitution of potassium ferrocyanide has not yet been satisfactorily explained, and it might be regarded simply as a mixture $4KCN, Fe(CN)_2$, were it not for the following facts, which effectually contradict this most natural assumption: (1) The iron cannot be detected by any of the common reagents used; for example, ammonium sulphide produces with ferrous salts a very dense black precipitate, but has no action whatever on potassium ferrocyanide. (2) Further, potassium cyanide is an extremely poisonous compound, as has been previously mentioned; potassium ferrocyanide, on the other hand, is not poisonous, so that it can hardly be assumed that potassium cyanide, as such, is present. (3) Moreover, the $K_4$ may be exchanged for hydrogen or other metals without affecting the iron and cyanogen, which leads to the conclusion that the group $Fe(CN)_6$ contains the iron in a state of intimate association with the cyanogen, whereby it loses its ordinary properties.

*Hydrogen ferrocyanide*, or *hydroferrocyanic acid* $H_4Fe(CN)_6$, is obtained as a white crystalline precipitate when hydrochloric acid is added to a saturated solution of potassium ferrocyanide. This precipitate is insoluble in an excess of the reagent, but soluble in water. If it be drained, dissolved in alcohol, and ether added, it may be obtained in large crystals. It is a strong acid. When exposed to air, it absorbs oxygen, and evolves hydrocyanic acid, leaving a residue of Prussian blue, or ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$. By boiling its solution the acid is decomposed into hydrocyanic acid and ferrous ferrocyanide $Fe_2[Fe(CN)_6]$,

$$3H_4Fe(CN)_6 = 12HCN + Fe_2[Fe(CN)_6]$$

Ferrous ferrocyanide is first white, but soon changes to blue on exposure to air.

Hydroferrocyanic acid is tetrabasic; its four hydrogen atoms may be replaced by a metal to form a ferrocyanide.

The ferrocyanogen group $Fe(CN)_6^{iv}$ is a tetrad group, consisting of ferrous iron, which is a diad ($Fe''$), and six monad cyanogen groups $(CN)'$, leaving four vacant bonds, thus, $[Fe''(CN)_6]^{iv}$, or $Fcy^{iv}$ or $Cfy^{iv}$, according to some authors.

**137. Ferric Ferrocyanide.** — Ferric ferrocyanide, or Prussian blue $Fe_4'''[Fe(CN)_6]_3$, forms the dark-blue precipitate obtained when a solution of potassium ferrocyanide is added to a solution of a ferric salt; as, for example,

$$\underset{\text{ferric chloride}}{2Fe_2Cl_6} + \underset{\text{potassium ferrocyanide}}{3K_4Fe(CN)_6} = 12KCl + \underset{\text{ferric ferrocyanide}}{Fe_4[Fe(CN)_6]_3}$$

When calcined in the air, ferric ferrocyanide leaves a residue of peroxide of iron. It is insoluble in water, alcohol, and in the weaker acids. Oxalic acid dissolves it, and the solution is employed as blue ink. Some ammonium salts, such as acetate and tartrate, also dissolve it. Alkalies destroy the blue color, leaving ferric hydrate and a solution of an alkali ferrocyanide:

$$Fe_4[Fe(CN)_6]_3 + 12KOH = 2Fe(OH)_6 + 3K_4[Fe(CN)_6]$$

This is turned to account in calico printing for producing a buff or white pattern on a blue ground. The material having been dyed blue by passing first through a solution of a ferric salt and afterwards through potassium ferrocyanide, the pattern is printed with an alkali, which leaves the brown ferric hydrate capable of being removed by a dilute acid, when the material has been rinsed, so as to leave the design white.

*Potassium ferricyanide* $K_3(CN)_6Fe$, which is also known as *red prussiate of potash*, is formed when a current of chlorine is passed into a solution of potassium ferrocyanide. Potassium chloride and potassium ferricyanide are formed, and the latter gives to the liquid a deep-brown color. On evaporation, it deposits the new salt, which is purified by a second crystallization. Potassium chloride remains in the mother liquor. The process of formation may be expressed by the following equation:

$$2K_4(CN)_6Fe + Cl_2 = 2KCl + 2K_3(CN)_6Fe$$

Potassium ferricyanide forms beautiful red crystals that are anhydrous. It is generally assumed that this salt contains the triad radical ferricyanogen $[Fe'''(CN)_6]'''$. Potassium ferricyanide dissolves in 3.8 parts of cold water and in a less quantity of hot water. The solution has a dark-yellow color, and if this solution is added to that of ferrous salt, a dark-blue precipitate of *ferrous ferricyanide*, known in the arts as *Turnbull's blue*, is obtained, as is seen from the following equation:

$$\underset{\substack{\text{potassium}\\\text{ferricyanide}}}{2K_3(CN)_6Fe} + \underset{\substack{\text{ferrous}\\\text{sulphate}}}{3FeSO_4} = \underset{\substack{\text{potassium}\\\text{sulphate}}}{3K_2SO_4} + \underset{\substack{\text{ferrous}\\\text{ferricyanide}}}{Fe_3[(CN)_6Fe]_2}$$

A solution of potassium ferricyanide, rendered alkaline by potash, acts as a powerful oxidizing agent, becoming reduced to potassium ferrocyanide:

$$2K_3(CN)_6Fe + 2KOH = 2K_4Fe(CN)_6 + H_2O + O$$

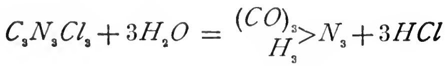
**138. Nitroferrocyanides.**—These salts are formed by the action of nitric acid on certain alkaline ferrocyanides. The best known of these compounds is *sodium nitroferrocyanide* $Fe(CN)_5(NO)Na_2$, or, as it is ordinarily called, *sodium nitroprusside*. It is prepared by oxidizing potassium ferrocyanide with dilute nitric acid. After filtration and evaporation, crystals of potassium nitrate and a deposit of oxamide are obtained. The mother liquor is saturated with sodium carbonate, and, on evaporation, yields sodium nitroprusside, which may be purified by recrystallization. Sodium nitroprusside crystallizes in large right rhombic prisms of a ruby-red color, which are readily soluble in water. It serves as a very delicate reagent for alkaline sulphides and hydrogen sulphide, which give with it an intense violet coloration.

**139. Mercuric Cyanide.**—Mercuric cyanide $Hg(CN)_2$ is prepared by dissolving finely powdered mercuric oxide in an aqueous solution of hydrocyanic acid until the odor of the latter has entirely disappeared, being careful to avoid an excess of the oxide. After concentration and cooling, colorless anhydrous prisms are obtained that are unaltered by air and light. This is mercuric cyanide. It is very poisonous, possesses a nauseous, metallic taste, and dissolves in 8 parts of cold water. It is decomposed by heat into mercury and cyanogen. The solution of mercuric cyanide dissolves mercuric oxide, and forms with it a compound more soluble than the cyanide, crystallizing in colorless scales.

**140. Chlorides of Cyanogen.** — Two chlorides of cyanogen are known to exist: *liquid cyanogen chloride* $CNCl$, and *solid cyanogen chloride* $C_3N_3Cl_3$. Liquid cyanogen chloride $CNCl$ is prepared by passing chlorine gas over mercury cyanide, or, better, into an aqueous solution of hydrocyanic acid, which is maintained at 0°. Hydrochloric acid and cyanogen chloride are formed:

$$HCN + Cl_2 = CNCl + HCl$$

When the solution is saturated with chlorine, it is gently heated, and the cyanogen chloride that is disengaged is passed through a tube containing calcium chloride, and condensed in a well cooled receiver. When properly purified, cyanogen chloride is a colorless liquid, having a penetrating odor that is very irritating to the eyes. It boils at 15.5°, and solidifies at about 6°. When pure, it can be preserved without alteration, but, if it contains a trace of chlorine, it soon becomes converted into the solid chloride. Solid cyanogen chloride $C_3N_3Cl_3$ results from the polymeric transformation that the liquid undergoes spontaneously under certain circumstances. It can also be obtained by exposing hydrocyanic acid to the action of chlorine in direct sunlight. It crystallizes in brilliant yellow needles or plates. It melts at 140°, and boils at 190°. It has a peculiar irritating odor, and is immediately decomposed by boiling water into hydrochloric and cyanuric acids:



$$C_3N_3Cl_3 + 3H_2O = \underset{\substack{\text{cyanuric}\\ \text{acid}}}{\begin{matrix}(CO)_3\\ H_3\end{matrix}\!>\!N_3} + 3HCl$$

**141. Cyanogen Bromide and Iodide.**—The bromide and iodide of cyanogen correspond in constitution to the liquid chloride. They are prepared by the action of bromine and iodine, respectively, on mercury cyanide. These elements decompose this compound with the formation of bromide and iodide of mercury, the excess of bromine or iodine combining with the cyanogen to form cyanogen bromide or iodide. Cyanogen bromide $CNBr$ is a solid, and crystallizes in brilliant cubes. Cyanogen iodide $CNI$ sublimes spontaneously in beautiful, colorless needles when a mixture of iodine and mercury cyanide is placed in a flask, mercuric iodide being formed. Cyanogen iodide has a penetrating odor, is very volatile, and, like the chloride and the bromide, is very poisonous.

**142. Cyanides of the Alcohol Radicals.**—*Methyl cyanide*, or *acetonitrile* $CH_3 \cdot CN$, is formed by heating a mixture of methyl iodide and potassium cyanide, the reaction being expressed by the equation:

$$CH_3I + KCN = KI + CH_3CN$$

or by distilling acetamide with phosphoric anhydride, which removes 1 molecule of water from the former compound:

$$C_2H_3O \cdot NH_2 - H_2O = CH_3 \cdot CN$$

Methyl cyanide is a colorless volatile liquid of rather pleasant odor. Its specific gravity is .8, and it mixes with alcohol and ether. The tendency for the nitrogen in the cyanogen group ($C \equiv N$) contained in it to become pentavalent enables it to combine with other bodies; thus, it unites with $Br_2$, $HBr$, and $HI$ to form crystalline compounds. A boiling solution of potassium hydrate decomposes methyl cyanide into ammonia and potassium acetate:

$$CH_3 \cdot CN + 2H_2O = CH_3 \cdot COOH + NH_3$$

An isomeride of methyl cyanide known as *methyl-carbyl amine* $CH_3 \cdot NC$ is formed, if, instead of potassium cyanide, silver cyanide is acted on by methyl iodide. Under the influence of acids, it decomposes into the formic acid and methyl amine:

$$\underset{\text{methyl-carbyl amine}}{CH_3{\cdot}NC} + 2H_2O = \underset{\text{formic acid}}{HCHO_2} + \underset{\text{methyl amine}}{NH_2{\cdot}CH_3}$$

*Ethyl cyanide* $C_2H_5{\cdot}CN$ is obtained when ammonium propionate is distilled with phosphoric anhydride:

$$(NH_4)C_3H_5O_2 = C_2H_5{\cdot}CN + 2H_2O$$

From this mode of formation results the name *propionitrile*, which is sometimes given to this compound. It may also be obtained when potassium cyanide and potassium ethyl sulphate are distilled together, as is seen from the following equation:

$$KCN + KC_2H_5SO_4 = K_2SO_4 + C_2H_5{\cdot}CN$$

but this product of distillation, which is a liquid and has a variable boiling point, contains, independent of the true ethyl cyanide, an isomeride of that body, namely, ethyl-carbyl amine. Ethyl cyanide, which in general resembles methyl cyanide, is a colorless liquid, having a penetrating and pleasant odor; it boils at 96.7°. When boiled with potassium hydrate, potassium propionate is formed, and ammonia liberated:

$$\underset{\text{ethyl cyanide}}{C_3H_5N} + KOH + H_2O = \underset{\text{potassium propionate}}{KC_3H_5O_2} + NH_3$$

When ethyl cyanide is brought in contact with dilute sulphuric acid and zinc, i. e., nascent hydrogen, it combines with 4 atoms of it, forming propyl amine:

$$\underset{\text{ethyl cyanide}}{C_2H_5CN} + 4H = \underset{\text{propyl amine}}{C_3H_9N}$$

*Ethyl-carbyl amine* $C_2H_5{\cdot}NC$ was the name given by Gautier to the isomeride of ethyl cyanide, previously mentioned. It is a colorless liquid, having an intensely and exceedingly offensive odor, and boils at 79°. Aqueous acids convert it into ethyl amine and formic acid:

$$\underset{\text{ethyl-carbyl amine}}{C_2H_5\cdot NC} + 2H_2O = \underset{\text{ethyl amine}}{C_2H_5NH_2} + \underset{\text{formic acid}}{HCHO_2}$$

**143. Isocyanides.**—Methyl- and ethyl-carbyl amine are known as *isocyanides;* their formulas show that their alkyl groups are united to the nitrogen and not to the carbon of the $CN$ group; their graphic formula must then be

$$H_3\equiv C-N\mathrel{\substack{\equiv\\=}}C \text{ or } H_3\equiv C-N''' = C''$$

That is, either the valence of the nitrogen atom has changed from 3 to 5, or the valence of the carbon atom of the original $CN$ group from 4 to 2. As the valence of carbon in all other organic compounds is always 4, while that of nitrogen changes quite freely, the former assumption appears to be the more likely one. The terms ethyl and methyl isocyanides are, recently, in more frequent use than ethyl- and methyl-carbyl amine.

**144. Hydroxy- and Thio-Cyanogen Compounds.** Cyanuric acid $C_3N_3(OH)_3$ is obtained by heating urea until the melted mass solidifies again:

$$\underset{\text{urea}}{3CO(NH_2)_2} = 3NH_3 + \underset{\text{cyanuric acid}}{C_3N_3(OH)_3}$$

This residue is washed with water, dissolved in potash, and the cyanuric acid precipitated by adding hydrochloric acid. A better result is obtained by passing dry chlorine over urea kept in fusion by a gentle heat:

$$3CO(NH_2)_2 + Cl_3 = 2NH_4Cl + HCl + N + C_3N_3(OH)_3$$

The residue is washed in cold water and crystallized from hot water. Cyanuric acid forms small, white crystals, soluble in 40 parts of cold water, and very soluble in boiling water and alcohol. It separates from its boiling solution in orthorhombic prisms containing 2 molecules of water of crystallization. It is a tribasic acid, forming salts in which 1, 2, or 3 atoms of the hydrogen are replaced by metal.

Examples of such salts are *trisodium cyanurate* $C_3N_3(ONa)_3$, *barium cyanurate* $C_3N_3O_3HBa$, *silver cyanurate* $C_3N_3(OAg)_3$, etc.

*Cyanic acid* $CN \cdot OH$ is obtained by the dry distillation of cyanuric acid. One molecule of the latter, which is polymeric with cyanic acid, breaks up into 3 molecules of the latter body:

$$C_3N_3(OH)_3 = 3CN \cdot OH$$

Cyanic acid condenses at a few degrees below 0° to a colorless liquid having a strong and irritating odor, resembling acetic acid. It is a rather unstable compound. As soon as it is removed from the freezing mixture in which it is condensed, and its temperature rises a few degrees above 0°, it produces a crackling noise, and is converted into an amorphous white mass, known as *cyamelide*, which appears to be polymeric with cyanic acid, and may be reconverted into it by redistillation. When cyanic acid is mixed with water, heat is evolved, and the liquid becomes alkaline, from the production of hydro-ammonium carbonate:

$$CN \cdot OH + 2H_2O = NH_4 \cdot HCO_3$$

*Potassium cyanate* $KO \cdot CN$ is obtained when gaseous cyanogen chloride is passed into a well cooled solution of potassium hydrate, as is seen from the following equation:

$$Cl \cdot CN + 2KOH = KO \cdot CN + KCl + H_2O$$

It crystallizes in needles that fuse when heated, and become metamerized into the isocyanate.

*Potassium isocyanate*, also known as *potassium pseudocyanate* $K \cdot NC : O$, is prepared by heating to dull redness, in a flat, iron tray, an intimate mixture of 2 parts of well dried potassium ferrocyanide and 1 part of well dried manganese dioxide. The mixture must be continually stirred; it soon blackens and enters into semifusion. After cooling, it is reduced to powder and exhausted with boiling alcohol. On cooling, the filtered alcoholic solution deposits potassium isocyanate in laminated transparent crystals that are anhydrous. Potassium isocyanate is very soluble in water, but only slightly so in cold alcohol. If hydrochloric acid is added to an aqueous solution of potassium isocyanate, carbon dioxide is evolved, together with some pungent vapor of cyanic acid.

*Ammonium cyanate* $NH_4 \cdot O \cdot CN$ is prepared by mixing vapor of cyanic acid with ammonia gas in excess, whereupon it is deposited in minute crystals, that effervesce with the acids, evolving carbon dioxide. If the cyanate is kept for some time, or if its aqueous solution is boiled, it no longer effervesces with the acids nor evolves ammonia with cold potassium-hydrate solution, having become changed into urea $CO(NH_2)_2$.

*Ammonium isocyanate* $NH_4 \cdot NC \cdot O$ is formed when potassium isocyanate is decomposed by ammonium sulphate. It is a solid, white mass, very soluble in water. When its aqueous solution is treated with the acids, it evolves carbon dioxide, similarly to ammonium cyanate, and it becomes likewise transformed into urea on standing.

**145. Thiocyanic Acid.**—Thiocyanic acid $HSCN$, also known as *sulphocyanic acid*, or *hydrogen thiocyanate*, is obtained by decomposing barium thiocyanate, dissolved in water, with sulphuric acid. The filtered solution is colorless, very acid, but not poisonous; it boils below 100°, and is easily decomposed in a very complex manner, by ebullition, and by exposure to the air. Thiocyanic acid and the thiocyanates give an intense blood-red color with ferric salts, producing ferric thiocyanate; the red color is bleached by mercuric chloride, which distinguishes it from ferric acetate.

*Potassium thiocyanate* $KSCN$, also known as *potassium sulphocyanate*, or *potassium sulphocyanide*, is prepared by heating a mixture of 2 parts of potassium ferrocyanide and 1 part of sublimed sulphur to redness in a covered crucible. After cooling, the mass is dissolved in water, the solution filtered, and potassium carbonate added to the liquid as long as a precipitate of ferrous carbonate is formed. The solution is again filtered, evaporated to dryness, the residue exhausted with alcohol, and the alcoholic solution allowed to evaporate spontaneously. Potassium thiocyanate crystallizes in long prismatic crystals, resembling potassium nitrate. It is deliquescent and very soluble in water and alcohol. It fuses easily, becoming dark blue, but fades again on cooling; it burns when heated in air, with the production of potassium sulphate. When hydrochloric acid is added to a strong solution of potassium sulphocyanate, a yellow precipitate of persulphocyanic acid is obtained; this may be crystallized from hot water, and yields a yellow precipitate of lead persulphocyanate $Pb(CN)_2S_3$ with lead nitrate. When heated with dilute sulphuric acid, potassium sulphocyanate yields carbon oxysulphide $COS$, according to the equation:

$$KSCN + 2H_2SO_4 + H_2O = KHSO_4 + NH_4HSO_4 + COS$$

Solution of potassium sulphocyanate produces an intense blood-red color with the ferric salts, due to the formation of ferric sulphocyanate.

*Ammonium sulphocyanate* or *ammonium thiocyanate* $NH_4CNS$ is formed on heating prussic acid with yellow ammonium sulphide. It is most readily obtained by heating carbon disulphide with alcoholic ammonia:

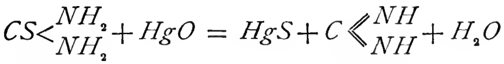
$$CS_2 + 4NH_3 = NH_4CNS + (NH_4)_2S$$

It crystallizes in prisms that readily dissolve in water and alcohol. It melts at about 150°. The thiocyanates of sodium, barium, strontium, calcium, manganese, and ferrous thiocyanate are colorless and very soluble; those of lead and silver are white and insoluble.

*Cyanogen sulphide* $(CN)_2S$ is formed when cyanogen iodide in ethereal solution acts on silver thiocyanate. It crystallizes in rhombic plates, melting at 65°, and is soluble in water, alcohol, and ether.

*Pseudo-cyanogen sulphide* $C_3N_3HS_3$ is formed in the oxidation of potassium sulphocyanate with nitric acid or chlorine. It is a yellow amorphous powder, insoluble in water, alcohol, and ether. It dissolves with a yellow color in alkalies. *Canarine* is similar to, and probably identical with, pseudocyanogen sulphide. It is obtained from $KCNS$ by electrolysis, or by oxidation with $KClO_3$ and $HCl$. It is applied as a yellow or orange dye for wool, and does not require a mordant.

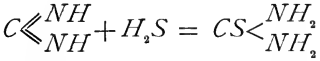
**146. Cyanamide.**—Cyanamide $CN_2H_2$ is formed by the action of cyanogen chloride or bromide on an ethereal solution of ammonia, or by the action of mercuric oxide or silver oxide on sulpho-urea, as is seen from the following equation:



$$CS<\begin{matrix}NH_2\\NH_2\end{matrix}+HgO = HgS + C\ll\begin{matrix}NH\\NH\end{matrix}+H_2O$$

sulpho-urea cyanamide

It forms crystals fusible at 40° and soluble in water, alcohol, and ether. Ammoniacal silver nitrate precipitates from its solution a yellow silver compound containing $CN_2Ag_2$. By the action of acids it combines with the elements of water, forming urea. Hydrogen sulphide reconverts it into sulpho-urea, as is shown by the following equation:



$$C\ll\begin{matrix}NH\\NH\end{matrix}+H_2S = CS<\begin{matrix}NH_2\\NH_2\end{matrix}$$

Dicyanimide $HN(CN)_2$ is obtained by the action of potash on a solution of potassium cyanate, according to the equation:

$$3KOCN + H_2O = (KO)_2CO + KOH + HN(CN)_2$$

On neutralizing the solution with $HNO_3$ and adding $AgNO_3$, a precipitate of $AgN(CN)_2$ is obtained.

**147. Mustard Oil.**—The iso-thiocyanates of the hydrocarbon radicals are known as *thiocarbimides*, or, more generally, as *mustard oils*. Allyl iso-thiocyanate $H_5C_3 \cdot NCS$ is the principal constituent of ordinary mustard oil, which is obtained by distilling powdered black mustard seeds with water. Mustard seeds contain *potassium myronate* and a peculiar ferment known as *myrosin*. Under the influence of water and this ferment, the potassium myronate breaks up into grape sugar, hydropotassium sulphate, and mustard oil. The reaction occurs even at 0°, and the seeds yield about

.5 per cent. of the oil. The reaction may be expressed by the subjoined equation:

$$\underset{\substack{\text{potassium}\\ \text{myronate}}}{C_{10}H_{18}KNO_{10}S_2} = \underset{\substack{\text{grape}\\ \text{sugar}}}{C_6H_{12}O_6} + \underset{\substack{\text{hydropotas-}\\ \text{sium sulphate}}}{KHSO_4} + \underset{\substack{\text{allyl iso-}\\ \text{thiocyanate}}}{H_5C_3\cdot NCS}$$

Mustard oil is also obtained artificially by distilling allyl iodide or bromide with an alcoholic solution of either potassium or silver thiocyanate, according to the equation:

$$KSCN + C_3H_5I = H_5C_3\cdot NCS + KI$$

Essential oil of mustard is a liquid that is insoluble in water, but readily dissolves in alcohol and ether. It boils at 150.7°, and has a specific gravity of 1.017 at 10°. It has a pungent odor and causes blisters on the skin. It is slowly decomposed by light, depositing a yellow precipitate. When heated with water or hydrochloric acid, it is decomposed, undergoing the following reaction:

$$H_5C_3\cdot NCS + 2H_2O = CO_2 + H_2S + NH_2\cdot C_3H_5$$

It unites with aqueous ammonia to form allyl thio-urea. When heated with water and lead oxide, it yields diallyl urea.

**148. Fulminates.**—The salts known as fulminates are prepared from the fulminates of mercury and silver, obtained when those metals are treated with nitric acid and alcohol.

*Mercuric fulminate* $HgO(CN)_2O$ and *silver fulminate* $(CN)_2(OAg)_2$ are prepared by dissolving mercury or silver in nitric acid and adding alcohol to the still hot solution. In a few minutes, a brisk effervescence takes place, and fulminate of mercury or silver is deposited as a white crystalline precipitate. When dry, these bodies explode violently by either heat or percussion. Fulminate of mercury is the basis of percussion caps.

Warm ammonia dissolves silver fulminate, and deposits, on cooling, crystals of *silver-ammonium fulminate* $NH_4O\cdot CN\cdot O\cdot NCAg$, a compound that is even more violently explosive than silver fulminate, and is even dangerous while moist. A similar compound is also formed with mercuric fulminate. Potassium chloride, added to a hot solution of silver fulminate, removes one-half of the silver as precipitated silver chloride, and the solution deposits shining plates of *silver-potassium fulminate* $KO{\cdot}CN{\cdot}O{\cdot}NCAg$, which is also dangerously explosive. By careful addition of nitric acid, the $K$ may be replaced by $H$, and the *silver-hydrogen fulminate* $HO{\cdot}CN{\cdot}O{\cdot}NCAg$ obtained, which readily dissolves in boiling water and crystallizes on cooling; by boiling with silver oxide or mercuric oxide, this is reconverted into either silver or mercuric fulminate. Zinc and copper fulminate may be obtained by decomposing moist mercuric fulminate with those metals; they are soluble, crystalline, and explosive.

*Sodium fulminate* $NaO{\cdot}CN{\cdot}O{\cdot}NCNa, 2H_2O$ is obtained by the action of sodium amalgam on an aqueous solution of mercuric fulminate. On evaporating over lime and sulphuric acid, the sodium salt is deposited in prisms that explode when rubbed.

*Fulminuric* or *isocyanuric acid* $HO{\cdot}NC(OC{\cdot}NH)_2$ is obtained as a potassium salt by boiling mercuric fulminate with potassium chloride, potassium fulminate being formed first:

$$\begin{aligned} &2(KO)_2(CN)_2 + 3H_2O \\ &= KO{\cdot}NC(OC{\cdot}NH)_2 + KOH + K_2CO_3 + NH_3 \end{aligned}$$

On adding silver nitrate, the sparingly soluble silver fulminurate $AgO{\cdot}NC(OC{\cdot}NH)_2$ crystallizes out, and by decomposing this with $H_2S$ and evaporating the filtrate, a solution of the acid is obtained; it crystallizes with difficulty, and is soluble in alcohol.

# ORGANIC CHEMISTRY

(PART 7)

## DERIVATIVES OF HYDROCARBONS

### PHENOLS

**1.** The phenols, or hydroxybenzenes, are, as the latter name implies, hydroxyl derivatives of benzene, and their position lies midway between the alcohols and the acids. They are derived from the benzene hydrocarbons in a similar manner to that by which the alcohols of the fatty series are derived from the paraffins, that is, by the replacement of hydrogen in the benzene nucleus by one or more hydroxyl groups; as, for instance, phenol $C_6H_5 \cdot OH$, orcinol $C_6H_3CH_3 \cdot (OH)_2$, pyrogallol $C_6H_3(OH)_3$. If the hydroxyl is introduced into the methyl group instead of into the phenyl group in the homologues of benzene, an alcohol is produced; thus, $C_6H_5 \cdot CH_2OH$ is benzyl alcohol, while $C_6H_4 \cdot OH \cdot CH_3$ is methyl phenol, or cresol.

The phenols are either liquids or solids, and are frequently characterized by a peculiar odor; some characteristic examples of phenols are carbolic acid, thymol, etc. Most of the phenols can be distilled without decomposition, and are readily soluble in alcohol and ether; some dissolve readily in water, while others dissolve but sparingly. Many of them possess antiseptic properties, as, for instance, phenol, cresol, and resorcin. Phenols are distinguished from alcohols by their tendency to combine very readily with the alkalies, which originally caused them to be mistaken for acids. As in the case of alcohols, phenols may contain one hydroxyl group (monohydric phenols), two hydroxyl groups (dihydric phenols), three hydroxyl groups (trihydric phenols), etc. All phenols possess a characteristic tendency to produce colored products of oxidation, and usually acquire an intense color by the addition of ferric salts.

The phenols are frequently products of the dry distillation of complex organic substances, as, for instance, coal, but they are also obtained by fusing the sulphonic acids with alkalies; thus, benzene sulphonic acid yields phenol, as is seen from the following equation:

$$\underset{\text{potassium-benzene sulphonate}}{C_6H_5\cdot SO_2OK} + KOH = \underset{\text{phenol}}{C_6H_5\cdot OH} + K_2SO_3$$

Another general method sometimes employed is the distillation of aromatic hydroxy-acids, either alone or with lime.

### MONOHYDRIC PHENOLS, OR MONOHYDROXYBENZENES

**2. Phenol.**—Phenol, or *phenic acid*, or *carbolic acid*, $C_6H_5\cdot OH$ was discovered in 1834 by Runge. It exists in coal tar, from which large quantities of phenol are obtained by distillation. That part of the coal tar which passes over into the receiver between 150° and 200° is collected separately, and mixed with a saturated solution of either potassium or sodium hydrate, to which solid potash, or soda, is added. A crystalline phenate of potassium or sodium is formed; this is dissolved in boiling water, the insoluble oil that floats is separated, and the alkaline solution is neutralized with hydrochloric acid, whereupon the phenol separates. It is collected, washed with a small quantity of water, dehydrated with calcium chloride, and rectified by distillation. The distilled product is cooled to $-10°$, and the crystals deposited are allowed to drain out of contact with the air.

Phenol may be prepared artificially from benzene by a process that is applicable to the preparation of all phenols, as has been already stated in Art. **1.** It consists in treating benzene with sulphuric acid, though fuming sulphuric acid is preferable. Benzene sulphonic acid is formed; this is diluted with water to separate the excess of hydrocarbon, and the solution is neutralized with chalk; calcium-benzene sulphonate, which is soluble, and sulphate, which is insoluble, are formed. The calcium-benzene sulphonate is converted into the sodium salt by double decomposition with sodium carbonate, and, after evaporation and desiccation, the product is fused in a silver crucible with an excess of potassium hydrate. The mass is exhausted with water, and the alkaline solution decomposed by hydrochloric acid. The phenol separates, and is dried and purified by distillation.

There is another very simple synthesis of phenol. In the presence of aluminum chloride, benzene absorbs oxygen directly, and phenol is formed:

$$C_6H_6 + O = C_6H_6O$$

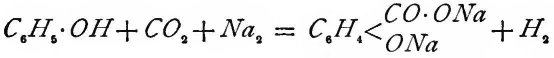
This reaction is one of the most unexpected and interesting applications of a general method of synthesis discovered by Friedel and Crafts.

**3.** Pure phenol crystallizes in long, colorless, prismatic needles, having a specific gravity of 1.084, melting at about 40°, and boiling at 183°. The commercial product forms a crystalline mass that turns reddish in a short time, and, in contact with moist air, deliquesces to a brown liquid. Its odor is peculiar and characteristic; its taste, acrid and burning. It is poisonous when taken internally, blisters the skin, and acts as an antiseptic. It freely dissolves in alcohol, ether, and acetic acid, and is soluble in 15 parts of water at about 20°. Its solution is colored a dark violet by ferric salts, and bromine water, even in very dilute solutions, forms a yellow precipitate of tribromphenol. A pine shaving moistened with hydrochloric acid assumes a blue color when dipped in phenol and exposed to the air.

Although phenol is neutral to litmus paper, it forms definite combinations with the alkalies. When it is mixed with a very concentrated solution of potassium hydrate, a crystalline mass is obtained that constitutes *potassium phenate* $C_6H_5 \cdot OK$. The same product is formed, with the disengagement of hydrogen, by the action of metallic potassium on phenol. The solubility of phenol in the alkaline hydrates is applied in the separation of this compound from the neutral oils that accompany it. The property is common to the phenols, and indicates the slightly acid character of this class of compounds. Phosphoric chloride converts phenol into phenyl chloride, as is seen from the following equation:

$$C_6H_5 \cdot OH + PCl_5 = C_6H_5 \cdot Cl + POCl_3 + HCl$$

The hydrogen in the group $C_6H_5$ in phenol can be readily replaced by chlorine, bromine, or such groups as $NO_2$, $NO$, $NH_2$, etc. The compounds so formed may sometimes be obtained directly (as the nitrophenols), and sometimes by indirect processes. In the presence of sodium, phenol directly combines with carbon dioxide, forming salicylic acid:



$$C_6H_5 \cdot OH + CO_2 + Na_2 = C_6H_4 < \begin{matrix} CO \cdot ONa \\ ONa \end{matrix} + H_2$$

sodium salicylate

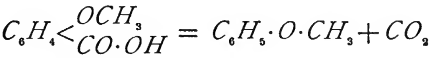
The following remarkable reaction of phenol was first noticed by Reimer and Tiemann: When it is heated with chloroform and an excess of sodium hydrate, in the proportion of 1 molecule each of phenol and chloroform, and 4 molecules of sodium hydrate, it is converted into salicyl aldehyde:

$$\underset{\substack{\text{sodium} \\ \text{phenate}}}{C_6H_5 \cdot ONa} + 3NaOH + CHCl_3 = \underset{\substack{\text{sodium} \\ \text{salicylite}}}{C_7H_6O_2Na} + 3NaCl + 2H_2O$$

The compound $C_7H_5O_2Na$ is the sodium compound of salicyl aldehyde, into which it is converted by hydrochloric acid.

**4. Ethers of Phenols.**—*Diphenyl oxide* $C_6H_5 \cdot O \cdot C_6H_5$, or $(C_6H_5)_2O$, is formed, together with other products, by the dry distillation of copper benzoate. It crystallizes in long needles that fuse at 28°. It boils at 246°, and is very soluble in alcohol and water. It is a very stable compound that cannot be reduced by either zinc or hydriodic acid.

*Methyl-phenyl oxide*, or *anisol*, or *methyl-phenyl ether*, $C_6H_5 \cdot O \cdot CH_3$ was first obtained by distilling anisic acid with barium oxide or lime:



$$C_6H_4 < \begin{matrix} OCH_3 \\ CO \cdot OH \end{matrix} = C_6H_5 \cdot O \cdot CH_3 + CO_2$$

anisic acid anisol

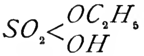
It may be prepared more readily by synthesis through the reaction of methyl iodide on potassium phenate:

$$C_6H_5 \cdot OK + CH_3I = KI + C_6H_5 \cdot O \cdot CH_3$$

It is a colorless liquid having an ethereal odor. It has a specific gravity of .991 at 15°, boils at 152°, and is insoluble in water.

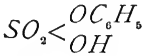
**5.** *Ethyl-phenyl oxide*, or *phenetol*, $C_6H_5 \cdot O \cdot C_2H_5$ may be obtained by a process analogous to the last method indicated for preparing anisol. It is an aromatic liquid that boils at 172°.

*Phenyl-sulphuric acid* is analogous to ethyl-sulphuric acid.



$$SO_2 < \begin{matrix} OC_2H_5 \\ OH \end{matrix}$$

ethyl-sulphuric acid



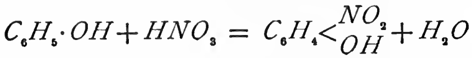
$$SO_2 < \begin{matrix} OC_6H_5 \\ OH \end{matrix}$$

phenyl-sulphuric acid

The acid is not known in the free state, but its potassium salt exists; it is formed when potassium phenate is heated with an aqueous solution of potassium pyrosulphate $K_2S_2O_7$. It exists in the urine of herbivorous animals. If phenol is ingested, it appears in the urine as potassium phenyl sulphate.

**6. Substituted Derivatives of Phenol.**—Among the very numerous compounds derived from phenol by the substitution of various elements or groups for the hydrogen of the group $C_6H_5$, only a few of the nitro and sulphonic compounds can be described here.

*Mononitrophenols* $C_6H_4<^{NO_2}_{OH}$ exist in three isomeric modifications. Two of them, the ortho- and the para-mononitrophenols, are formed by the action of nitric acid on phenol:



$$C_6H_5\cdot OH + HNO_3 = C_6H_4<^{NO_2}_{OH} + H_2O$$

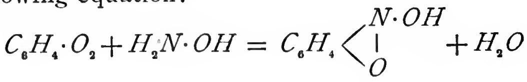
The meta derivative is obtained by indirect process.

*Orthonitrophenol* crystallizes in large yellow prisms, slightly soluble in water, fusible at 45°, and boiling at 214°. It is readily carried over with vapor of water, and may be separated from the para-isomeride.

*Metanitrophenol* is obtained in yellow crystals, fusible at 96°, and quite soluble in water. It does not distil with vapor of water.

*Paranitrophenol* deposits from its boiling aqueous solution in long colorless needles, fusible at 114°. They redden on exposure to air. Nascent hydrogen converts the mononitrophenols into amido-phenols $C_6H_4<^{NH_2}_{OH}$.

*Nitrosophenol*, or *quinone monoxime*, $C_6H_4\left\langle\begin{matrix}NOH\\ |\\ O\end{matrix}\right.$ is obtained by the action of hydroxylamine on quinone, as is seen from the following equation:



$$C_6H_4\cdot O_2 + H_2N\cdot OH = C_6H_4\left\langle\begin{matrix}N\cdot OH\\ |\\ O\end{matrix}\right. + H_2O$$

Nitrosophenol crystallizes from hot aqueous solutions in fine colorless needles. It dissolves in water, alcohol, and ether, forming pale-green solutions. It becomes brown on exposure to air, and explodes when heated to from 110° to 120°.

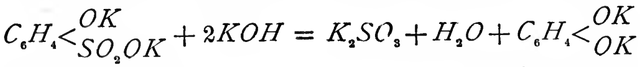
**7.** The most important of this class of compounds is *trinitrophenol* $C_6H_2(NO_2)_3\cdot OH$, or *carbazotic acid*, probably best known under the name of *picric acid*. It is prepared by dissolving 1 part of phenol in 1 part of strong sulphuric acid, and by degrees adding the solution of phenol-sulphonic acid thus obtained to 3 parts of strong nitric acid. When the violent action is over, the mixture is heated on the water bath as long as considerable red gas is evolved. On cooling, a crystalline mass of picric acid that is purified by dissolving in boiling water, filtering, and crystallizing, is obtained. It is deposited in yellow plates or prisms that are sparingly soluble in cold water, but more easily on heating, imparting a bright yellow color to a large volume of water; alcohol dissolves it readily. Its solution has an intensely bitter taste, and stains the skin and other organic matters yellow, a property that is turned into account in dyeing silk, wool, etc. When heated, the crystals fuse at 112° with partial sublimation, and explode slightly at a higher temperature, in consequence of the sudden formation of gas and the evolution of heat by the action of the $NO_2$ on the $C$ and $H$. The conversion of phenol into picric acid by the action of nitric acid may be represented by the following equation:

$$C_6H_5\cdot OH + 3HNO_3 = C_6H_2(NO_2)_3OH + 3H_2O$$

**8.** Picric acid is one of the very few acids that form sparingly soluble potassium salts. A cold saturated aqueous solution of picric acid is even a better test for potassium than is tartaric acid, giving, especially on stirring, a yellow, adherent, crystalline precipitate of *potassium picrate* $C_6H_2(NO_2)_3OK$. This salt explodes violently when heated or struck and has been used as an explosive. *Ammonium picrate* is also a very explosive salt. Picric acid precipitates several of the alkaloids. An alcoholic solution of picric acid forms crystalline compounds with several hydrocarbons in alcoholic solutions, particularly with benzene, naphthalene, and anthracene. Reducing agents, such as glucose in alkaline solutions, convert picric acid into *picramic acid* $C_6H_2(NO_2)_2(NH_2)OH$, which forms red salts. Gently heated with solution of chloride of lime, picric acid yields *chloropicrin*, or *nitrochloroform* $C(NO_2)Cl_3$, which is readily recognized by its pungent, tear-provoking odor.

**9.** Picric acid is a very common product of the action of nitric acid on organic substances; indigo, silk, and many resins furnish it in considerable quantity, especially the fragrant red resin known as "Botany Bay gum," obtained from one of the grass trees of New South Wales, which is sometimes used for preparing picric acid. It is said that picric acid is sometimes used as a hop substitute in beer; its presence may be easily and quickly determined by gently heating the suspected beer and soaking a thread of white wool in the warm liquid; should the wool take a fast yellow color, the presence of picric acid is established.

**10. Phenol-Sulphonic Acids.**—Phenol-sulphonic acid $C_6H_4{<}\begin{matrix}OH\\SO_2OH\end{matrix}$ exists in three isomeric modifications. The ortho and para compounds are formed when phenol is dissolved in concentrated sulphuric acid. The first is formed in large quantities in the cold, and is readily converted into the para derivative by heat. The excess of sulphuric acid is separated by neutralizing it with chalk, removing the calcium sulphate by filtration, and decomposing the solution of the calcium salts with potassium carbonate. When evaporated, the solution first deposits potassium para-phenol sulphonate in hexagonal plates, and the potassium ortho-phenol sulphonate afterwards crystallizes out in needles containing two molecules of water. The latter salt is very soluble in water; if heated with an excess of potassium hydrate, it is converted into pyrocatechin, as is seen from the subjoined equation:



$$C_6H_4{<}\begin{matrix}OK\\SO_2OK\end{matrix} + 2KOH = K_2SO_3 + H_2O + C_6H_4{<}\begin{matrix}OK\\OK\end{matrix}$$

potassium phenol sulphonate of potassium

potassium compound of pyrocatechin

The ortho-acid is used as an antiseptic under the name of *aseptol.* Metaphenol-sulphonic acid has also been isolated. It crystallizes in fine needles containing two molecules of water. When heated with an excess of potassium hydrate, it yields resorcinol.

**11. Cresols.**—Cresols, or *methyl phenols*, or *hydroxy toluenes*, $C_6H_4(CH_3)OH$ accompany phenol in coal tar. The *coal-tar creosote* is a mixture of phenol and cresol. The cresols may be prepared by dissolving the corresponding toluidines in sulphuric acid, adding potassium nitrite, and distilling by steam:

$$C_6H_4(CH_3)NH_2 + HNO_2 = C_6H_4(CH_3)OH + H_2O + N_2$$

Orthocresol is solid and fuses at 31°; paracresol is solid and fuses at 36°, and boils at 198°; they are metameric with benzyl alcohol $C_6H_5 \cdot CH_2 \cdot OH$. Paracresol occurs in urine, and is a product of the putrefaction of albumin; its dinitro derivative is a yellow dye, commercially known as *Victoria orange*. Metacresol and paracresol give a blue color with ferric chloride.

**12. Naphthols.**—Naphthols $C_{10}H_7 \cdot OH$ are phenols from naphthalene, and are prepared from naphthalene sulphonic acids or naphthyl amines; α-naphthol melts at 95° and boils at 282°; β-naphthol melts at 122° and boils at 285°; the latter is more soluble in water, and is used as an antiseptic. The naphthols are true phenols, but they resemble the alcohols more than do the benzene phenols. They give rise to a number of important dyestuffs that are chiefly nitro derivatives and diazo derivatives. Thus, dinitro α-naphthol $C_{10}H_5(NO_2)_2OH$ is *Martius' yellow*, or *naphthalene yellow*. The photographic developer *eikonogen* is sodium amido β-naphthol sulphonate $C_{10}H_5(OH)(NH_2)(SO_3Na)$.

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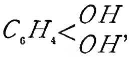
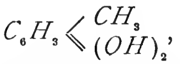
### DIHYDRIC PHENOLS OR DIHYDROXY BENZENES

**13.** Three isomeric bodies having the composition $C_6H_4(OH)_2$ are known; they are derived from benzene by the substitution of two hydroxyl groups for two atoms of hydrogen. These three bodies are pyrocatechin, resorcinol, and hydroquinone. The latter compound also belongs to this class, and will be considered in connection with the quinones.

**14. Pyrocatechin.**—Pyrocatechin 1:2  $C_6H_4{<}^{OH}_{OH}$, or *catechol*, obtained its name from the fact that it was first obtained by the destructive distillation of catechu, an astringent body extracted by boiling water from the inner bark wood of *acacia catechu*, and used in tanning. It is also produced by the distillation of gum kino and various tannins. It is generally prepared by conducting hydriodic-acid gas into guaiacol $C_6H_4(OH)(OCH_3)$ heated to 195°. The latter is obtained by distilling guaiacum, a resinous exudation from the West Indian tree, known as *lignum vitæ*. Pyrocatechin is a solid body, very soluble in water and alcohol, but only very slightly soluble in ether; it crystallizes from its aqueous solution in prisms. It melts at 104°, and sublimes below that temperature in brilliant, colorless plates. It boils between 240° and 245°. Its odor is strong and excites sneezing. It has the character of an acid like phenol itself. It dissolves in the alkalies and in the alkaline carbonates. When exposed to the air, these solutions become colored, first green, then brown, and finally black. An aqueous solution of pyrocatechin produces a deep-green color with ferric chloride, which changes to dark red on the addition of an alkali.

**15. Resorcinol.**—Resorcinol 1:3 $C_6H_4(OH)_2$ was named from *resin*, being formed when certain gums, such as galbanum, asafetida, gum ammoniac, etc., are fused with potassium hydrate. It is made on a large scale for the manufacture of colors, by fusing benzene disulphonic acid with caustic potash. The fused mass is dissolved in water, supersaturated with sulphuric acid, filtered, and the filtered solution shaken with ether, which dissolves the resorcinol. After having driven off the ether on a water bath, a residue is obtained, which is distilled; the resorcinol sublimes and condenses in radiated crystals. Resorcinol crystallizes in prisms or tables that fuse at 118°, and boil at 276°, but may be sublimed at a much lower temperature. It has a sweet taste, and dissolves readily in water, alcohol, and ether. Its solutions give a violet color with ferric chloride. Exposed to air, it absorbs oxygen and becomes brown; ammoniacal copper and silver solutions are reduced when heated with it.

The most characteristic test for resorcinol consists in heating it with phthalic anhydride, dissolving in dilute sulphuric acid, and adding ammonia, when a beautiful green fluorescence is produced.

**16. Orcinol.**—Orcinol  $C_6H_3\begin{cases}CH_3\\(OH)_2\end{cases}$, also known as 1:3:5 *dihydroxy toluene* or *orcin*, was discovered by Robiquet in 1829. It is prepared from certain lichens, which are used by dyers for preparing the colors known as litmus, cudbear, and archil; such as, *Lecanora tartarea*, or rock moss; *Roccella tinctoria*, or orchella weed, and others. The lichens are boiled with lime and water for some time, the solutions filtered, evaporated to about one-fourth of their volume, treated with $CO_2$ to precipitate the lime, and shaken with ether to extract the orcin. Some orcin appears to exist already formed in the lichens, but the greater part of it is formed by the action of the lime and water on certain acids that may be extracted from the lichens by lime in the cold, and obtained as gelatinous precipitates by adding $HCl$. Thus, *orsellinic acid* $C_6H_2CH_3(OH)_2CO_2H$, when boiled with lime, yields carbon dioxide and orcin $C_6H_3CH_3(OH)_2$. Orcin crystallizes in colorless six-sided prisms containing 1 molecule of water. It fuses at 58°, loses its molecule of water at 86°, and boils at 290°. It has a sweet taste and is soluble in water, alcohol, and ether. Its solutions are colored violet by ferric chloride. It forms a crystalline compound with 1 molecule of ammonia, and, when its solution in ammonia is exposed to air, it absorbs oxygen, giving a purple solution, from which acetic acid precipitates a red coloring matter, *orcéin* $C_7H_7NO_3$:

$$\underset{\text{orcin}}{C_7H_8O_2} + NH_3 + O_3 = 2H_2O + \underset{\text{orcéin}}{C_7H_7NO_3}$$

This substance is the chief coloring matter of the dyes prepared from lichens by mixing them with lime and urine (the latter to furnish ammonia), and exposing them to the air for some weeks. The color is pressed out, and made into cakes with chalk or plaster of Paris. Orcin only dissolves sparingly in water, but is quite readily soluble in alcohol and alkaline liquids, yielding purple solutions that are reddened by acids, orcéin being precipitated.

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## TRIHYDRIC PHENOLS OR TRIHYDROXY BENZENES

**17. Pyrogallol.**—Pyrogallol $C_6H_3(OH)_3$, also known as *pyrogallic acid*, is formed by the dry distillation of gallic acid:

$$C_6H_2(OH)_3CO_2H = C_6H_3(OH)_3 + CO_2$$

It is also formed when one of the chlorphenol-sulphonic acids is melted with caustic potash, as is seen from the following equation:

$$\underset{\text{potassium chlorphenol sulphonate}}{C_6H_3 \cdot Cl \cdot OH \cdot SO_3K} + 2KOH = \underset{\text{pyrogallol}}{C_6H_3(OH)_3} + KCl + K_2SO_3$$

It crystallizes in laminæ or needles, melts at 132°, and boils at 210°, and is easily soluble in water, ether, or alcohol. In an alkaline solution, it absorbs oxygen rapidly and becomes brown. On account of this power to absorb oxygen, it is used in gas analysis. It is a strong reducing agent, precipitating silver and mercury in the metallic state; its action on silver salts renders it useful in photography. With a solution of ferrous salt, it gives no color; but if a trace of ferric salt is mixed with the ferrous salt, a blue coloration is at once obtained. Ferric salt alone gives a red color. When heated with phthalic anhydride, it yields pyrogallol phthalein, or gallein, $C_{20}H_{10}O_7$, which is used as a red dye. When chlorine is passed through a cooled solution of pyrogallol in acetic acid, trichlorpyrogallol $C_6Cl_3(OH)_3$ is obtained, and may be crystallized in needles.

**18. Phloroglucinol.**—Phloroglucinol 1 : 3 : 5 $C_6H_3(OH)_3$, also known as *phloroglucol*, is isomeric with pyrogallol; it was first obtained from a glucoside called *phlorizin*, existing in the bark of the apple tree. It is formed in many reactions, especially when resorcinol, gum kino, dragon's blood, and other resins are fused with potassium hydrate.

Phloroglucinol crystallizes in hard rhombic prisms that have a very sweet taste. It dissolves readily in water, alcohol, and ether. Its aqueous solution is neutral, and produces a deep-violet color with ferric chloride. Its ethereal solution, evaporated upon a microscope slide, deposits prisms in tangled, tree-like forms that are very characteristic. The crystals deposited from ether are anhydrous, while those formed in water contain 2 molecules of water of crystallization, which they lose at about 100°. The dry crystals melt at 220°. The chemical character of phloroglucinol is very peculiar. While in many respects it behaves like a trihydric phenol—it forms salts with the alkalies and a triacetate with acetyl chloride—it is also capable of reacting like a triketone; with hydroxyl amine, for example, it yields the trioxime $C_6H_6(N \cdot OH)_3$. Such bodies that react as if they belonged to two distinct chemical classes are said to be *tautomeric*.

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## QUINONES

**19.** The quinones are peculiar compounds that in some way are related to the ketones. The simplest example of the class and the one that is best known, is called *quinone*. Its formula is $C_6H_4O_2$, and it appears, therefore, to be benzene in which 2 hydrogen atoms are replaced by 2 oxygen atoms. All quinones contain the group $(O \cdot O)''$, and bear the same relation to hydrocarbons that quinone bears to benzene, and they must, therefore, be regarded as oxidation products of the hydrocarbons.

**20. Quinone.**—Quinone $C_6H_4(O_2)$, which is also known as *benzoquinone*, is a product of the oxidation of quinic acid, which exists in cinchona bark. It may be obtained by distilling that acid with a mixture of manganese dioxide and sulphuric acid. The mass swells up and disengages vapors of quinone, which condense in the receiver in brilliant, golden-yellow needles. They are pressed between folds of filter paper, and purified by resublimation. It may also be obtained by heating benzene with chromyl chloride, when hydrochloric acid is evolved and a brown, solid compound produced; this is decomposed by water, with the formation of quinone, which remains dissolved in the excess of benzene:

$$(1)\quad C_6H_6 + 2CrO_2Cl_2 = 2HCl + C_6H_4(CrO_2Cl)_2$$

$$(2)\quad C_6H_4(CrO_2Cl)_2 + H_2O = C_6H_4(O_2)'' + Cr_2O_3 + 2HCl$$

Many benzene derivatives also yield quinone when oxidized. It is most easily prepared by oxidizing aniline with potassium dichromate and sulphuric acid. Quinone crystallizes in long, brilliant, transparent needles of a golden-yellow color. It melts at 115.7° to a yellow liquid; it has a pungent tear-exciting odor, and dissolves sparingly in cold water, easily in hot water, and also in alcohol and ether. Its solution stains the skin brown. Quinone acts as an oxidizing agent, liberating iodine from hydriodic acid, and becoming converted into hydroquinone $C_6H_4(OH)_2$, which is 1 : 4 dihydroxy benzene.

**21.** In many reactions, quinone behaves like a diketone; for instance, with hydroxyl amine it yields both a monoxime $O:C_6H_4:N \cdot OH$ and a dioxime $HO \cdot N:C_6H_4:N \cdot OH$. The graphic formula shown in Fig. 1 has therefore been proposed

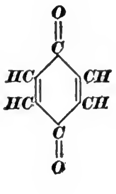


FIG. 1

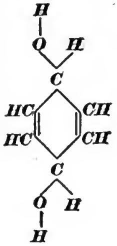


FIG. 2

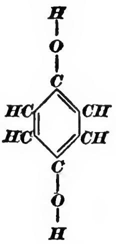


FIG. 3

by Fittig for quinone. It has been pointed out, however, that, if quinone contains true ketone groups, it should yield, when reduced, a secondary alcohol having the graphic formula shown in Fig. 2, instead of yielding, as is actually the case, the quasi-tertiary alcohol, hydroquinone, whose graphic formula is seen in Fig. 3. Moreover, when substituted quinones react with $PCl_5$, each of the $O$ atoms is replaced by one $Cl$ atom, instead of by two, as would be expected if the $O$ were doubly linked to carbon as shown in Fig. 1. These considerations led Graebe to the graphic formula shown in Fig. 4. That the oxygen atoms in quinone occupy the 1 : 4 position is shown by its easy conversion into 1 : 4 dihydroxy benzene, and by the fact that its dioxime yields 1 : 4 diamidobenzene when reduced.

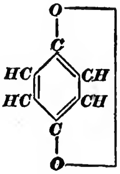


FIG. 4

**22. Hydroquinone.**—Hydroquinone $C_6H_4(OH)_2$ is formed when para-iodophenol 1:4 $C_6H_4<^{OH}_{I}$ is fused with potassium hydrate; it is formed more readily by the action of reducing agents, such as nascent hydrogen, hydriodic acid, or sulphurous acid, on quinone:

$$C_6H_4(O)_2+2H = C_6H_4(OH)_2$$

It is also found among the products of the dry distillation of quinic acid. Hydroquinone crystallizes in 6-sided prisms that fuse at 162° and sublime in monoclinic tables, so that it may be considered dimorphous. It is odorless and has a sweetish taste. It dissolves in 17 parts of water at 15°, and is very soluble in alcohol and ether. It partially decomposes when suddenly heated. When its vapor is passed through a tube heated to redness, it breaks up into quinone and hydrogen. Various oxidizing agents, such as chlorine, ferric chloride, nitric acid, silver nitrate, and potassium dichromate, convert hydroquinone into fine green metallic prisms of *green hydroquinone*, or *quinhydrone*, $C_6H_4O_2 \cdot C_6H_4(OH)_2$, which may also be obtained by mixing aqueous solutions of quinone and hydroquinone. This beautiful substance is sparingly soluble in cold water, but dissolves readily in hot water to a reddish-brown solution that deposits splendid green crystals on cooling. It dissolves in alcohol and ether with a yellow color. When heated, it fuses to a brown liquid, and partly sublimes in green plates, the remainder decomposing and giving the yellow crystalline sublimate of quinone. On boiling its aqueous solution, quinone volatilizes and hydroquinone remains in solution. It dissolves in ammonia with a deep-green color that becomes brown on exposure to air. Oxidizing agents, such as ferric chloride, added in excess, convert quinhydrone into quinone; while reducing agents, such as sulphurous acid, convert it into hydroquinone. Hydroquinone is used as a photographic developer.

**23. Tetrachloroquinone.**—Tetrachloroquinone $C_6Cl_4(O_2)$ is usually known as *chloranil;* this name was given to it by Erdmann, who first obtained this body by the action of chlorine on indigo, of which the Portuguese name is *anil.* Chloranil is formed, together with trichloroquinone $C_6HCl_3(O_2)$, from many benzene derivatives, such as phenol, aniline, salicin, isatine, etc., by the action of chlorine, or of potassium chlorate and hydrochloric acid. It is most readily prepared by gradually adding a mixture of 1 part of crystallized phenol, and 4 parts of potassium chlorate to hydrochloric acid diluted with an equal volume of water, and slowly heating the liquid. Red crystals then separate, which, on further addition of potassium chlorate, are converted into a yellow mixture of trichloroquinone and tetrachloroquinone. To separate these compounds, they are converted by sulphurous acid into the corresponding chlorohydroquinones. The tetrachloro-hydroquinone $C_6Cl_4(OH)_2$ is insoluble in water, while the trichloro-hydroquinone $C_6HCl_3(OH)_2$ dissolves. The former is then oxidized by strong nitric acid, which converts it into chloranil. This body, which is used in color making, is insoluble in water, and only sparingly soluble in alcohol, and it dissolves in ether and benzene; from the latter two liquids it is deposited in golden-yellow shining crystals. It is unattacked by even concentrate acids. It dissolves with a purple-red color in potash, and yields purple crystals of potassium chloranilate:

$$\underset{\text{chloranil}}{C_6Cl_4O_2} + 4KOH = 2KCl + 2H_2O + \underset{\substack{\text{potassium}\\ \text{chloranilate}}}{C_6Cl_2(OK)_2O_2}$$

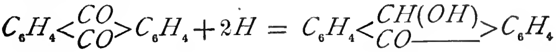
*Potassium chloranilate* is only sparingly soluble in water, but if dilute hydrochloric acid is added these crystals dissolve, and *chloranilic acid* $C_6Cl_2(OH)_2O_2,Aq$ separates out in reddish shining needles. *Bromanil* $C_6Br_4O_2$ has also been obtained from phenol.

**24. Anthraquinone.**—Anthraquinone $C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_4$ is prepared by dissolving anthracene $C_{14}H_{10}$ in glacial acetic acid, and adding chromic anhydride to the hot solution; then, on adding water, the anthraquinone is precipitated, and may be purified by sublimation. Anthraquinone forms rhombic crystals and does not possess the odor of quinone. It sublimes in yellow needles, is insoluble in water, but slightly soluble in alcohol and ether. It is an extremely stable compound, resisting the action of alcoholic potash and all oxidizing agents. Melted with solid potassium hydrate, it yields potassium benzoate, as is seen from the subjoined equation:

$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_4 + 2KOH = 2C_6H_5\cdot COOK$$

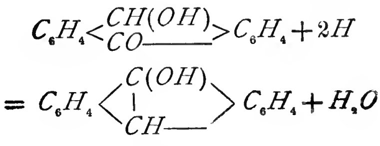
anthraquinone potassium benzoate

Reducing agents convert it into the secondary alcohols, oxanthranol, or hydroxy anthranol, $C_{14}H_{10}O_2$ and *anthranol* $C_{14}H_{10}O$, and, finally, into anthracene $C_{14}H_{10}$. These changes may be represented thus:



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_4 + 2H = C_6H_4{<}\begin{matrix}CH(OH)\\CO\text{———}\end{matrix}{>}C_6H_4$$

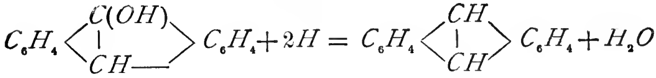
oxanthranol



$$C_6H_4{<}\begin{matrix}CH(OH)\\CO\text{———}\end{matrix}{>}C_6H_4 + 2H$$

$$= C_6H_4\left\langle\begin{matrix}C(OH)\\ | \\ CH\text{——}\end{matrix}\right\rangle C_6H_4 + H_2O$$

anthranol



$$C_6H_4\left\langle\begin{matrix}C(OH)\\ | \\ CH\text{——}\end{matrix}\right\rangle C_6H_4 + 2H = C_6H_4\left\langle\begin{matrix}CH\\ | \\ CH\end{matrix}\right\rangle C_6H_4 + H_2O$$

anthracene

Hence, anthraquinone is more nearly a true diketone than is benzoquinone. When heated with zinc dust, it yields anthracene. A great many derivatives of anthraquinone have been prepared. Among the best known are the hydroxyl derivatives, some of which are much prized dyes and manufactured on a very extensive scale.

**25. Alizarine.**—Alizarine $C_6H_4(CO)_2C_6H_2(OH)_2$, or *dihydroxy anthraquinone*, is the name applied to the coloring substance of madder, the root of *Rubia tinctorum*, which Robiquet was the first to extract in the pure state. Graebe and Liebermann made its synthesis in 1868 by heating dibrom anthraquinone to 200° with potassium hydrate:

$$\underset{\text{dibrom anthraquinone}}{C_6H_4(CO)_2C_6H_2Br_2} + 2KOH$$
$$= 2KBr + \underset{\text{alizarine}}{C_6H_4(CO)_2C_6H_2(OH)_2}$$

Alizarine does not exist already formed in the madder plant, but the latter contains a glucoside, to which Robiquet has given the name *ruberythric acid*, that undergoes hydrolysis when acted on by acids or when allowed to ferment, and thus is converted into alizarine and glucose, as is seen from the equation:

$$\underset{\substack{\text{ruberythric}\\\text{acid}}}{C_{26}H_{28}O_{14}} + 2H_2O = \underset{\text{alizarine}}{C_{14}H_8O_4} + \underset{\text{glucose}}{2C_6H_{12}O_6}$$

**26.** Alizarine may be extracted from madder by boiling the latter with a solution of alum. The filtered liquid, if left standing for some days, deposits impure alizarine as a brown-red precipitate, and holds in solution another coloring matter that is known as *purpurin*. The precipitated alizarine is then filtered off and purified by washing with dilute hydrochloric acid and by dissolving in alcohol and crystallizing it therefrom. These crystals are again treated with a boiling solution of alum, in order to remove any traces of purpurin that might have been precipitated with the alizarine, and finally dissolved in ether, which again deposits it in pure crystals.

Alizarine is now exclusively prepared on a large scale from anthracene. This hydrocarbon is converted into anthraquinone, and the latter body treated with fuming sulphuric acid, to convert it into anthraquinone sulphonic acid. The sodium salt of this acid, sodium anthraquinone sulphonate, is fused with sodium hydrate, and a small quantity of potassium chlorate is added to the fused mass.

$$\underset{\substack{\text{sodium anthraquinone}\\ \text{sulphonate}}}{C_6H_4(CO)_2C_6H_3\cdot SO_3Na} + 3NaOH + O_2$$

$$= \underset{\text{sodium alizarate}}{C_6H_4(CO)_2C_6H_2(ONa)_2} + Na_2SO_4 + 2H_2O$$

The sodium alizarate is dissolved in water, precipitated by hydrochloric acid, and the precipitate purified by crystallization from toluene, and, finally, by sublimation.

Alizarine crystallizes in long, brilliant, orange-yellow prisms with 3 molecules of water. It is very sparingly soluble in cold water, more readily in boiling water, and easily dissolves in alcohol and ether. It fuses at about 275°, and may be sublimed. It dissolves in strong sulphuric acid with a deep-red color, and is precipitated by water. It acts like a dibasic acid, dissolving in alkalies to purple solutions that give purple-blue precipitates with salts of barium and calcium. The insolubility and the brilliant colors of the alizarates are of great value in dyeing and calico printing. Alizarine gives red precipitates (technically known as *madder lakes*) with salts of tin and aluminum, and a dark violet with salts of iron.

**27. Purpurin.**—Purpurin $C_6H_4(CO)_2C_6H(OH)_3$ is another coloring matter that may be extracted from madder, and has been mentioned in Art. **26.** It appears, like alizarine, to exist in the plant as a glucoside, and may be separated from alizarine by boiling with alum, which only dissolves the purpurin. Purpurin also dissolves readily in alcohol and ether, producing red solutions. It crystallizes from weak alcoholic solutions in orange-colored needles with 1 molecule of water of crystallization, while from absolute alcohol it deposits in red anhydrous needles. It melts at about 254°, and sublimes in red needles. Purpurin is oxyalizarine or 1:2:4 trihydroxy-anthraquinone. It may also be obtained by oxidizing natural alizarine with $MnO_2$ and $H_2SO_4$. It undergoes a complete reduction, and is converted into anthracene when heated with zinc dust.

Isomeric with purpurin is *flavopurpurin* and *anthrapurpurin* $C_6H_3 \cdot OH \cdot (CO)_2 \cdot C_6H_2(OH)_2$, both of which are contained in commercial alizarine. Anthrapurpurin closely resembles alizarine, but it fuses at a higher temperature (330°), and is more soluble in water. The colors of its metallic salts are far more brilliant than those of the alizarates, so that their presence in commercial alizarine, when used as a dye, is rather of advantage than otherwise. Flavopurpurin crystallizes in golden needles that are soluble in alcohol.

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### TRIPHENYL-METHANE DYESTUFFS

**28.** These compounds include the greater number of the colors commonly known as *aniline dyes*. It is, of course, impossible to treat all the aniline dyes and their manufacture here, and for information as to the chemical constitution of less important dyes, the student must consult a work on aniline dyes or dyestuffs. Although these compounds are amido or hydroxyl derivatives, consideration of them has been postponed until quinone has been described, on account of the fact that these dyestuffs contain a benzene nucleus to which other groups are attached in a manner similar to that in which the oxygen atoms of quinone are attached to the benzene ring—a formation that is generally known as *quinonoid structure*. The parent substance of the aniline dyes, *triphenyl methane* $CH(C_6H_5)_3$, has been described in a previous Section. When a solution of this compound in acetic acid is oxidized by chromic acid, it yields *triphenyl carbinol* $(C_6H_5)_3C \cdot OH$, a tertiary alcohol that crystallizes in prisms and melts at 159°.

**29.** When three amido groups or three hydroxyl groups are introduced into triphenyl methane, compounds are produced that are colorless, but readily become colored when oxidized and treated with an acid. For example, triamido-triphenyl methane $CH(C_6H_4NH_2)_3$ is a colorless substance; when oxidized it becomes triamido-triphenyl carbinol $C(OH)(C_6H_4NH_2)_3$, which is also a colorless substance, and yields colorless salts when treated with cold acids, but colored salts when treated with warm acids. The latter salts are dyestuffs; they are formed from the carbinol with the loss of 1 molecule of water, and, since the only oxygen in the carbinol is that of the alcoholic group $OH$, it must be supposed that this group forms water with the hydrogen of the acid. The loss of the $OH$ group entails the conversion of the ordinary benzene linking of one of the benzene rings into the quinonoid linking, the change being accompanied by a development of color, just as the conversion of the ordinary linking of the colorless hydroquinone (see Fig. 3) into the quinonoid linking of quinone (see Fig. 1) develops a color, $HO\cdot C_6H_4\cdot OH$ becoming $O:C_6H_4:O$. The following equation will make this change clearer:

$$HCl,NH_2\cdot C_6H_4\cdot C(OH)(C_6H_4\cdot NH_2)_2$$

triamido-triphenyl-carbinol
hydrochloride (colorless)

$$= ClNH_2:C_6H_4:C(C_6H_4\cdot NH_2)_2+H_2O$$

pararosaniline chloride
(colored salt)

**30.** The foregoing reactions are typical of the behavior of every triphenyl-methane dyestuff; that is to say, each may be obtained by oxidizing a derivative of triphenyl methane and treating the product with a warm acid. The parent triphenyl-methane derivative is called the *leuco-base* of the dyestuff; the carbinol into which it is converted by oxidation is called the *color base* of the dyestuff, while the colored salt is the dyestuff itself. Thus, triamido-triphenyl methane is called *leuco-pararosaniline;* triamido-triphenyl carbinol is the pararosaniline base; while the colored salt with the quinonoid linking is pararosaniline chloride. The converse changes are possible; that is to say, by treating the dyestuff with a caustic alkali, the colorless base is precipitated, and, if this is treated with a reducing agent (nascent hydrogen, for instance), it yields the leuco-base.

**31. Classification of Triphenyl-Methane Dyestuffs.** The triphenyl-methane dyestuffs are classified into derivatives of:

1. Diamido-triphenyl methane $C_6H_5 \cdot CH(C_6H_4 \cdot NH_2)_2$; the type of these is *malachite green.*
2. Triamido-triphenyl methane $CH(C_6H_4 \cdot NH_2)_3$; the type of these is *rosaniline* (magenta).
3. Trihydroxyl-triphenyl methane $CH(C_6H_4 \cdot OH)_3$; the type of these is *aurine.*
4. $CH(C_6H_5)_2(C_6H_4 \cdot CO_2H)$, or triphenyl-methane carboxylic acid; the type of these is *eosin.*

**32. Malachite Green.**—Malachite green is *tetramethyl 1:4 diamido-triphenyl-methane chloride*

$$ClN(CH_3)_2 : C_6H_4 : C(C_6H_5)[C_6H_4 \cdot N(CH_3)_2]$$

The leuco-base of this dyestuff is prepared by heating benzaldehyde with dimethyl aniline and zinc chloride (the latter compound to act as a dehydrating agent):

$$C_6H_5 \cdot CHO + 2C_6H_5 \cdot N(CH_3)_2$$
$$= C_6H_5 \cdot CH[C_6H_4 \cdot N(CH_3)_2]_2 + H_2O$$

The leuco-base is oxidized by $PbO_2$ (when it yields the corresponding carbinol or color base; see Art. **30**), in the presence of $HCl$ (to produce the color salt). The dyestuff is then precipitated by zinc chloride and sold in the form of a double zinc salt.

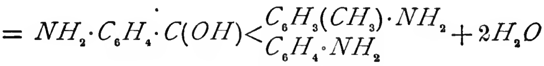
**33. Rosaniline Salts.**—Rosaniline salts constitute the bulk of the dyestuff known as *magenta* (fuchsine). They are formed by the action of acids on a rosaniline base, which is triamido-tolyl-diphenyl carbinol

$$NH_2 \cdot C_6 \cdot H_3(CH_3) \cdot C(OH)(C_6H_4 \cdot NH_2)_2$$

The chloride $ClNH_2 : C_6H_3(CH_3) : C(C_6H_4 \cdot NH_2)_2$, nitrate, and acetate are the salts most frequently used in commerce. They are prepared by heating aniline oil, which should contain equal molecular proportions of aniline, orthotoluidine, and paratoluidine, with an oxidizing agent, for which purpose either arsenic acid or nitrobenzene is generally used.

$$NH_2 \cdot C_6H_4 \cdot CH_3 + C_6H_4(CH_3) \cdot NH_2 + C_6H_5 \cdot NH_2 + O_3$$

aniline oil*



$$= NH_2 \cdot C_6H_4 \cdot C(OH) < \begin{matrix} C_6H_3(CH_3) \cdot NH_2 \\ C_6H_4 \cdot NH_2 \end{matrix} + 2H_2O$$

triamido-tolyl-diphenyl carbinol

The rosaniline base obtained in this way is converted into the chloride by adding hydrochloric acid, and this salt is precipitated by adding sodium chloride. When recrystallized, rosaniline salts form bronze-green crystals that are sparingly soluble in cold water, but more readily in hot water, forming a red solution. When the hot solution is mixed with ammonia and filtered quickly, the rosaniline base crystallizes from the filtrate in colorless plates, which become red when exposed to the air, from the absorption of $CO_2$. Reducing agents bleach the red solution with formation of *leucoaniline* $NH_2 \cdot C_6H_3(CH_3) \cdot CH(C_6H_4 \cdot NH_2)_2$, the leuco-base of rosaniline.

**34.** *Pararosaniline* $C(OH)(C_6H_4 \cdot NH_2)_3$, or *triamido-triphenyl carbinol*, is prepared by oxidizing a mixture of paratoluidine (1 molecule) and aniline (2 molecules) in the same way as was described for rosaniline. The salts are red dyestuffs like those of rosaniline. Many derivatives of pararosaniline and rosaniline containing methyl, ethyl, and phenyl groups, in place of the amido-hydrogen atoms, are prepared by heating pararosaniline or rosaniline hydrochloride with alkyl or phenyl halides; these are also used as dyestuffs, the shades produced by them becoming more blue as successive alkyl or phenyl groups are introduced. Thus, *pentamethyl pararosaniline* is known as *methyl violet*, and *triphenyl-rosaniline chloride* is known as *aniline blue*. The combination of hexamethyl rosaniline (which is saturated with methyl groups)

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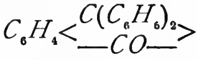
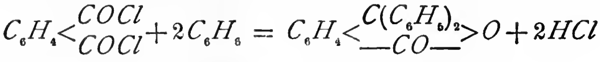
* Aniline oil contains a mixture of equal molecular proportions of aniline, ortho-, and para-toluidine.

with methyl chloride or iodide produces a green dyestuff known as *iodine green.*

**35. Aurine.**—When a pararosaniline base is diazotized, the three $NH_2$ groups are converted into diazo groups, and when the resulting compound is boiled with water, it yields *trihydroxyl-triphenyl carbinol* $(C_6H_4 \cdot OH)_3C \cdot OH$. This is a rather unstable compound that readily loses 1 molecule of water, becoming *aurine* $O : C_6H_4 : C(C_6H_4OH)_2$. It crystallizes in green needles that dissolve in alkalies to a red solution, but are precipitated again by acids. Thus, aurine behaves as an acid substance, as, indeed, is to be anticipated, from the presence of phenolic $OH$ groups. It may be mentioned that, while pararosaniline is a type of basic dyestuffs tending to combine with acid mordants, aurine is a type of acid dyestuffs tending to combine with basic mordants.

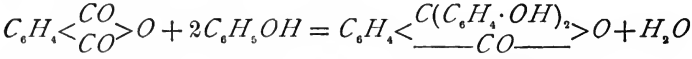
**36. Eosin.** — Triphenyl-methane carboxylic acid (see Art. **31**), or rather its hydroxyl derivative, triphenyl carbinol 1 : 2 carboxylic acid $(C_6H_5)_2(C_6H_4 \cdot COOH)C \cdot OH$, gives rise to the dyestuffs of this class. *Phthalophenone* is the anhydride of this latter acid, its formula being  $C_6H_4{<}\genfrac{}{}{0pt}{}{C(C_6H_6)_2}{—CO—}{>}O$, and it is prepared by the interaction of phthalic chloride with benzene in the presence of aluminum chloride.



$$C_6H_4{<}\genfrac{}{}{0pt}{}{COCl}{COCl}+2C_6H_6 = C_6H_4{<}\genfrac{}{}{0pt}{}{C(C_6H_6)_2}{—CO—}{>}O+2HCl$$

phthalic chloride benzene phthalophenone

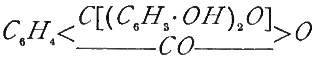
It yields triphenyl-methane carboxylic acid when reduced. By substituting phthalic anhydride for the chloride, and hydroxyl benzenes for benzene in this reaction, the eosin dyestuffs are obtained. Thus, *phenol phthalein* (dihydroxyl phthalophenone) is obtained when phthalic anhydride is heated with two molecular proportions of phenol in the presence of a dehydrating agent:



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}O+2C_6H_5OH = C_6H_4{<}\genfrac{}{}{0pt}{}{C(C_6H_4 \cdot OH)_2}{——CO——}{>}O+H_2O$$

phthalic anhydride phenol phenol phthalein

The mass is dissolved in an alkali solution, and the phenol phthalein precipitated by an acid. Its alkaline salts are pink in solution, and being derived by the displacement of hydrogen from the phenolic hydroxyl, are decomposed by the feeblest acid, so that phenol phthalein is a very useful substance as an indicator in acidimetry; but it can hardly claim to be a dyestuff.

**37.** *Fluorescein*  $C_6H_4<\genfrac{}{}{0.4pt}{}{C[(C_6H_3\cdot OH)_2O]}{CO}>O$ is obtained when phthalic anhydride is heated with resorcinol, 2 molecules of water being liberated. It forms red crystals and dissolves in dilute alkalies, giving a red solution with a green fluorescence; this is also noticeable on the dyed material, hence the dyestuff is frequently mixed with others for producing a fluorescent green.

**38.** Eosin itself is a tetrabromo derivative of fluorescein, and is made by brominating the latter in an acetic-acid solution. It dissolves in alkalies, giving a deep-red solution that fluoresces green when diluted.

## CARBOHYDRATES

**39.** Among the more widely distributed products of the vegetable kingdom must be included the various kinds of sugar, starch, gum, and the matter of young vegetable cells, or cellulose.

Most of these compounds contain carbon, hydrogen, and oxygen in such proportions that the oxygen is present in exactly sufficient quantity to form water with the hydrogen. Their composition is then expressed by the general formula $C_m(H_2O)_n$. If all the oxygen and hydrogen were removed in the form of water, only carbon would remain, hence the name *carbohydrates*, or *hydrated carbons*. The carbohydrates may be suitably divided into two classes: (1) the sugars and (2) the starches and celluloses.

## SUGARS

**40.** The sugars may be subdivided into *glucoses*, *monosaccharides*, or *monoses*, having the general formula $C_n(H_2O)_n$, and disaccharides, or sucroses, or dioses, having the general formula $C_n(H_2O)_{n-1}$. Hydrolysis resolves the sugars of the second class into those of the first class. The type of the sugars of the glucoses is grape sugar, and that of the disaccharides is cane sugar. Since the sugars contain asymmetric carbon atoms, they give rise to a large number of stereoisomerides.

### GLUCOSES OR MONOSACCHARIDES

**41.** The glucoses are the simplest carbohydrates. Those that are best known have the composition $C_6H_{12}O_6$, and are related to the hexatomic alcohols, sorbite and mannite $C_6H_8(OH)_6$. There are, however, simpler ones, such as arabinose $C_5H_{10}O_5$, erythrose $C_4H_8O_4$, etc.; and, again, some are more complex, as, for instance, *heptose* $C_7H_{14}O_7$ and *octose* $C_8H_{16}O_8$. The monosaccharides, therefore, fall into classes that are called *trioses*, *tetroses*, *pentoses*, *hexoses*, *heptoses*, etc. according to the number of oxygen atoms contained in them. Constitutionally, they are either *aldehyde alcohols* containing the group $\cdot CH(OH) \cdot CHO$ or *ketone alcohols* containing the group $\cdot CO \cdot CH_2 \cdot OH$.

**42. Trioses and Tetroses.**—*Glycerose* $C_3H_6O_3$ deserves special mention as being the simplest member of the monosaccharides, and as having been obtained synthetically. It is formed by treating glycerine with oxidizing agents, such as sodium hydrate and bromine. It is a syrupy liquid that undergoes fermentation and reduces alkaline solutions of copper salts, thus acting like many of the sugars, as will be seen further on. *Erythrose* $C_4H_8O_4$ has been obtained from erythrite in the same way that glycerose is obtained from glycerine.

**43. Pentoses.**—These are the lowest well known members of the monosaccharides; they are natural sugars occurring in various plants. *Arabinose* $C_5H_{10}O_5$ is obtained from gum arabic by boiling it with dilute sulphuric acid. It crystallizes in prisms, has a sweet taste, and is strongly dextrorotary. *Xylose* $C_5H_{10}O_5$ is obtained from wood gum by boiling it with dilute acids. *Rhamnose* $C_6H_{12}O_5$ has been obtained by decomposing a number of natural substances, such as quercitrin, etc. It has been shown to be a methyl derivative of a pentose, and is, therefore, more correctly represented by the formula $CH_3 \cdot C_5H_9O_5$.

**44. Hexoses.**—These are the compounds generally called *glucoses*. They are widely distributed in nature, but are mainly found in unripe fruit, the chief compounds being dextrose (grape sugar) and levulose (fruit sugar). They are produced by the hydrolysis of the disaccharides and polysaccharides, the change being effected mostly by either dilute acids or alkalies.

**45.** *Grape sugar*, or *glucose* (formerly called *dextrose*), $CH_2OH(CHOH)_4 \cdot CHO$ is the crystallized sugar found in honey, raisins, and many other fruits; it is nearly always accompanied by levulose, which is far more difficult to crystallize, and which is metameric with it. Dextrose is also found in small quantities in several animal fluids, and in the liver, and is always present in diabetic urine. Glucose may be obtained from honey by mixing it with cold alcohol to dissolve the levulose, which forms about one-third of its weight, and leaves about an equal quantity of dextrose, which may be dissolved in boiling alcohol and crystallized therefrom. To extract grape sugar from fruits, these are crushed with water and strained, and the liquid is then boiled to coagulate the albumin, filtered, evaporated to a syrup, and set aside for some days, when crystals of glucose are deposited. Fresh fruits contain chiefly levulose, which, however, is gradually converted into glucose.

**46. Glucose Manufacture.**—In this country, glucose is prepared on the large scale from corn starch, and in Germany from potato starch, the transformation being usually effected by boiling with dilute sulphuric acid. The excess of acid is removed by treating the solution with chalk, and filtering. The filtered solutions are evaporated down, either to a syrupy consistency and sent into the market as "glucose," "mixing syrup," etc., or to dryness, the solid product being known in commerce as "grape sugar." By evaporating the solutions down to such a concentration that they contain from 75 to 80 per cent. glucose, and crystallizing at a temperature of 32° crystals are formed that closely resemble those of cane sugar. They consist of anhydrous grape sugar; their formation is facilitated by adding a little of the crystallized substance to the concentrated solutions. If, in the treatment of starch with sulphuric acid, the transformation is not complete—and this is usually the case—the product will be a mixture of glucose, maltose, and dextrin. The longer the action continues, the larger the percentage of glucose.

Glucose crystallizes from concentrated solutions at ordinary temperature in small, white, rounded masses with 1 molecule of water of crystallization. The mass as seen in commercial "granulated grape sugar" looks very much like ordinary granulated sugar. These crystals remain unchanged in the air, but melt when heated on the water bath, and at 100° lose their water of crystallization. Anhydrous glucose deposited from alcoholic solutions melts at 146°. Glucose dissolves in about its own weight of water at 17°. It is one-third as soluble as cane sugar, and, in solutions of equal concentration, is about one-third as sweet. It is much less soluble in alcohol than in water. Its solutions turn the plane of polarization to the right, and the deviation varies with the strength of the solution. When heated to 170°, glucose loses the elements of water and its sweetness, and is converted into a colorless mass known as *glucosan:*

$$\underset{\text{glucose}}{C_6H_{12}O_6} = \underset{\text{glucosan}}{C_6H_{10}O_5} + H_2O$$

Glucose forms true compounds with metals and salts; among the better known compounds may be mentioned *sodium glucose* $C_6H_{11}O_6Na$, *sodium-chloride glucose* $2C_6H_{12}O_6 \cdot NaCl, H_2O$, and *calcium glucose* $C_6H_{10}O_6Ca, H_2O$. If potassium hydrate is added to a solution of glucose, and the liquid heated, it first becomes yellow, and then rapidly assumes a deep-brown color. The same color is produced when glucose is heated with either calcium or barium hydrate. As ordinary cane sugar does not produce this reaction, this may serve as an easy means to distinguish between glucose and cane sugar. Glucose reduces various metallic solutions. Gold and silver are precipitated by it from their solutions. If a solution of cupric sulphate is poured into a solution of glucose, and potassium or sodium hydrate is added, no precipitate is formed, but the liquid acquires a dark-blue color. On heating, a red precipitate of cuprous oxide is formed (method of detecting sugar in urine). Glucose is much used by brewers and distillers for making alcohol, as well as by confectioners; dyers use it to reduce indigo.

**47.** *Levulose* $CH_2OH \cdot (CHOH)_3 \cdot CO \cdot CH_2OH$, or *fruit sugar*, is distinguished from glucose by turning the plane of polarization to the left. It occurs, together with glucose, in honey, many fruits, and various other substances. The mixture of equal parts of glucose and levulose constitutes *invert sugar*, which is levorotary, because the specific rotary power of levulose, at ordinary temperature, is greater than that of glucose.

Cane sugar may be inverted, that is, transformed into a mixture of equal parts of glucose and levulose, by gently warming with dilute acids:

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{levulose}}{C_6H_{12}O_6}$$

The same reaction is brought about by contact with yeast, or when a solution of cane sugar is allowed to stand for some time. To separate the levulose, the invert sugar obtained from 10 grams of cane sugar is mixed with 6 grams of slaked lime and 100 cubic centimeters of water, whereby a solid calcium compound of levulose is formed, while the whole of the glucose remains in solution and may be readily separated from the precipitate. The calcium salt of levulose, suspended in water and decomposed by $CO_2$, yields a solution of pure levulose, which may be filtered and concentrated by evaporation.

Levulose is much sweeter than glucose, rivaling cane sugar in this respect. It does not ferment as readily as glucose, so that, when invert sugar is mixed with yeast, the glucose is the first to disappear. It also reduces alkaline cupric solutions (Fehling's solution) less rapidly. Levulose rotates the plane of polarization to the left—whence its name—but a dextro and an inactive levulose also exist. When heated to 170°, levulose loses 1 molecule of water, and is converted into *levulosan*:

$$\underset{\text{levulose}}{C_6H_{12}O_6} = \underset{\text{levulosan}}{C_6H_{10}O_5} + H_2O$$

This compound is dextrorotary.

**48.** *Galactose* $CH_2 \cdot OH \cdot (CH \cdot OH)_4 CHO$ is produced, together with glucose, by boiling milk sugar with dilute sulphuric acid. It is soluble in water, but sparingly soluble in cold alcohol; it crystallizes in rhombic prisms that are less sweet than cane sugar, and melts at 163°. It has a dextrorotary power, and is very easily fermentable. It resembles glucose in most of its reactions.

**49.** *Mannose* $CH_2 \cdot OH(CH \cdot OH)_4 CHO$ is another stereoisomerism of glucose. It was first obtained as a product of the oxidation of mannitol. It has since been observed among the substances that result from the hydrolysis of certain naturally occurring carbohydrates, such as reserve cellulose. Mannose forms friable masses that are very soluble in water, difficultly soluble in alcohol, and insoluble in ether. It is dextrorotary and fermentable with yeast.

**50.** *Sorbinose* $CH_2OH \cdot (CH \cdot OH)_3 \cdot CO \cdot CH_2 \cdot OH$ is crystallized from the juice of the mountain-ash berry, after it has been allowed to ferment. It is levorotary, and ferments only slowly with yeast.

### DISACCHARIDES

**51.** The members of this class of sugars are characterized by being converted by hydrolysis into 2 molecules of glucose; hence, the name *bioses* is given to this class of compounds.

**52. Cane Sugar.**—Cane sugar $C_{12}H_{22}O_{11}$, also known as *saccharose*, or *sucrose*, is not only found in sugar cane, but is found widely distributed in nature. It occurs in sorghum, the Java palm, the sugar maple, beets, madder roots, coffee, walnuts, sweet and bitter almonds, in the blossoms of many plants, in honey, etc. It is mainly obtained from sugar cane and white-beet roots, the former containing about 18 per cent. and the latter between 13 and 18 per cent. of sugar, varying according to climate, soil, and cultivation. As the manufacture of sugar from beet roots is a comparatively new industry in the United States, but one that promises to assume enormous proportions, it is deemed appropriate to describe here the process of extracting the sugar.

The beets, after reaching maturity, are loosened from the soil by means of special plows, the tops removed with one stroke of the knife, at a point that is marked by the lower circle of dried leaves, and the beets thrown into wagons. The wagon load of beets, on reaching the factory, is first weighed, and then driven up an inclined bridge that reaches the dumping platform of the beet sheds. A chain attached to one side of the platform is then connected with the body of the wagon to prevent it from sliding off the platform when being dumped. The platform is then partially inverted, which results in the beets falling into the bins below. At the bottom of these bins is a covered concrete flume about 18 inches deep and 14 inches wide. When these covers, which are about 2 feet long, are removed, the beets fall into the flume and are carried along by a swift current of water to the factory. The first process, on arriving there, is a purely mechanical one, and is called the *washing*. By this operation, adhering particles of dirt and leaves (called *tare*)

are separated from the beets in a specially devised apparatus that keeps the beets agitated in a flow of clean pure water. The washer is about 10 feet long and 3 feet deep, and has a shaft running through the center, to which are attached about a dozen arms. The clean beets overflow into iron buckets attached to an elevator chain that delivers them to the slicer on the third floor of the factory, where they are cut up into small strips, called *cossettes*, about 2 inches long, $\frac{1}{4}$ inch wide, and $\frac{1}{16}$ inch thick. The cutter consists of a rapidly revolving disk, about 3 feet in diameter, in which are placed sets of knifes so arranged that at every revolution a certain number of cossettes are sliced off the beets, which are placed directly over the knives. The cossettes are collected by means of a chute directly under the cutter or slicer, down which they slide into the cell of the diffusion battery. The diffusion battery consists of 14 cells placed in a circle, and so connected by pipes that water or juice can flow through one from top to bottom, and immediately pass to the next, which it traverses in like manner, and so on throughout the entire circle. At the top and bottom of each cell are doors that are used for filling the vats with the cossettes, and after the sugar is extracted those at the bottom are used for emptying out the pulp (exhausted cossettes). The cells are about 10 feet high and 4 feet in diameter, and contain about $2\frac{1}{2}$ tons of cossettes when filled. The cells are filled and emptied in regular order in conformity with their position in the circle and at the rate of about 8 to 10 an hour. Each time a cell is filled, a certain quantity of the fresh juice, which has traveled the entire circle and has been through this particular cell last, is drawn off into the workings of the factory, into what is known as the *measuring tank.* The juice has the appearance of black, muddy water, in which flocculent particles are clearly seen. The pulp from which the sugar has been extracted is conveyed from the bottom of the battery by means of a helix to a press, where the surplus of water is pressed out; thence by carts, or otherwise, to the silo, where, after it has become sour, it is fed to cattle, etc.

**53.** The charge of juice, after having passed the measuring tank, is forced through the "calorizators," or heaters, to the carbonators. There the juice is heated to about 70°, to cause coagulation of the albuminoids. A calorizator has the appearance of a very short steam boiler, except that in this case the juice flows through the tubes and the steam is in the interior. This is the first process of clarification, and it is a very important one. At the carbonators, a quantity of milk of lime, equal in bulk to about one-tenth of the juice therein contained, is allowed to flow in from a small tank situated directly above. This milk of lime is added, not only to separate certain impurities that form insoluble compounds with the lime, but also to prevent the juice from becoming altered by reason of its acidity. As the sugar itself dissolves a large quantity of lime, the latter must be eliminated. A current of carbon dioxide is consequently passed into the solution, and decomposes the saccharate of lime formed there. The precipitates still remaining are removed at the filter presses, of which we will speak later on. The carbonators are usually nine in number, and are arranged so that each will hold two charges from the measuring tank; they are about 12 feet long, 9 feet deep, and 5 feet wide, being supplied on the inside bottom with steam coils and gas injectors. There are two sets of carbonators, called *first* and *second.*

The operation is practically the same in both, except that in the second, less lime is used, and the heating is conducted differently. After the juice has been brought down to a certain degree of alkalinity by means of the carbon dioxide, it is forced through filter presses, which remove the precipitate and other mechanical impurities.

The presses are made of about forty frames, hollow on the inside, and about 3 feet high, 3 feet deep, and 1 inch thick. Between these frames is placed canvas, and the whole arrangement is tightened by using a screw at one end. The turbid juice is forced into the cavities in the frames, and, in order to get out, it must pass through the cloth, thereby leaving the sediment behind. The juice, on leaving this stage, has a bright amber color. It is pumped to the sulphuring tanks, where fumes, produced by burning sulphur, are forced into it. The action of the sulphur dioxide is mainly for the purpose of decolorizing, although some lime is at the same time precipitated. The sulphuring is controlled by making tests of the alkalinity of the juice, and by observing the color. If properly conducted, the juice should have, after passing through this treatment, the appearance of clean water. The juice, after being sulphured, undergoes another filtering in what are called *mechanical filters*. These filters are iron boxes about 4 feet square on top, and 3 feet deep, and are supplied with a cover, which may be removed to take out the bags. The action of these filters is just the reverse of pouring a liquid into a bag and having it filtered through, for in this case the juice flows from the outside of the bag to the inside, and then over and out of the top of the filter. The bags are stretched over copper frames to prevent them from collapsing during the operation.

This process completes the clarification, and the juice is then ready to be concentrated, an operation that is done in the apparatus known as the *quadruple effects*. These are, as the name indicates, four in number, and each is composed of two apartments—one for the steam, and the other, occupying over two-thirds of the space of the "effect," for the juice and vapors that arise from the boiling. The arrangement is such that a vacuum pump connected to the condenser of the fourth effect causes a vacuum in each (of different degrees), so that the juice can be readily drawn from one to the other, as desired. Another reason why this process is conducted in a vacuum is to prevent the loss of sugar due to excessive heat. Each effect is about 12 feet long, 11 feet wide, and 10 feet high. A large vapor pipe 20 inches in diameter runs from the top of the first to the steam chest of the second, and, in a like manner, from the second to the third, and so on, uniting them all. The idea of the arrangement is this: The steam turned into the steam chest of the first boils the juice in that effect; the vapor arising from this goes over and boils the juice in the next, and so on, until they are all boiling at once. As the juice is concentrated, they draw from one to the other to maintain a constant level. When the density of the last is at the required point, about 25° Baumé, the juice is pumped into the vacuum pan where it is boiled to grain.

The vacuum pan has the general appearance of a large hollow globe; it is about 11 feet in diameter, and is made of cast iron, put together in segments.

The vacuum is caused by a large pump, and the operation of boiling is conducted in the following manner: A vacuum is produced by means of the pump, then the juice is drawn in to a certain level, steam is turned into the copper coils situated in the bottom, and the juice boils. When the juice has boiled down to a certain density (about 43° Baumé), small grains of sugar appear. When the grains are sufficient in number, in the opinion of the operator, more juice is drawn in. The new lot, instead of starting new grains, deposits on the first; the operation from here on is a continual drawing in and boiling down, until the pan is full. It is then let out into the mixer by a large valve placed directly in the bottom. The mixer is a large **V**-shaped trough with a shaft, on which are placed arms that keep the *melada* from solidifying. This melada, or boiled juice, has the appearance of a thick pasty mass of sugar and molasses. The mixer is about 30 feet long, 10 feet wide at the top, and 7 feet deep. Attached directly below are the centrifugals, eight in number, which receive the melada through short spouts that are controlled by means of a tight-fitting gate. The centrifugals are of the general appearance of those used in laundries, being supplied with a screen on the side, and revolve about a thousand times a minute. A charge of melada (about 200 pounds) is drawn into the centrifugal, and the apparatus is set revolving. After about 10 minutes, the molasses is thrown off and a small spray of water is directed against the sugar adhering to the sides of the machine; this completes the operation, leaving the sugar pure white. When the centrifugal is stopped, this sugar then falls through a trap door in the bottom of the machine, to a carrier that takes it to the granulator, or dryer, where the slight amount of moisture is driven off, after which it falls down a chute to a hopper, where it is placed in bags for shipment.

**54.** Going back to the centrifugals, the molasses that runs off from the melada is collected in tanks made for that purpose, and when enough has accumulated, it is sent to the vacuum pan and reboiled; but, in this case, it is not boiled to grain, but simply concentrated as much as is consistent. This operation usually takes 2 hours, whereas the graining takes about 5 hours. This "blank melada" is then run into crystallizers that are of the exact capacity of the vacuum pan, where it is kept in a slow, constant motion, to promote graining, for about 3 or 4 hours; it is then treated in the centrifugal. The sugar coming from this, being very unpalatable, is melted in a special mixer, and is pumped back into the thick juice. If, on analysis, the molasses is found to contain no more available sugar, it is used for making vinegar and shoe blacking, or, more frequently, thrown away, although it contains a number of by-products, such as trimethyl amine, etc. which are obtained from it in some of the German factories. A factory with a capacity of, say, 750 tons of beets, would have an output of about 75 tons of sugar, and would require daily about 45 tons of limestone.

**55. Properties of Sucrose.**—Sugar crystallizes from water in large, well formed prisms, that are hard, anhydrous, and unalterable in the air. It is dextrorotary, and dissolves in one-third its weight of cold water, resulting in a thick solution known as *single syrup*. Sugar is insoluble in ether and in cold absolute alcohol. Boiling absolute alcohol dissolves a little more than 1 per cent.; ordinary alcohol will take up more, owing to the presence of water. When heated to from 210° to 220°, sucrose loses water, and is converted into the substance called *caramel*, which is more or less brown in color, according to the duration of the heating and the temperature reached. Cane sugar does not reduce alkaline copper solutions. By the action of dilute acids, sugar is converted, slowly in the cold, but rapidly on boiling, into a mixture of equal parts of two isomeric sugars that have opposite rotary power, namely, glucose and fructose; the mixture is called *invert sugar:*

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O = \underbrace{\underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}}_{\text{invert sugar}}$$

The same transformation is effected by the soluble matter of yeast, and also by the peculiar ferment that exists in most fruits, but no one has succeeded as yet in effecting the union of glucose and fructose to form sucrose. The character of the relation between sucrose and the two monosaccharides is not understood.

It is only after having undergone this transformation into inverted sugar that sugar is acted on by ferments. It is converted into saccharic acid $C_6H_{10}O_8$ and oxalic acid by nitric acid; and is carbonized by concentrated sulphuric acid. Sugar resists the action of the alkalies better than glucose, forming with them and the bases in general definite compounds known as *saccharates.* If a mixture of sugar and slaked lime is triturated with water and the whole is thrown on a filter, the liquid that passes through will be colorless and strongly alkaline; on heating this mixture to ebullition, it changes into a solid mass that again becomes liquid on cooling, being then known as a solution of saccharate of calcium $(C_{12}H_{22}O_{11})_2 \cdot 3CaO$; the compound $C_{12}H_{22}O_{11} \cdot CaO$ is precipitated from it by the addition of alcohol. An excess of strontium hydrate precipitates cane sugar completely from a hot solution, the resulting disaccharate $C_{12}H_{22}O_{11} \cdot 2SrO$ being readily decomposed by carbon dioxide into sugar and strontium carbonate. When sugar is fused with potassium hydrate, hydrogen is disengaged, and carbonate, oxalate, formate, and propionate of potassium are formed. When distilled with quicklime, sugar is decomposed, with the formation of carbon dioxide, water, acetone, and *metacetone* $C_3H_6O$ (a liquid having a pleasant odor, and boiling at 84°). Sugar forms a crystalline compound with sodium chloride.

**56. Sugar of Milk.**—Sugar of milk, *milk sugar* or *lactose*, $C_{12}H_{22}O_{11}, H_2O$ occurs in the milk of all mammals, and is extracted from the whey that remains after the manufacture of cheese. To obtain the sugar of milk, it is only necessary to evaporate the whey to crystallization, when hard, colorless, rhombic crystals are obtained together with 1 molecule of water, which is lost on heating the crystals to about 140°. The sugar of milk that comes into the market has been crystallized on strings or wood splinters.

Milk sugar dissolves in 6 parts of cold water and in 2 parts of boiling water; it has a slightly sweet taste, and is dextrorotary. It reduces Fehling's solution, but much more slowly than glucose. Oxidized with nitric acid, it yields mucic and saccharic acids. Nascent hydrogen converts milk sugar into mannite, dulcite, and other similar substances. Like glucose and cane sugar, it forms compounds with bases, dissolving lime, baryta, lead oxide, etc. When boiled with dilute sulphuric acid, milk sugar is converted into glucose and galactose. Milk sugar ferments under certain conditions, and is thus converted into lactic acid. The souring of milk is a result of this fermentation. The lactic acid coagulates the casein, hence the thickening of sour milk.

**57. Maltose.**—Maltose $C_{12}H_{22}O_{11}, H_2O$ is formed by the action of malt on starch, and was for some time mistaken for dextrose. Malt, which is made by steeping barley in water until it germinates and then drying it, contains a substance called *diastase*, which has the power of effecting changes similar to some of those effected by the ferments. Thus it acts on starch and converts it into dextrin and maltose, as is seen from the following equation:

$$\underset{\text{starch}}{3C_6H_{10}O_5} + H_2O = \underset{\text{maltose}}{C_{12}H_{22}O_{11}} + \underset{\text{dextrin}}{C_6H_{10}O_5}$$

Maltose is also formed by the action of dilute sulphuric acid on starch, and is always found in commercial glucose. Maltose forms masses composed of hard white needles, and loses its water of crystallization when heated to about 100°.

A solution of maltose is dextrorotary, reduces Fehling's solution, and is easily fermented by yeast, yielding alcohol and carbon dioxide; thus,

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{alcohol}}{4C_2H_6O} + 4CO_2$$

Boiling with dilute acids converts maltose into glucose:

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

**58. Other Disaccharides.**—*Isomaltose* $C_{12}H_{22}O_{11}$ is formed by the action of hydrochloric acid on glucose, and is also formed from starch in the presence of diastase. It has an intensely sweet taste, and is dextrorotary. It is decomposed by heating gently, but does not seem to be directly fermentable.

**59.** *Mycose*, or *trehalose*, $C_{12}H_{22}O_{11}, 2H_2O$ is found in the ergot of rye, and has been obtained from the trehala manna, or nest sugar, of Persia, an edible substance produced by an insect from the tree on which it lives. Mycose crystallizes in hard, rectangular octahedra, is gritty between the teeth, and has a sweet taste. The crystals fuse at 100°, and lose their water of crystallization at 130°. It is strongly dextrorotary, and is soluble in water and alcohol. The latter property distinguishes it from cane sugar.

**60.** *Raffinose*, or *melitose*, $C_{18}H_{32}O_{16}, 5H_2O$ occurs in Australian manna, cotton seeds, and sugar beets. It crystallizes in fine needles, that lose their water of crystallization at 100°, while the residue melts at 118°. Raffinose is but slightly sweet, dissolves in water and alcohol, and is dextrorotary. It does not react with Fehling's solution, but is completely fermentable.

**61.** *Melezitose* $C_{18}H_{32}O_{16}, 2H_2O$ is extracted by alcohol from the manna exuding from the larch. It crystallizes in monoclinic prisms with 2 molecules of water of crystallization, which it loses when heated to 108°. It is about as sweet as cane sugar, is dextrorotary, and melts at 157°.

**62. Fermentation.**—If yeast is introduced into a solution of glucose, and exposed for some time to a temperature of from 20° to 30°, bubbles of carbon dioxide will soon be disengaged and seen to arise. After all the carbon dioxide has been evolved, and the liquid subjected to distillation, a small quantity of alcohol will be obtained. The glucose, as such, has disappeared; it is decomposed into alcohol and carbon dioxide. This decomposition has been effected by the yeast, the process that took place being called *fermentation*. The sugar is the fermentable substance, and the yeast is the ferment.

The ferment is an organized matter that develops and multiplies and lives at the expense of the fermentable substance. It was formerly thought that this organized matter was the direct cause of fermentation. Modern investigations, however, tend to show that this is not the case. It appears that the organisms produce an unorganized ferment, an enzyme, and this enzyme is the real cause of the fermentation.

**63.** *Alcoholic Fermentation.*—The decomposition of glucose under the active influence of yeast constitutes alcoholic fermentation, and the principal reaction that occurs may be expressed by the subjoined equation:

$$\underset{\text{glucose}}{C_6H_{12}O_6} = \underset{\text{alcohol}}{2C_2H_6O} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{2CO_2}$$

It has been shown by the experiments of Pasteur that only about 94 per cent. of the quantity of glucose that is decomposed undergoes the change indicated by the above equation. The remaining 6 per cent. is employed partly in the formation of small quantities of higher alcohols, succinic acid, and glycerol, and partly in the development of new yeast cells.

**64. Yeast.**—Yeast is composed of a mass of cells or ovoid corpuscles having a diameter of $\frac{1}{100}$ millimeter, and arranged in clusters, as shown in Fig. 5. Their walls are an elastic membrane, and their contents appear liquid or granular when viewed through the microscope. They contain cellulose, albuminoid matter, and mineral salts. When they are introduced into a substance that contains the material necessary for their development, they multiply rapidly. Pasteur has made a large number of decisive experiments on this point. He planted some yeast cells in a solution of sugar to which he had added a small quantity of an ammoniacal salt and some phosphates. The solution of sugar fermented, and the ferment developed by budding, the new cells absorbing the ammonia and phosphates. They obtained from the sugar the matter necessary to form cellulose, and from the ammonia the nitrogen required for the elaboration of the albuminoid matters. However, these artificial conditions are not those that are best adapted for the propagation of cells. The latter increase with extraordinary energy in liquids that contain, besides the yeast and glucose, a quantity of albuminoid matter ready formed.

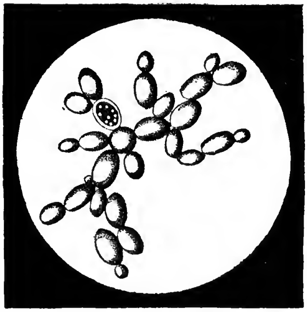


FIG. 5

**65.** *Lactic Fermentation.*—Lactic fermentation is of a vegetable nature, and is accomplished by the action of a peculiar ferment, formed of small round or elongated cells, very short, and isolated or in masses, which are considerably smaller than the yeast cells, and constitute the lactic yeast of Pasteur. It only acts on glucose or lactose in either neutral or alkaline solution—hence the necessity of adding sodium carbonate or chalk to the solution. The reaction consists in a splitting of the glucose molecule, as is seen from the following equation:

$$\underset{\text{glucose}}{C_6H_{12}O_6} = \underset{\text{lactic acid}}{2C_3H_6O_3}$$

**66.** *Butyric Fermentation.*—Butyric fermentation consists in the transformation of calcium lactate into butyrate—a transformation that is accompanied by a disengagement of hydrogen. According to Pasteur, this fermentation is caused by a low organism that can live and thrive only in situations where its members cannot obtain free oxygen. Such is the energy of their respiratory functions that, according to Pasteur, free oxygen kills them. They decompose oxidized bodies and assimilate the oxygen. Acetic fermentation has been briefly mentioned, previously. It may be added, however, that, by the action of a certain ferment, glucose is converted into mannitol, and a gummy matter that is very soluble in water and gives a viscous consistency to the fermented liquid. This is called the *viscous fermentation.*

There are many other kinds of fermentation, an exceedingly large number of organic compounds being capable of decomposition in this manner; the ferments are also very numerous, and the special fermentation undergone by a substance depends on the peculiar ferment present.

## STARCHES AND CELLULOSES

**67. Starch.**—Starch, or *amylose*, $(C_6H_{10}O_5)_n$ is found everywhere in the vegetable kingdom in large quantities, particularly in all kinds of grain, as corn and wheat, and in tubers, as potatoes, arrowroot, etc.

In this country, starch is manufactured mainly from corn, but in Europe it is generally extracted from potatoes. The processes involved in the manufacture of starch are mostly mechanical. The corn is first treated with warm water, and the softened grain is then ground between stones, a stream of water running continuously into the mill. The thin paste that is carried away is brought upon sieves of silk bolting cloth, which are kept in constant motion. The starch, as a milky liquid, passes through these sieves with the water, and is then allowed to settle, when the water is drawn off. The starch is next treated with water containing a little alkali (either caustic soda or sodium carbonate), the object of which is to dissolve the gluten, oil, etc. The mixture is now brought into long, shallow, wooden runs, where the starch is deposited, the alkaline water running off. Finally, the starch is washed with water, and dried at a low temperature.

Starch is a white powder, formed of minute grains of organized structure. Their size and shape vary according to the origin of the starch. Starch made from potatoes has larger grains than starch made from grain. The size of these minute grains varies from $\frac{2}{1000}$ to $\frac{185}{1000}$ of a milligram, and they are made up of concentric layers that become denser as they approach the surface.

Starch in its usual condition is insoluble in water, alcohol, and ether. If ground with cold water, it is partly dissolved; if heated with water, the membranes of the starch cells are broken, and the contents form a partial solution. On cooling, it forms a transparent jelly called *starch paste.* With iodine, starch paste gives a blue color, and with bromine it gives a yellow color. The conversion of starch into maltose and dextrin by the action of diastase has been previously mentioned.

**68. Dextrin.**—Dextrin $C_6H_{10}O_5$ is prepared by moistening starch with one-third its weight of a weak solution of nitric acid, drying it in the air, and heating to 115°. It is converted, by further treatment with acids, into glucose. The substance ordinarily called dextrin has been shown to be a mixture of several isomeric substances that resemble one another very closely. The mixture is an uncrystallizable solid. It is strongly dextrorotary, hence its name; it also gives a red color with iodine, and does not reduce Fehling's solution. It is employed by calico printers for thickening their colors; it is used as a mucilage for labels and postage stamps, and for the preparation of immovable surgical dressings.

**69. Inulin.**—Inulin $(C_6H_{10}O_5)_6, H_2O$ occurs widely diffused throughout the vegetable kingdom, and may be extracted from dahlia roots, which contain 10 per cent. of inulin, by boiling with water, which, on cooling, deposits it in minute granules that are analogous to starch. It swells in cold water, in which it is only very slightly soluble; it is very soluble, however, in boiling water, which again deposits it in a pulverulent form on cooling. The aqueous solution of inulin turns the plane of polarization to the left. Inulin is not colored blue by iodine, but takes a transient yellow-brown tint when mixed with the latter. When boiled with dilute sulphuric acid, it gives fruit sugar.

**70. Glycogen.**—Glycogen $(C_6H_{10}O_5)_n$ was obtained by Bernard from the liver of several animals (calf or pig) by exhausting with water, and precipitating with boiling alcohol. The precipitate is purified by boiling with dilute potash, repeatedly dissolving in strong acetic acid, and precipitating by alcohol. Glycogen is a white, starch-like substance, without odor or taste, yielding an opalescent solution with water, but insoluble in alcohol. It does not reduce any alkaline solution of copper, and does not ferment with yeast, but is converted into glucose by boiling with dilute acids, or by contact with diastase, saliva, or blood.

**71. The Gums.**—The gums $(C_6H_{10}O_5)_n$ are amorphous, transparent substances, widely disseminated in plants; they form sticky masses with water, and are precipitated by alcohol. They are odorless and tasteless, and some of them yield clear solutions with water, while others swell up in that menstruum and will not filter through paper. The first are called the *real gums*, and the second *vegetable mucilages*. Nitric acid oxidizes them to mucic and oxalic acids.

**72. Cellulose.**—The framework of plant tissues consists of a more or less delicate membrane that is a secretion of protoplasmic activity and is known as the *cell wall*. In the earlier stages of its growth and development, it consists of cellulose $(C_6H_{10}O_5)_n$ with a varying amount of water. Gradually, however, it is transformed into bodies of more complex constitution—the compound celluloses—and, at the same time, mineral matters are deposited in it.

The name *cellulose* does not denote a chemical individual, but a group of closely related isomers of similar properties. Cotton, hemp, flax, and the pith of certain trees consist essentially of cellulose. All these bodies are permeated by foreign substances, such as nitrogenous, coloring, and mineral matters. White filter paper, prepared cotton wool, and well washed linen consist of nearly pure cellulose.

Cellulose is prepared by drying sawdust at 110°, and boiling it with a mixture of alcohol and benzene to extract the resinous matter it contains. It is then washed with alcohol, and boiled two or three times with weak ammonia, after which it is washed and digested with weak bromine water, until it no longer decolorizes the bromine water after standing 24 hours. This oxidizes the vasculose, and converts it into acids. The residue is washed and heated nearly to boiling with water containing $\frac{1}{250}$ of its volume of strong ammonia; this dissolves the oxidized acids, and acquires a brown color. When this brown color no longer increases, the residue is again washed, and the treatment with bromine water is repeated until no more brown color is imparted to the ammonia; a final washing with water and boiling with alcohol leaves the cellulose pure.

**73.** When pure, cellulose is a white, opaque solid, exhibiting an organized structure. It is infusible and insoluble in all simple solvents, but in the presence of certain metallic compounds, it forms gelatinous hydrates that are soluble in water. Cellulose dissolves completely on warming with concentrated aqueous solution of zinc chloride, but more rapidly, and in the cold, when a solution of the salt in strong hydrochloric acid is employed. Another valuable solvent is *Schweitzer's reagent*, which is made by dissolving cupric hydrate in ammonia. When submitted to dry distillation, cellulose leaves a residue of carbon, and yields numerous gaseous and liquid products. The gas obtained by the distillation of wood is used for illuminating purposes in some localities. The liquid product ordinarily separates into two layers; one of these layers is aqueous and contains acetic acid, wood spirit, acetone, etc.; the other is insoluble in water, and constitutes wood tar. Cellulose is rapidly attacked by concentrate sulphuric acid; the resulting viscous solution probably contains a compound of sulphuric acid and cellulose, and also various other products resulting from a rapid disintegration of this sulphate. When the solution is diluted with water, and boiled, glucose is formed, and sulphuric acid regenerated. When paper is dipped into a cold mixture of sulphuric acid and half its volume of water, and then carefully washed and dried, a semitransparent matter is obtained that has a certain rigidity, and is similar to parchment in aspect and toughness. This parchment paper is extensively used as a substitute for animal parchment.

**74.** Colloidal cellulose is formed by the action of sulphuric acid (Sp. Gr. 1.53) on cellulose, and forms, with water, a milky liquid that can be filtered. The action of sulphuric acid or zinc chloride on cellulose produces a body known as *amyloid*, that is analogous to starch. Cellulose moistened with iodine tincture and then treated with strong sulphuric acid assumes a blue color. By treatment with acetic anhydride, cellulose is converted into the triacetate $C_6H_7O_2(C_2H_3O_2)_3$ and the tetra-acetate $C_6H_6O(C_2H_3O_2)_4$; and there are indications that higher acetates may exist.

**75. Guncotton.**—Cellulose has some of the properties of alcohols; among these properties is the power to form ethereal salts with acids. Thus, when treated with nitric acid, it forms several nitrates, just as glycerine forms the nitrate known as *nitroglycerin*. Treated for a short time with sulphuric and nitric acids, cellulose is converted into lower nitrates, particularly the tetranitrates and pentanitrates. A solution of these in a mixture of ether and alcohol is known as *collodion solution*, which is quite extensively used in photography and surgery. When poured upon any surface, such as glass, the ether and alcohol rapidly evaporate, leaving a thin coating of the nitrates that were in solution.

When treated for 24 hours, at a temperature of 10°, with a mixture of nitric and sulphuric acids, cellulose yields hexanitrate $C_{12}H_{14}O_4(ONO_2)_6$, which is used as an explosive under the name of *guncotton*, or *pyroxylin.* Guncotton looks like ordinary cotton, but is more harsh to the touch and sometimes has a light yellowish tint. It burns with a sudden flash, leaving no residue, and produces a great volume of gaseous products consisting of carbon monoxide, carbon dioxide, nitrogen dioxide, vapor of water, etc. It is chiefly used in blasting.

An intimate mixture of guncotton and camphor has come into extensive use, under the name of *celluloid*, as a substitute for ivory, bone, and horn. As it is plastic at a slightly elevated temperature, it can easily be molded into any desired shape, when on cooling it hardens.

Nitro powders, largely used on account of their smokeless explosion, are prepared by gelatinizing finely divided guncotton by means of a solvent such as ethyl acetate or acetone. The solvent is removed by high pressure and evaporation, and the gelatinous residue is cut into slices and pressed into suitable forms. Other substances are usually added to modify the force of the explosion.

# ORGANIC CHEMISTRY

(PART 8)

## DERIVATIVES OF HYDROCARBONS

### GLUCOSIDES

**76.** Glucosides is the name given to a class of bodies, very widely diffused in the vegetable kingdom, that are resolved by boiling with dilute acids, or alkalies, or by the action of ferments, into a sugar (mostly dextrose) and some other compound. While sharing this method of decomposition in common, they show in other respects a wide divergence. Most of the glucosides are neutral bodies, though they frequently combine with metallic oxides, such as lead and mercuric oxides. They are usually soluble in water and in alcohol, often insoluble in ether, and generally crystallizable. Many glucosides are optically active, most of them showing a levorotary character. This rotary power does not, however, correspond in any way to that of the sugar that is obtained by the decomposition of the glucoside. As these compounds have little practical value, only the most important of them will be mentioned here.

**77. Amygdalin.**—Amygdalin $C_{20}H_{27}NO_{11}$ is extracted from bitter almonds, the kernels of the fruit of *Amygdalus communis*. It dissolves freely in alcohol and water, and crystallizes from the former with 2 molecules and from the latter with 3 molecules of water of crystallization. An aqueous solution of amygdalin is levorotary. Dilute acids decompose it into glucose, hydrocyanic acid, and benzaldehyde, as is seen from the subjoined equation:

$$\underset{\text{amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{glucose}}{2C_6H_{12}O_6} + \underset{\text{hydrocyanic acid}}{CHN} + \underset{\text{benzaldehyde}}{C_7H_6O}$$

The same decomposition takes place by the action of a peculiar ferment, known as *emulsin*, or *synaptase*, which is present in bitter and sweet almonds. This ferment is soluble in water, and acts on amygdalin only in the presence of water; hence the odor of prussic acid is only noticeable when bitter almonds are moistened with water. Sweet almonds do not contain amygdalin.

**78. Salicin.**—Salicin $C_{13}H_{18}O_7$ is a crystallizable bitter substance contained in the leaves and young bark of the poplar, willow, and various other trees. It may be prepared by exhausting willow bark with boiling water, concentrating the solution to a small bulk, digesting the concentrate solution with lead hydrate, precipitating the excess of lead by $H_2S$, and then evaporating until the salicin crystallizes out. Salicin forms small, colorless, and bitter tasting needles that melt and decompose by heat, burning with a bright flame and leaving a residue of charcoal. Salicin is soluble in about 30 parts of water, more soluble in alcohol, but insoluble in ether, and is readily distinguished by the bright-red color that it gives with strong sulphuric acid, by which it is detected when applied to the inner bark of the willow. Under the influence of emulsin, salicin is resolved into glucose and saligenin:

$$\underset{\text{salicin}}{C_{13}H_{18}O_7} + H_2O = \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{saligenin}}{C_7H_8O_2}$$

Salicin yields, with chlorine, substitution products that are decomposed by emulsin in the same manner as salicin itself, yielding chlorsaligenin $C_7H_7ClO_2$ and dichlorsaligenin

$C_7H_6Cl_2O_2$. When salicin is fused with potassium hydrate, hydrogen is evolved, and salicylic and oxalic acids formed. By the action of a mixture of potassium dichromate and sulphuric acid, salicin yields carbon dioxide, formic acid, and an oxidized oil, which is salicyl aldehyde $C_7H_6O_2$.

**79. Populin.**—Populin $C_{20}H_{22}O_8,2H_2O$ exists in the bark and leaves of the aspen (*Populus tremula*), from which it may be extracted in a similar way to that employed in the extraction of salicin. When properly purified, it crystallizes in very fine, silky, and colorless needles with 2 molecules of water. Its taste is sweet, and it is only slightly soluble in water, but dissolves freely in alcohol. By the action of dilute acids, it is decomposed into benzoic acid, saliretin, and glucose; the latter two compounds result also from the decomposition of salicin, so that populin really appears to be a combination of benzoic acid and salicin:

$$\underset{\text{populin}}{C_{20}H_{22}O_8} + H_2O = \underset{\text{benzoic acid}}{C_7H_6O_2} + \underset{\text{salicin}}{C_{13}H_{18}O_7}$$

**80. Phlorizin.**—Phlorizin $C_{21}H_{24}O_{10},2H_2O$ exists in the bark and in the roots of most fruit trees, such as the apple, pear, plum, cherry, etc. It may be extracted by boiling the roots with water, decanting the boiling solution, concentrating it, and allowing it to stand in a cool place for some time. The phlorizin deposits on cooling, and may be purified by recrystallization, after decolorizing it with animal charcoal. When pure, it forms colorless, silky needles, having a bitter taste, and an aftertaste that is sweet. It is very insoluble in cold water, but readily dissolves in boiling water and alcohol. Its alcoholic solution is levorotary. Dilute sulphuric and hydrochloric acids decompose it into phloretin and glucose:

$$\underset{\text{phlorizin}}{C_{21}H_{24}O_{10}} + H_2O = \underset{\text{phloretin}}{C_{15}H_{14}O_5} + \underset{\text{glucose}}{C_6H_{12}O_6}$$

**81.** *Phloretin* is a white substance that crystallizes in little scales, slightly soluble in water, and very soluble in alcohol. When phloretin is heated with potassium hydrate, it breaks up into phloretic acid and phloroglucinol, as is seen from the following equation:

$$\underset{\text{phloretin}}{C_{15}H_{14}O_5} + H_2O = \underset{\text{phloretic acid}}{C_9H_{10}O_3} + \underset{\text{phloroglucinol}}{C_6H_6O_3}$$

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### VEGETABLE COLORING MATTER

**82.** Although the vegetable kingdom is so rich in variety and beauty of tints, comparatively few plants yield coloring matters that are sufficiently permanent to be employed in the arts, most of them fading rapidly as soon as the plant dies, since they are unable to resist the decomposing action of light, oxygen, and moisture, unless supported by the vital influence in the plant; some of them even fade during the life of the plant, as may be seen in some varieties of roses, for instance, that are only fully colored in those parts that are hidden from the light. Vegetable coloring matter is usually divided into three classes; namely, (1) those that exist ready formed in the plant, such as turmeric and safflower; (2) those that are formed by the joined action of alkalies and oxygen, as in the cases of logwood and archil; (3) those that belong to the class of glucosides.

**83. Various Vegetable Coloring Matters.**—*Chlorophyl*, or *leaf green*, is contained, together with wax and other substances, in the chlorophyl granules that are found in all the green parts of plants. Owing to its inability to crystallize or volatilize, it has never been obtained in a perfectly pure state. It may be obtained impure by exhausting leaves with ether, and treating the residue with alcohol, in which chlorophyl is readily soluble. Chlorophyl dissolves in cold strong sulphuric acid to a green solution that gives a dark-green precipitate on being diluted. If the green precipitate or the original chlorophyl is boiled with an alcoholic solution of potash, the solution, when neutralized with hydrochloric acid, gives a yellow precipitate (phylloxanthin), and the solution retains a blue coloring matter (phyllocyanin) that contains nitrogen. It has been suggested that the autumnal color of leaves might be due to the disappearance of phyllocyanin. Green leaves assume an autumnal tint when immersed in chlorine. The blue coloring matter contained in many flowers, such as the violet, has been named *cyanin*. Acids redden it, and, hence, only those flowers that have a neutral juice are blue; red flowers yield an acid juice. The coloring matter of grapes and of red wine is probably cyanin.

*Saffron* is a yellow coloring matter, obtained from the flowers of *Crocus sativus*, which are purple with yellow anthers. When these are dried and pressed into cakes, they form the saffron of commerce, which has an agreeable odor. It is imported chiefly from Spain. It gives up to water and alcohol a yellow amorphous substance termed *polychroite* $C_{48}H_{60}O_8$—a glucoside that, when boiled with dilute sulphuric acid, yields glucose, crocin $C_{16}H_{18}O_6$, and a volatile oil $C_{10}H_{16}O$ smelling of saffron.

**84.** *Annatto*, or *arnotto*, is another yellow coloring matter that forms the pulp surrounding the seeds of *Bixa Orellana*, a West Indian plant. It is used for coloring butter and cheese, for which purpose, however, it is entirely unfit, as it is extracted with stale urine, and swarms with bacteria, some of which may be morbific.

*Turmeric* is the dried root of *Curcuma longa* and *Curcuma rotunda*, plants cultivated chiefly in Bengal. It contains a crystalline, yellow body, *curcumin* $C_{14}H_{14}O_4$, which may be extracted by boiling with benzene. It is insoluble in water, but dissolves in alcohol. Alkalies dissolve it, forming red salts, from which acids throw it down as a yellow precipitate. Paper dyed with turmeric is used as a delicate test for alkalies, which turn it brown. When acted on by boric acid and strong sulphuric acid, it is converted into *rosacyanin*, which crystallizes, in green needles dissolved by alcohol, with a red color that is changed to deep blue by alkalies. Turmeric paper is also used in testing for boric acid.

**85.** *Weld* is the *Reseda luteola*, a plant of the mignonette order, the leaves of which give a yellow solution when boiled with water. The decoction, mixed with alum and chalk, gives a yellow precipitate that is used in paper staining. It contains a crystalline yellow body, luteolin $C_{20}H_{14}O_{6}$, sparingly soluble in water, but dissolved by alkalies and by alcohol.

*Fustic* is a yellow dyestuff, two kinds of which exist, called *old fustic* and *young fustic*. The former is the wood of a tree of the mulberry order, *Morus* or *Maclura tinctoria*, grown in the West Indies, while the latter is the wood of the Venice sumach (*Rhus cotinus*), which grows in Italy and the southern parts of France. When old fustic is boiled with water, the solution deposits yellow needles of *morin* $C_{13}H_{8}O_{6}$ which is soluble in alcohol. The mother liquor of morin, when evaporated, yields *maclurin*, a nearly colorless compound. When fused with potassium hydrate, morin yields *phloroglucol*, and maclurin yields, in addition, *protocatechuic acid*.

*Gamboge* is a yellow gum resin, originally obtained from Camboja, in Asia. It contains about 30 per cent. of a yellow gum, soluble in water, and 70 per cent. of resin, soluble in alcohol and alkalies, called *gambodic acid*.

*Safflower*, which yields rouge, consists of the dried flowers of *Carthamus tinctorius*, which is cultivated in Egypt. It contains a yellow substance, which may be extracted by water, and a red color, *carthamin* $C_{14}H_{16}O_{17}$, which may be dissolved out by sodium carbonate, and precipitated by acetic acid. Alcohol dissolves it to a red solution. It is used in dyeing, but has the disadvantage, together with many other vegetable coloring matters, that it soon fades. *Brazilin* $C_{16}H_{14}O_{5}$, the coloring matter in Brazil wood, crystallizes in small yellow prisms that dissolve in alcohol with a reddish-yellow color, and in alkalies with crimson color; the solution is decolorized by sulphurous acid and zinc dust.

**86. Indigo.**—Indigo $C_{16}H_{10}N_{2}O_{2}$ is the product of several species of plants of the genus *Indigofera*, growing in India and South America, and also of *Iatis tinctoria* and other plants. It does not exist in these plants ready formed, but is produced by the decomposition of a glucoside $C_{26}H_{31}NO_{17}$, called *indican*, which may be extracted from them by cold alcohol, and forms a brown, bitter syrup, easily soluble in water and alcohol. This substance, when boiled with dilute acids or substances subjected to the action of ferments, is resolved into indigo blue and indiglucin:

$$\underset{\text{indican}}{2C_{26}H_{31}NO_{17}} + 4H_2O = \underset{\text{indigo}}{C_{16}H_{10}N_2O_2} + \underset{\text{indiglucin}}{6C_6H_{10}O_6}$$

A substance similar to indican sometimes occurs in urine, and gives rise, by its conversion into indigo blue, to a blue coloration of the liquid when left in contact with the air or treated with sulphuric acid.

In India, indigo is prepared from the stems and leaves of the indigofera, collected at the time of flowering. The stems and leaves are macerated with water in vats, where they are allowed to ferment. After 12 or 15 hours the liquid is drawn off into other vats, where it is thoroughly stirred to bring it, as much as possible, in contact with the air, an operation that produces a blue precipitate. The brown liquid is then drawn off, and the deposit is boiled in copper vessels; it is then pressed between cloths and cut into cubical pieces and dried. It is in this form that indigo appears in commerce. It contains from 50 to 90 per cent. of coloring matter, and occurs in pieces the shade of which varies from violet blue to dense black blue. Pure indigo is known as *indigotin* or *indigo blue*, and may be obtained by heating the indigo of commerce in a current of hydrogen, or by subliming it in small quantities.

Indigotin is insoluble in water, in cold alcohol, and in ether, but dissolves in hot oil of turpentine and in aniline. When carefully heated, in small quantities at a time, it volatilizes. Concentrate, or, better, fuming, sulphuric acid dissolves indigo readily at about 50° or 60°, forming a beautiful blue solution that contains two acids, *indigo monosulphonic acid* $C_{16}H_9N_2O_2SO_3H$ and *indigo disulphonic acid*

$C_{16}H_8N_2O_2(SO_3H)_2$. The solution of indigo in sulphuric acid is used in dyeing; it is prepared by dissolving indigo in a hot mixture of fuming and ordinary sulphuric acids. The blue solution thus obtained is known as *sulphate of indigo*, or *Saxon blue*. The precipitate produced by $K_2CO_3$ in the solution of indigo in sulphuric acid is known as *indigo carmine*. Boiling dilute nitric acid converts indigo into isatine. The concentrate acid converts it first into nitrosalicylic acid $C_7H_5(NO_2)O_3$ and then into picric acid. When heated with potassium hydrate, indigo is converted into potassium anthranilate:

$$C_{16}H_{10}N_2O_2 + 2KOH = 2C_6H_4(NH_2)CO_2K + C_2$$

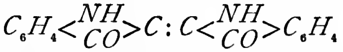
indigo potassium anthranilate

and afterwards into aniline $C_6H_5NH_2$, which distils over.

$$C_6H_4(NH_2)CO_2K + KOH = C_6H_5NH_2 + K_2CO_3$$

potassium anthranilate aniline

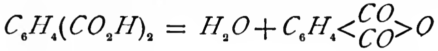
The constitution indigo is probably to be represented



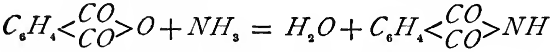
$$C_6H_4{<}\substack{NH\\CO}{>}C:C{<}\substack{NH\\CO}{>}C_6H_4$$

Only one method for the synthesis of indigo will be given. Naphthaline by heating with very concentrate sulphuric acid is oxidized, yielding phthalic acid, which on heating yields phthalic anhydride; this with dry ammonia yields phthalimide, which by the action of bromine and sodium hydrate yields anthranitic acid; this combines with monochloracetic acid to form phenyl-glycocoll-orthocarborylic acid, which on fusion with sodium hydrate yields indoxyl, and this latter in an alkaline solution is converted by atmospheric oxygen into indigo. The following equations represent the reactions:

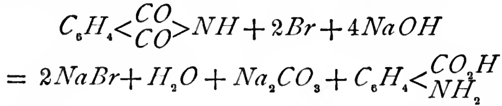
$$C_{10}H_8 + 9O = C_6H_4(CO_2H)_2 + H_2O + 2CO_2$$



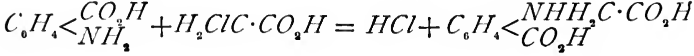
$$C_6H_4(CO_2H)_2 = H_2O + C_6H_4{<}\substack{CO\\CO}{>}O$$



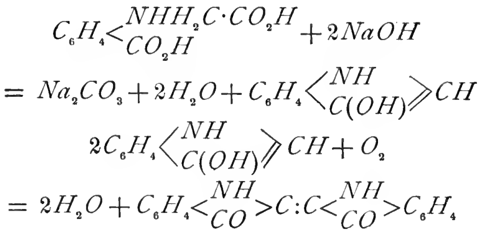
$$C_6H_4{<}\substack{CO\\CO}{>}O + NH_3 = H_2O + C_6H_4{<}\substack{CO\\CO}{>}NH$$



$$C_6H_4{<}\substack{CO\\CO}{>}NH + 2Br + 4NaOH$$
$$= 2NaBr + H_2O + Na_2CO_3 + C_6H_4{<}\substack{CO_2H\\NH_2}$$



$$C_6H_4{<}\substack{CO_2H\\NH_2} + H_2ClC{\cdot}CO_2H = HCl + C_6H_4{<}\substack{NHH_2C{\cdot}CO_2H\\CO_2H}$$



$$C_6H_4<\begin{matrix}NHH_2C\cdot CO_2H\\ CO_2H\end{matrix} + 2NaOH$$
$$= Na_2CO_3 + 2H_2O + C_6H_4\left\langle\begin{matrix}NH\\ C(OH)\end{matrix}\right\rangle CH$$
$$2C_6H_4\left\langle\begin{matrix}NH\\ C(OH)\end{matrix}\right\rangle CH + O_2$$
$$= 2H_2O + C_6H_4<\begin{matrix}NH\\ CO\end{matrix}>C:C<\begin{matrix}NH\\ CO\end{matrix}>C_6H_4$$

**87. Indigo White.**—Indigo white $C_{16}H_{12}N_2O_2$, or *leucindigo*, which was discovered by Chevreul in 1812, results from the action of nascent hydrogen on indigo. It is produced when the latter substance is submitted to the action of alkaline solutions in the presence of reducing matters, such as sulphurous or phosphorous acid, hydrogen sulphide, zinc, ferrous hydrate, or grape sugar. It is ordinarily prepared by introducing a mixture of indigo, ferrous sulphate, slaked lime, and water into a vessel that should be entirely filled with the mixture and then hermetically sealed and allowed to stand for 48 hours. A clear, alkaline solution is thus obtained, which is decanted, and supersaturated with hydrochloric acid, out of contact with the air. A deposit of indigo white is formed; this is collected on a filter, rapidly washed with boiled water, and dried in a vacuum. The compound thus obtained has a dirty white color, and is tasteless and odorless, insoluble in water, but dissolves with a yellow color in alcohol, ether, and alkaline solutions. On contact with air it absorbs oxygen and is converted into indigo blue.

Indigo is largely used in dyeing. The principle of its application depends on the conversion of the indigo blue into indigo white by reducing agents. The reduced indigo white is soluble in alkaline solutions, and in this form is fixed on the fabrics; it is reconverted into indigo blue by exposure to the air. The mixture given above for the preparation of indigo white is most frequently employed.

**88. Isatine.**—Isatine $C_8H_5NO_2$, or $C_6H_4\left\langle\begin{matrix}N\\ CO\end{matrix}\right\rangle COH$, was discovered by Erdmann and Laurent in 1841. It is the product of the oxidation of indigo by chromic or dilute nitric acid:

$$\underset{\text{indigo}}{C_{16}H_{10}N_2O_2} + O_2 = \underset{\text{isatine}}{2C_8H_6NO_2}$$

Pure isatine crystallizes sometimes in large, dark, gold-colored prisms, and sometimes in small orange-colored or reddish-yellow prisms that have a brilliant luster and are soluble in boiling water and alcohol, giving brown-red solutions. When heated, it sublimes with partial decomposition. It dissolves in solutions of the alkaline hydrates, forming violet solutions that become yellow when boiled, the isatine being converted into *isatic acid;* thus:

$$\underset{\text{isatine}}{C_8H_5NO_2} + H_2O = \underset{\text{isatic acid}}{C_8H_7NO_3}$$

Isatine is reprecipitated by acids from these alkaline solutions. Silver nitrate added to the potash solution gives a carmine-red crystalline precipitate of *silver isatine* $C_8H_4AgNO_2$. Isatine forms crystalline compounds with alkali bisulphites. When distilled with a strong solution of potassium hydrate, isatine yields aniline, as is seen from the following equation:

$$C_8H_5NO_2 + 4KOH = 2K_2CO_3 + \underset{\text{aniline}}{C_6H_7N} + H_2$$

Nitric acid converts it into nitrosalicylic acid and picric acid. With chlorine it yields chlorsatine $C_8H_4ClNO_2$ and dichlorsatine $C_8H_3Cl_2NO_2$, which are also formed when chlorine acts on indigo. When these compounds are distilled with potash, they yield monochloraniline and dichloraniline. Reducing agents convert isatine into *hydroxy isatine* or *isatyde* $C_{16}H_{12}N_2O_4$.

**89. Indole.**—Indole $C_8H_7N$, or  $C_6H_4\left\langle\begin{matrix}CH\\NH\end{matrix}\right\rangle CH$, is formed when indigo is distilled with zinc dust, or when nitrocinnamic acid $C_8H_6NO_2 \cdot CO_2H$ is reduced by zinc and potassium hydrate. It crystallizes in colorless plates, melts at 52°, and boils with partial decomposition, although it may be distilled with steam or in a vacuum. It possesses a disagreeable odor, dissolves readily in boiling water, alcohol, and ether, and has feebly basic properties. Indole is formed normally during the pancreatic digestion by the breaking up of albuminoid matters. It occurs, together with its methyl derivative, *skatole*, in human excrements.

**90. Skatole.**—Skatole, or *methyl indole*, $C_9H_9N$, or  $C_6H_4\left\langle\begin{matrix}NH-\\C(CH_3)\end{matrix}\right\rangle\!\!\!\gg CH$, is the chief constituent of the volatile portion of human excrements. It has been obtained synthetically in shining leaflets, having a strong, disagreeable odor, and melting at 95°.

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### ALBUMINOID COMPOUNDS

**91. Proteids.**—Under this head are classed several nitrogenous products of animal and vegetable life that are neither crystalline nor volatile. They resemble one another very closely in composition, containing from 50 to 55 per cent. of carbon, 21 to 25.5 per cent. of oxygen, 15 to 18 per cent. of nitrogen, 6.7 to 7.3 per cent. of hydrogen, and .4 to 1.7 per cent. of sulphur. The composition and properties of proteids are generally represented by those of the coagulated matter (called *albumen*) that exists in the white of egg and in the serum of blood. They are closely related to the epidermic productions and insoluble substances that are converted into gelatine or chondrin by boiling, although they differ from these in chemical composition as well as in many of their properties. These compounds seem to be the closest approximation of unorganized matter to organized matter, that is, to the living cell, and they have therefore been called *proteids*. They may be characterized by the following chemical reactions:

Most insoluble albuminoid matter, when brought in contact with water containing traces of hydrochloric acid, swells up, and is slowly converted into a transparent jelly that is partially soluble in water.

Hot concentrated hydrochloric acid dissolves albuminoid matters, the former assuming a dark-blue or violet color.

Nitric acid colors albuminoid matter yellow.

Albuminoid substances are precipitated from neutral or slightly alkaline aqueous solutions by alcohol, tannin, phenol, and a number of metallic salts, as, for instance, those of mercury, lead, and copper. The albuminoid precipitate thrown down by a copper salt is soluble in a concentrate solution of potassium hydrate, whereby the liquid assumes a beautiful violet color.

Millon's reagent, consisting of a solution of mercuric nitrate in dilute nitric acid, assumes a red color when boiled with albuminoid matter.

All albuminoid substances are levorotary, but their optical activity varies considerably. The insoluble albuminoid matter, such as coagulated albumen, fibrin, and casein, dissolves in hot potassium-hydrate solution. It is impossible to subject the proteids to an exact chemical classification, but they may, however, be conveniently arranged as follows:

1. *True albumins*, which are soluble in pure water and coagulable by heat, of which egg albumen and serum albumin are characteristic representatives.

2. *Globulins*, which are insoluble in water and soluble in neutral salts solution, such as sodium chloride, the solutions coagulating by heat. The albumen in the yolk of eggs is the best known representative of this group.

3. *Fibrins*, which are insoluble in water and which swell up in solutions of dilute acids and neutral salts; blood fibrin and gluten fibrin are the most characteristic types.

4. *Coagulated albumins;* these substances are insoluble in water and are only slightly swelled up by acid and neutral salt solutions.

5. *Amyloid*, which is insoluble and is colored violet, brown, or red, by iodine.

6. *Acid albumins*, which are insoluble in water, alcohol, or neutral salt solutions, but soluble in acid and alkaline solutions. It should be here remarked that a small quantity of calcium carbonate, suspended in water, prevents their solution.

7. *Alkali albumins* are only slightly soluble in water,

alcohol, and saline solutions, but they are soluble in water holding calcium carbonate in suspension.

8. *Albumoses*, which are really transition products between the preceding bodies and the peptones; they are soluble in a dilute solution of sodium chloride.

9. *Peptones* are compounds that are very soluble in water, not coagulable by heat, and not precipitated from solutions by acids or salts.

10. *True proteids*, which may be decomposed into an albuminoid body with some other substance, such as hemoglobin, casein, etc.

11. *Albuminoids*, which are insoluble matters that in general are not dissolved by the digestive juices.

12. *Gelatinoids*, which readily dissolve in hot water without alteration; of these, gelatine is the best known representative.

13. *Spongy* matters, such as compose sponge.

A few of the more important of these bodies will be briefly considered here.

**92. Albumin.**—Albumin, or *white of egg*, $C_{72}H_{112}N_{18}O_{22}S$ may be extracted from the aqueous solution contained in the egg, by stirring it briskly to break up the membrane, adding a little acetic acid to neutralize the soda present in the white, filtering, placing for 12 hours on a dialyzer to separate the sodium chloride and acetate, evaporating the contents of the dialyzer below 50°, powdering the residue, and treating with ether to extract fatty matters. The albumin so prepared is an amorphous solid, of Sp. Gr. 1.31. When heated, albumin swells up, carbonizes, and evolves offensive alkaline vapors, usually leaving a slightly alkaline ash containing a trace of calcium phosphate, which is very difficult to separate completely. In cold water, albumin becomes soft and finally dissolves, like gum; if this solution is heated to about 70°, the albumin is converted into an insoluble form, becoming a white, soft solid, as in boiled eggs, if the albumin amounts to 12 per cent., and a flocculent precipitate if the solution is diluted. The *coagulated albumin* is not easily dissolved by acids or alkalies, and it is believed to be the anhydride of soluble albumin, for if it be heated with water in a sealed tube to above 150°, it is dissolved to a reddish liquid, which behaves like a solution of ordinary albumin, but is not coagulated by heat. Raw white of egg is inodorous and does not blacken silver; but, after boiling, it smells of $H_2S$, and blackens silver, showing that it suffers some decomposition during coagulation. When dried, the coagulated albumin forms a translucent brittle mass that becomes white and opaque in water. The soluble form of albumin, completely dried below 50°, may afterwards be heated to 100°, without becoming insoluble.

Sulphuric, nitric, and hydrochloric acids precipitate albumin in thick flakes, which retain a certain quantity of acid; the latter may be removed by prolonged washings with water, the residue constituting *acid albumin*. The action of nitric acid on albumin is often used for the detection of that substance in pathological urine and is known as *Heller's* test. When white of egg is beaten up with a few drops of a very concentrate solution of potassium hydrate, it sets in a few minutes in a soft, transparent, semisolid mass, from which the excess of potassium hydrate may be removed by washing with cold water. The residue is albuminate of potassium, which readily dissolves in boiling water. Acetic acid precipitates from the solution an *alkali albumin*, which may be freed from salts by dialysis. Coagulated albumin dissolves in alkalies and alkaline carbonates, forming albuminates. Albumin combines with calcium hydrate, as with potassium hydrate.

Many salts precipitate solutions of albumin. Acetate and subacetate of lead form dense precipitates of albuminate of lead. Cupric sulphate produces a blue precipitate, and mercuric chloride yields a dense white precipitate, even in very dilute solutions of albumin. The insolubility of this precipitate explains the use of the white of egg as a well-known antidote in cases of poisoning by corrosive sublimate. Solutions of albumin are not precipitated by solutions of sodium chloride or sodium sulphate, but when acetic acid is added to the mixture, a precipitate is formed. Reciprocally, a solution of albumin to which acetic acid has been added is precipitated by adding a solution of sodium chloride or sodium sulphate.

The putrefaction of the albumins gives rise to the *ptomaines* and *toxines;* such poisonous products are also formed by the bacilli of diseases like diphtheria, and it is on the introduction into the system of antidotes (antitoxines) derived from animals that have been able to survive the poisons, that the principle of inoculation depends.

**93. Globulin and Fibrin.**—The name *globulin* has been given to the coagulable albuminoid that can be obtained from red-blood corpuscles. It resembles albumin in many of its properties, but coagulates completely only at 90°. Neither acetic acid nor alkalies precipitate it, but carbon dioxide throws it down from its solution. When recently drawn blood is left to itself, it coagulates spontaneously in a very short time, and soon separates into a yellow liquid, called *serum*, and a red coagulum, which is the *clot*. The clot contains the red corpuscles, surrounded by an insoluble albuminoid matter. This matter is fibrin; it is formed by the reaction of two globulins that exist in solution in the liquid portion of the blood, which is called *plasma*. One of these substances is known as *fibrinogen;* the other is *serum globulin*. These two bodies have been isolated; when they are mixed in the presence of water and a certain portion of sodium chloride, the whole dissolves at first, and the liquid soon coagulates spontaneously; the coagulum is fibrin. When left to itself during the heat of summer, fibrin putrefies very rapidly, and is converted into a blackish liquid that contains albumin, leucine and butyric and valeric acids being formed at the time. When treated with hydrochloric acid, fibrin dissolves, forming a blue solution. When moist fibrin is introduced into water containing a mere trace of concentrated hydrochloric acid, it swells and becomes transparent, forming a jelly. After some time it dissolves in the liquid, although with difficulty, and the solution contains an acid albumin, known as *syntonin*. Dilute sodium chloride solutions dissolve fibrin. When such a solution is dialyzed, most of the salt passes into the exterior liquid, and there remains in the dialyzer a limpid solution of the two globulins, coagulable by heat, and presenting many of the properties of egg albumin.

**94. Myosin.**—Myosin separates from muscle plasma (the liquid contained in living muscle) after death, producing *rigor mortis*. It may be prepared from chopped flesh by triturating the flesh to a pulp with common salt, adding 9 parts of water for 1 of salt, digesting for some time at 24°, pressing through linen, and filtering; the myosin is precipitated on adding much water, or by saturating it with salt.

**95. Peptones.**—The gastric juice dissolves coagulated albumin digested with it at about 37°, and the solution is not precipitated by potassium ferrocyanide nor coagulated by heating. In this condition albumin is said to have been *peptonized* or converted into *peptone*. The constituent of the gastric juice that produces this change is termed *pepsin*, and may be precipitated from the juice by alcohol. It resembles albumin in composition, but it is much less subjected to putrefaction. When dissolved in dilute hydrochloric acid, it yields a mixture that peptonizes most albuminoids if digested at about 40°. The pepsin prepared from the stomach of pigs and other animals is administered medicinally to aid digestion.

**96. Hemoglobin and Oxyhemoglobin.**—The coloring matter contained in the red globules of the arterial blood is called *oxyhemoglobin*, and closely resembles albumin in composition, except that it contains less sulphur and some iron; its composition is

| | |
|---|---|
| Carbon | 54.18 |
| Hydrogen | 7.20 |
| Nitrogen | 16.00 |
| Oxygen | 21.50 |
| Iron | .42 |
| Sulphur | .70 |
| | 100.00 |

Oxyhemoglobin is usually obtained in an amorphous condition, but from the blood of human beings and some animals, as, for instance, dogs, cats, rats, mice, and many fish, it can be separated in the crystalline form. The crystals generally belong to the type of right-rhombic prisms, but differ according to the blood from which they are obtained. Those from human blood present, under the microscope, the forms shown in Fig. 6. These crystals contain oxygen in a loosely combined form, which they evolve when exposed in a vacuum, especially if warmed, becoming thus converted into *hemoglobin*, which again absorbs oxygen on exposure to air; this change is attended with the production of a much brighter red color, and with a difference in its action on transmitted light, for if white light be allowed to pass through the solution of oxyhemoglobin contained in a test tube placed before the slit of the spectroscope, the green portion of the spectrum is seen to be crossed by two black bands, which are also seen when arterial blood is employed, while the solution of hemoglobin exhibits only one band in the middle of the green, which is also seen when venous blood is employed. The difference in the absorption spectrum is best shown by reducing the solution of oxyhemoglobin with a little ferrous sulphate, mixed with tartaric acid and ammonia in excess. The oxygen of oxyhemoglobin is also displaced by passing hydrogen or carbon dioxide through it, hemoglobin being left, and the color changing from red to purple. Oxyhemoglobin, when shaken with carbon monoxide gas, parts with its oxygen and absorbs an equal volume of carbon monoxide, its color changing to purple. The compound of hemoglobin and carbon monoxide may be obtained in bluish-red crystals. When solution of oxyhemoglobin is heated above 70°, it is

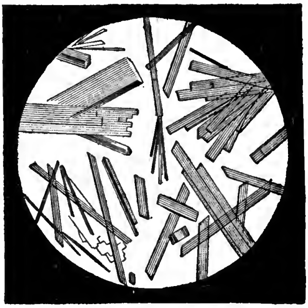


FIG. 6

decomposed into albumin, which coagulates, and another red-coloring matter known as hematin.

**97. Hematin.**—Hematin, which has the formula $C_{34}H_{34}N_4FeO_5$, is formed when oxyhemoglobin is decomposed by acids. If a solution of that substance, mixed with a little sodium chloride, is evaporated over sulphuric acid to a thick liquid, mixed with fifteen times its volume of glacial acetic acid, and heated on a steam bath for several hours, it yields, on cooling, flat rhombic prisms of hematin hydrochloride of dark violet-red color and metallic luster, containing single molecules of hematin and hydrochloric acid. The formation of these crystals has been employed for the identification of blood stains, the suspected matter being placed on a microscope slide, a little sodium chloride added, and glacial acetic acid allowed to run under the cover glass; on heating till bubbles appear, and cooling, the dark-red hematin hydrochloride crystals become visible.

**98. Casein.**—When an acid is added to milk, a thick precipitate of casein is at once formed. The lactic acid that forms in milk by the fermentation of the milk sugar produces the same precipitation. The milk is then said to curdle. Casein dissolves in alkaline liquids and even in certain alkaline salts, such as carbonate and phosphate of sodium. It exists in this state in the milk, which is alkaline when fresh. When this solution of alkaline albuminate, to which the name "soluble casein" has been given, is evaporated, it becomes covered with a pellicle. Acetic acid precipitates casein in flakes, combining with the alkali. A distinct property of casein is its coagulation by *rennet*, the mucous membrane of the stomach of the calf, a small quantity of which, or of its solution in brine, coagulates the casein in a large quantity of milk; the coagulation does not appear to depend on the formation of lactic acid, but on a specific action of the rennet; the curd thus produced contains calcium and magnesium phosphates, and is not easily soluble in sodium carbonate. The casein of milk is more readily coagulated by acids and rennet when the milk is warmed, hence milk that has undergone very slight fermentation is curdled when heated, but if fresh milk is heated to boiling, the decomposition will be prevented.

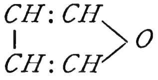
**99.** *Legumin*, or *vegetable casein*, occurs in peas, beans, and most leguminous seeds. It may be obtained by crushing and digesting peas in warm water; the resulting turbid liquid, holding starch in suspension, is allowed to settle, and is then filtered. Acetic acid is added to the filtrate, which precipitates the legumin, and this is filtered off and purified from fat by washing with alcohol and ether. Legumin closely resembles casein in its properties, being coagulated by rennet and its solution forming a pellicle, when heated; but slightly differing from casein in composition, legumin containing about 1 per cent. more of nitrogen, and only half as much of sulphur as casein.

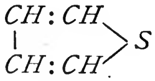
**100. Gelatine.**—The bones contain a cartilaginous substance, which may be isolated by dissolving out the mineral salts, that consists of calcium carbonate and phosphate, with hydrochloric acid. There remains a semitransparent, elastic substance that retains the form of the bone. This substance, which has been called *ossein*, or *collagene*, is insoluble in cold water, but by prolonged boiling, or, more rapidly, by digesting with water heated above 100°, it dissolves and forms a solution that sets into a transparent jelly on cooling. It consists of 50 per cent. carbon, 25.7 per cent. oxygen, 17.7 per cent. nitrogen, and 6.6 per cent. hydrogen, numbers that approximate to $C_{42}H_{66}N_{13}O_{16}$; its molecular formula, however, has not been finally determined, because it cannot be converted into vapor and does not form well defined compounds with other bodies. The body formed by the transformation indicated above dissolves slightly in cold water, and abundantly in boiling water, and the hot solution forms a jelly on cooling, hence the name gelatine. Other tissues of the animal economy may be converted into gelatine by boiling with water. It is so with the cellular tissue, the skin, scales, and swimming bladder of fish. The swimming bladder of the sturgeon, known in commerce as fish glue, furnishes very pure gelatine on boiling with water. The substances that may be converted into gelatine possess very nearly the same composition as gelatine itself, hence nothing precise is known concerning the nature of the change produced in them by the action of the boiling water.

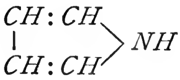
**101.** Dry gelatine occurs in more or less transparent sheets, varying in color from yellowish to dark brown, according to their purity and thickness. The aqueous solution of gelatine is precipitated in white flakes by alcohol. The acids, except tannic acid, do not precipitate it, but with tannic acid it forms a thick coagulum, a combination of tannin and gelatine. This action of tannin on gelatinous matter is, as has been previously mentioned, applied in the manufacture of leather, which is obtained by leaving fresh or green skins, previously swelled by soaking in water, in contact with tan, that is, coarsely ground oak bark, which is well known to contain considerable tannin. When chlorine water is added to a solution of gelatine, a white cloud is formed, which an excess of chlorine converts into a white, flocculent precipitate. Solutions of gelatine are precipitated by platinic chloride and by mercuric chloride, but not by alum or the salts of lead, copper, silver, etc. When boiled with dilute sulphuric acid, gelatine is converted into leucine and glycocoll.

## CLOSED-CHAIN COMPOUNDS IN WHICH *N*, *O*, OR *S* APPEARS AS PART OF THE NUCLEUS RING

**102.** A few compounds, which, strictly speaking, belong to this class, have been already treated on, some of which are succinic anhydride and the various lactones. These are, however, more of the nature of open-chain derivatives than are those that remain to be dealt with. The prototypes of these compounds are furfurane, thiophene, and pyrrol, which are believed to possess constitutions expressed by the following formulas:


furfurane


thiophene


pyrrol

They resemble benzene in that they yield derivatives similar to those of that hydrocarbon, and, as a whole, show little inclination to form addition products with the halogens. In fact, the arguments previously given that led to the closed-chain formula for benzene are equally applicable to these compounds.

Two classes of monosubstitution products are known from these compounds—the *α* derivatives, which contain the substituent attached to a carbon atom adjacent to the $O$, $S$, or $N$, and the *β* derivatives, in which a hydrogen atom of one of the far carbon atoms has been displaced. A third class is possible in the case of pyrrol, for the $H$ of the $NH$ group can be substituted. The possible diderivatives are more numerous than in the case of benzene; their orientation is expressed by numbering the near carbon atoms 1 and 4 and the far carbon atoms 2 and 3.

**103. Furfurane.**—Furfurane $C_4H_4O$ is contained in pine tar. It boils at 32°, is insoluble in water, but miscible with alcohol and ether. It is a colorless liquid, with an odor resembling chloroform. Its most important derivative, furfurol $C_4H_3O \cdot CHO$, has been considered in a preceding Section.

**104. Thiophene.**—Thiophene $C_4H_4S$ is invariably present in commercial benzene, but its isolation from this source offers considerable difficulty; a very pure product, however, may be obtained synthetically by heating a mixture of dry sodium succinate and phosphorus trisulphide. Thiophene is a colorless, mobile liquid, its specific gravity is 1.06 at 23°, and it boils at 84°. It smells like benzene, and yields a blue color when mixed with isatine and strong sulphuric acid; this reaction—due to the formation of indophenine $C_{12}H_7NOS$—serves to detect thiophene in benzene.

Of the homologues of thiophene, thiotolenes $C_4H_3(CH_3)S$ and thioxenes $CH_4(CH_3)_2S$ occur in coal tar. Having nearly the same boiling points as the corresponding benzene derivatives, they accumulate in the fractions constituting commercial toluene and xylene.

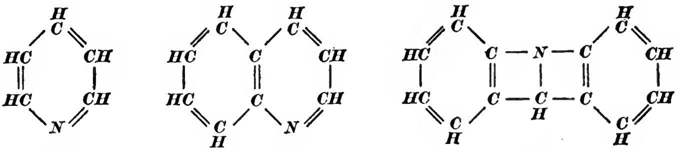
**105. Pyrrol.**—Pyrrol $C_4H_4NH$ is a feeble base, occurring in coal tar and bone oil, and is produced in the dry distillation of ammonium mucate. When freshly prepared it is a colorless liquid that turns brown when exposed to the air; it boils at 131°, and its odor resembles that of chloroform. It is insoluble in water, but mixes readily with alcohol and ether. Metallic potassium converts it into potassium pyrrol $C_4H_4(NK)$, a crystalline body that is decomposed by water into pyrrol and potassium hydrate. When treated with nascent hydrogen, pyrrol is reduced to *pyrroline* $C_4H_6(NH)$, a strong base that boils at 91°. By heating this base with hydriodic acid, it takes up more hydrogen and is converted into *pyrrolidine* $C_4H_8(NH)$, an alkaline liquid that boils at 83°.

The most characteristic test for pyrrol consists in exposing to its vapor a pine shaving moistened with hydrochloric acid, which soon assumes a red color.

**106. Pyrazole.**—Pyrazole  $\begin{matrix}HC:N\\HC:CH\end{matrix}\!>NH$ is related to pyrrol as pyridine (see Art. **109**) is to benzene; that is to say, it contains $N$ in place of $CH$. It is a feeble base, and crystallizes in needles.

**107.** *Antipyrine* $C_{11}H_{12}N_2O$, which is a *pyrazolone*, is prepared by heating ethyl aceto-acetate with phenyl hydrazine, and further heating the product with methyl iodide and methyl alcohol. It crystallizes in white plates, melts at 130°, and is very soluble in water. It has a bitter taste, and is used in medicine as a preventive of fever.

Among the most important members of this class of carbon compounds are the substances *pyridine*, *quinoline*, and *acridine*. These may be regarded as analogous in constitution to benzene, naphthalene, and anthracene, respectively, containing, in each case, $N$ in place of $CH$. Their graphical formulas, shown in Fig. 7, will make this clear.



pyridine quinoline acridine

FIG. 7

They behave towards reagents in a manner which indicates that they are closed-chain compounds (compare the stucture of benzene), and a study of their substitution products shows that the number of position isomerides that has been prepared is in accord with that prophesied on the supposition that the above formulas represent the constitution of the parent compounds. An inspection of the formulas shows that there should be three isomeric monosubstituted pyridines, seven isomeric monosubstituted quinoles, and five monosubstituted acridines. The orientation is expressed similar to that of the corresponding hydrocarbons, the $N$ in pyridine being 1 and that in quinoline 1′.

**108. Pyridine Bases.**—These bases, metameric with aniline and its homologues, are found in coal tar, naphtha, and in the offensive smelling oil known as *Dippel's animal oil*, which is obtained by distilling bones, from which they may be extracted. They are all liquids at ordinary temperature, possess an extremely offensive odor, and belong to the class of tertiary monamines, being substituted ammonias. They are separated from each other by fractional distillation. Their names, formulas, and boiling points are given below:

| | | | | | |
|---|---|---|---|---|---|
| Pyridine | $C_5H_5N$ | 115° | Parvoline | $C_9H_{13}N$ | 188° |
| Picoline | $C_6H_7N$ | 130° | Coridine | $C_{10}H_{15}N$ | 211° |
| Lutidine | $C_7H_9N$ | 142° | Rubidine | $C_{11}H_{17}N$ | 230° |
| Collidine | $C_8H_{11}N$ | 179° | Viridine | $C_{12}H_{19}N$ | 251° |

Pyridine bases are frequently present in commercial ammonia, and cause it to become pink when neutralized with hydrochloric acid.

**109.** *Pyridine* $C_5H_5N$, besides being formed in the distillation of bones, may be obtained in several other ways. Great interest has been aroused in the substance and its derivatives by the observation that several of the alkaloids that occur in nature, such as quinine, nicotine, cinchonine, and others, when oxidized, yield acids containing nitrogen, which bear to pyridine the same relations that benzoic, phthalic acids, etc. bear to benzene. Thus, by oxidizing nicotine, nicotinic acid $C_6H_5NO_2$ is obtained, and when this compound is distilled with lime, it breaks up into pyridine and carbon dioxide:

$$\underset{\text{nicotinic acid}}{C_6H_5NO_2} = \underset{\text{pyridine}}{C_5H_5N} + CO_2$$

This naturally leads to the conclusion that nicotinic acid is pyridine-carboxylic acid $C_5H_4N \cdot CO_2H$, which bears to pyridine the same relation that benzoic acid bears to benzene, acetic acid to marsh gas, etc. It is a colorless liquid, having a characteristic odor and a specific gravity of .986 at 0°. It boils at 115°, and is soluble in water and alcohol. It is an energetic base, forming deliquescent salts. Sodium converts it into a polymeride *dipyridine* $C_{10}H_{10}N_2$.

Piperidine, or hexahydropyridine, $C_5H_{11}N$, which is a strong base that forms salts with acids, is formed by the action of sodium on a hot alcoholic solution of pyridine; it is a colorless liquid, with a faint odor suggesting pepper, that boils at 106°, and is soluble in both water and alcohol. The remaining pyridine bases, all of which exist in more or less numerous isomeric modifications, need not be described here.

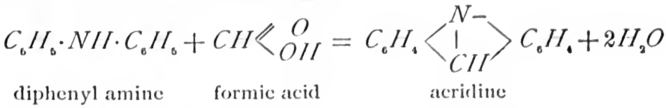
**110. Quinoline Bases.**—Quinoline bases occur in bone oil and coal tar; three bases of this series, namely, *quinoline* $C_9H_7N$, *lepidine* $C_{10}H_9N$, and *cryptidine* $C_{11}H_{11}N$, are also produced by the distillation of quinine and a few other natural alkaloids similar to the pyridine bases. These and other bases isomeric with them pass over when coal tar or bone oil is distilled, after the pyridine bases, at about 200°. They are oily liquids, insoluble in water, but soluble in alcohol and ether. They are tertiary amines, yielding ammonium bases when treated with moist silver oxide.

**111.** *Quinoline*, or *chinoline*, $C_9H_7N$ may be prepared synthetically by a method that was discovered by Skraup, and which consists in heating aniline and glycerine in the presence of sulphuric acid and nitrobenzene:

$$\underset{\text{aniline}}{C_6H_5NH_2} + \underset{\text{glycerine}}{C_3H_8O_3} + O = C_9H_7N + 4H_2O$$

The sulphuric acid aids the condensation by its dehydrating action, and the nitrobenzene plays the part of an oxidizing agent. Quinoline is a colorless, mobile liquid with an odor suggesting tar; its specific gravity is 1.08, it has a boiling point of 238°, and it is only sparingly soluble in water. Quinoline combines with amyl iodide to form a compound that, when heated with potash, yields a fine blue color, soluble in alcohol, and known as *quinoline cyanine*, or *quinoline blue*. A similar blue color is obtained with lepidine, and a mixture of the two has been used for dyeing silk.

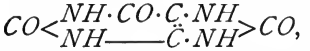
**112. Acridine Bases.**—*Acridine* $C_{13}H_9N$ occurs in crude anthracene, in which it may be recognized by its giving a fluorescent solution in dilute acids, and from which it can be precipitated by potassium bichromate; it crystallizes in colorless needles, melts at 110°, and readily sublimes, yielding a very irritating vapor. Acridine is obtained synthetically by heating diphenyl amine with formic acid in the presence of a dehydrating agent:



$$\underset{\text{diphenyl amine}}{C_6H_5\cdot NH\cdot C_6H_5} + \underset{\text{formic acid}}{CH\langle{}^{O}_{OH}} = \underset{\text{acridine}}{C_6H_4\left\langle\begin{matrix}N-\\ |\\ CH\end{matrix}\right\rangle C_6H_4} + 2H_2O$$

Several dyestuffs, such as chrysaniline, or phosphine, and acridine yellow, are substitution products of acridine homologues.

## URIC ACID AND ITS DERIVATIVES

**113. Uric Acid.**—Uric acid $C_5H_4N_4O_3$, or  $CO<\begin{matrix}NH\cdot CO\cdot C\cdot NH\\ NH\text{———}C\cdot NH\end{matrix}>CO$, was discovered by Scheele; its numerous metamorphoses were the subject of a classic research by Liebig and Wöhler, and they have been more recently studied by Baeyer and other chemists. Uric acid, or, as it was formerly called, *lithic acid*, is generally prepared from the excrement of the boa constrictor (serpent's urine), which consists chiefly of *hydroammonium urate* $H(NH_4)C_5H_2N_4O_3$; this is dissolved by boiling with dilute potassium hydrate, which expels $NH_3$, and converts it into normal potassium urate $K_2C_5H_2N_4O_3$. By passing $CO_2$ through the potassium urate, the sparingly soluble *hydropotassium urate* $HKC_5H_2N_4O_3$ is precipitated, which is washed, dissolved in hot water, and decomposed by $HCl$, thus precipitating the uric acid. Human urine also yields uric acid in small crystals when concentrated by evaporation, mixed hot with hydrochloric acid or nitric acid, and set aside; the crystals are usually much tinged with urinary coloring matter, and may be purified by dissolving in potassium hydrate solution and treating as above. *Guano*, the partly decomposed excrement of sea birds, contains a considerable quantity of uric acid that may be extracted by boiling it with a 5-per-cent. solution of borax, and adding hydrochloric acid to the filtered solution. Uric acid may be obtained synthetically by heating a mixture of urea and glycocoll to about 230°.

$$\underset{\text{urea}}{3CON_2H_4} + \underset{\text{glycocoll}}{C_2H_5NO_2} = \underset{\text{uric acid}}{C_5H_4N_4O_3} + 3NH_3 + 2H_2O$$

**114.** Pure uric acid is a glistening snow-white powder that shows, under the microscope, a minute but regular crystalline structure; is inodorous, tasteless, and only sparingly soluble, requiring 1,800 parts of hot and 15,000 parts of cold water for its solution, and is entirely insoluble in alcohol and ether, but dissolves in sulphuric acid without apparent decomposition, precipitating from this acid solution by the addition of water. It dissolves in solutions of the alkalies, forming neutral urates, which contain 2 atoms of the alkaline metals; hence, uric acid must be considered a dibasic acid. When carbon dioxide is led into a solution of a neutral urate, an acid urate that is nearly insoluble is precipitated. Hydrochloric acid forms a thick, white, gelatinous precipitate of uric acid when added to the solution of a urate. Heated to 160° or 170° with an excess of hydriodic acid, uric acid absorbs water, and is decomposed into glycocoll, carbon dioxide, and ammonia, as is seen from the following equation:

$$\underset{\text{uric acid}}{C_5H_4N_4O_3} + 5H_2O = \underset{\text{glycocoll}}{C_2H_5NO_2} + 3CO_2 + 3NH_3$$

If uric acid is gently heated with a little nitric acid, it is dissolved with a disengagement of red vapors, and the solution, evaporated at a gentle heat, leaves a residue that assumes a purple color on the addition of a drop of ammonia. This is used as a general test for uric acid, permitting the detection of the smallest trace of it. The purple substance thus obtained is known as *murexide*.

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### DERIVATIVES OF URIC ACID

**115.** Among the numerous compounds that are derived from urea, some are closely related to oxalic acid or other acids containing 2 carbon atoms, while others are derived from mesoxalic acid $CO(CO_2H)_2$, which contains 3 carbon atoms. All of these derivatives are more or less closely related to urea; they are, in fact, substituted ureas, and are more specially designated by the name *ureides*. Those related to mesoxalic acid are the more direct derivatives.

**116. Alloxan.**—Alloxan, or *mesoxalyl urea* $C_4H_2N_2O_4$, is the product of the action of strong nitric acid on uric acid in the cold, urea being formed at the same time:

$$\underset{\text{uric acid}}{C_5H_4N_4O_3} + H_2O + O = \underset{\text{alloxan}}{C_4H_2N_2O_4} + \underset{\text{urea}}{CH_4N_2O}$$

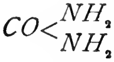
It is best prepared by adding 1 part of pulverized uric acid to 3 parts of nitric acid (Sp. Gr. 1.43) in a shallow basin standing in cold water. The resulting white, crystalline mass, after standing for some hours, is drained from the acid liquid into a funnel having its neck stopped with powdered glass; it is then dried on a porous plate, and purified by crystallization from a moderate amount of water. Alloxan crystallizes by slow cooling from a hot, saturated solution, in voluminous crystals with 4 molecules of water of crystallization; from a solution evaporated by heat, it separates in rhombic octahedra, containing but 1 molecule of water of crystallization. Alloxan is very soluble in water; the solution has an acid reaction, a disagreeably astringent taste, and, after a time, stains the skin red or purple. By the action of alkalies (baryta water, for instance), alloxan is converted into *alloxanic acid* $C_4H_4N_2O_5$, which is formed by the direct combination of the elements of 1 molecule of water with 1 molecule of alloxan, as is seen from the equation:

$$\underset{\text{alloxan}}{C_4H_2N_2O_4} + H_2O = \underset{\text{alloxanic acid}}{C_4H_4N_2O_5}$$

The alloxanates are decomposed by boiling into mesoxalic acid and urea. Thus, if a solution of alloxanic acid, or even alloxan, is added to a boiling solution of lead acetate, a precipitate of lead mesoxalate is formed:

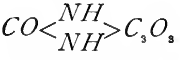
$$\underset{\text{alloxanic acid}}{C_4H_4N_2O_5} + H_2O = \underset{\text{mesoxalic acid}}{C_3O_5H_2} + \underset{\text{urea}}{CH_4N_2O}$$

Mesoxalic acid $C_3O_5H_2$, or $CO\cdot OH\cdot CO\cdot CO\cdot OH$, is a dibasic acid, and it is assumed that its divalent radical, mesoxalyl, exists in alloxan itself, which is mesoxalyl urea, i. e., urea in which 2 atoms of hydrogen have been replaced by the divalent mesoxalyl radical $(C_3O_3)''$. The graphic formulas given below will make this readily understood:



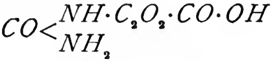
$$CO<\begin{matrix}NH_2\\NH_2\end{matrix}$$

urea



$$CO<\begin{matrix}NH\\NH\end{matrix}>C_3O_3$$

mesoxalyl urea
or alloxan



$$CO<\begin{matrix}NH\cdot C_2O_2\cdot CO\cdot OH\\NH_2\end{matrix}$$

mesoxaluric acid
or alloxanic acid

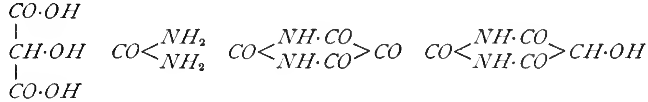
**117. Dialuric Acid.**—Dialuric acid $C_4H_4N_2O_4$, or $CO<\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}>CHOH$, is the product of the action of reducing agents on alloxan or on alloxantin, and is formed when hydrogen sulphide is passed through a boiling solution of one of these compounds until no further action takes place.

$$\underset{\text{alloxan}}{C_4H_2N_2O_4}+H_2S = \underset{\text{dialuric acid}}{C_4H_4N_2O_4}+S$$

Dialuric acid is also formed by the action of sodium amalgam on a hot solution of alloxan, and it crystallizes in long needles, which, when exposed to the atmosphere, soon assume a red color, and are converted into alloxantin. The crystals of dialuric acid are freely soluble in water. When a solution of alloxan is added to an aqueous solution of dialuric acid, *alloxantin* is formed, as may be seen from the following equation:

$$\underset{\text{dialuric acid}}{C_4H_4N_2O_4}+\underset{\text{alloxan}}{C_4H_2N_2O_4} = \underset{\text{alloxantin}}{C_8H_4N_4O_7}+H_2O$$

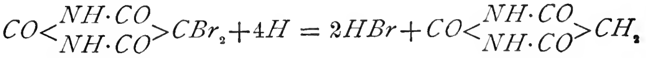
Dialuric acid is regarded by some chemists as tartronyl urea; that is, urea in which 2 atoms of hydrogen are replaced by the dibasic radical of tartronic acid. The graphic formulas of these compounds makes this assumption very probable:



$$\begin{matrix}CO\cdot OH\\ |\\ CH\cdot OH\\ |\\ CO\cdot OH\end{matrix}\quad CO<\begin{smallmatrix}NH_2\\ NH_2\end{smallmatrix}\quad CO<\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}>CO\quad CO<\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}>CH\cdot OH$$

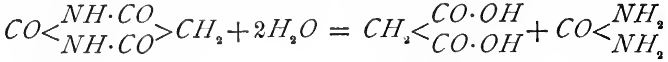
tartronic acid urea alloxan dialuric acid or tartronyl urea

**118. Barbituric Acid.**—Barbituric acid $C_4H_4N_2O_3$ crystallizes in large colorless prisms with 2 molecules of water of crystallization. It is obtained from alloxantin by heating it with strong sulphuric acid, or by the action of nascent hydrogen on dibromo alloxan, as is seen from the following equation:



$$\underset{\text{dibromo alloxan}}{CO<\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}>CBr_2}+4H = 2HBr+\underset{\text{barbituric acid}}{CO<\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}>CH_2}$$

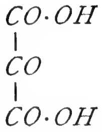
It is also called *malonyl urea*, as it may be prepared synthetically by heating malonic acid and urea to 100° in the presence of $POCl_3$. When barbituric acid is boiled with alkalies, it is reconverted into malonic acid and urea:



$$CO{<}\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}{>}CH_2 + 2H_2O = CH_2{<}\begin{matrix}CO\cdot OH\\ CO\cdot OH\end{matrix} + CO{<}\begin{matrix}NH_2\\ NH_2\end{matrix}$$

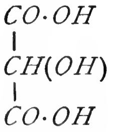
barbituric acid malonic acid urea

**119.** Alloxan and dialuric and barbituric acids, which have previously been described, are *ureides* derived from 1 molecule of urea by the substitution of the radical of a dibasic acid for 2 atoms of hydrogen. The groups $C_2O_2$, $C_3O_3$, $C_2O_2\cdot CHOH$, $C_2O_2\cdot CH_2$, which in oxalic, mesoxalic, tartronic, and malonic acids are united by two hydroxyls, are divalent:



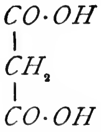
$$\begin{matrix}CO\cdot OH\\ |\\ CO\\ |\\ CO\cdot OH\end{matrix}$$

mesoxalic acid



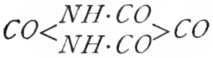
$$\begin{matrix}CO\cdot OH\\ |\\ CH(OH)\\ |\\ CO\cdot OH\end{matrix}$$

tartronic acid



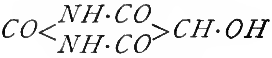
$$\begin{matrix}CO\cdot OH\\ |\\ CH_2\\ |\\ CO\cdot OH\end{matrix}$$

malonic acid



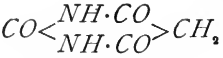
$$CO{<}\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}{>}CO$$

mesoxalic urea
alloxan



$$CO{<}\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}{>}CH\cdot OH$$

tartronyl urea
dialuric acid



$$CO{<}\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}{>}CH_2$$

malonyl urea
barbituric acid

The following compounds are *diureides;* they are derived from 2 molecules of urea, in which 4 atoms of hydrogen are replaced by two dibasic acid radicals, each of which contains 3 atoms of carbon and is related to mesoxalyl.

**120. Alloxantin.**—Alloxantin $C_8H_4N_4O_7$, or  $CO{<}\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}{>}C\overset{O}{\triangle}C{<}\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}{>}CO$, is obtained by reducing alloxan with $SnCl_2$, zinc, and hydrochloric acid, or hydrogen sulphide, in the cold, or mixing solutions of alloxan and dialuric acid, as has been previously stated.

Alloxantin crystallizes from hot water with 3 molecules of water of crystallization in small, hard prisms, and turns red when exposed to air containing ammonia; it has an acid reaction, and is but slightly soluble in cold water. Nitric acid converts alloxantin into alloxan, and reducing agents transform it into dialuric acid.

**121. Purpuric Acid, or Murexide.**—Purpuric acid, or murexide, $C_8H_5N_5O_6$ is not known in the free state, because as soon as it is liberated from its salts by mineral acids, it immediately decomposes into alloxan and uramyl. The ammonium salt $C_8H_4(NH_4)N_5O_6,H_2O$ is the dyestuff *murexide*, that is formed by heating alloxantin to 100° in a stream of ammonia gas:

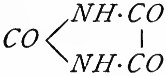
$$\underset{\text{alloxantin}}{C_8H_4N_4O_7} + 2NH_3 = \underset{\substack{\text{murexide} \\ \text{(ammonium purpurate)}}}{C_8H_4(NH_4)N_5O_6} + H_2O$$

or by evaporating uric acid with dilute nitric acid, and dissolving the residue in ammonia, when the murexide separates from the solution on cooling. Murexide crystallizes in quadrangular prisms, of a beautiful gold-green color, with 1 molecule of water of crystallization. These crystals dissolve in water, producing a fine, purple-red solution; they also dissolve in potassium-hydrate solution, producing a dark-purple color, which, on boiling, decolorizes with the disengagement of $NH_3$. They are insoluble in alcohol and ether.

**122. Allantoin.**—Allantoin $C_4H_6N_4O_3$ occurs in the urine of sucking calves, in the allantoic liquid of the cow, that is, the urine of the fetal calf, and in human urine after injections of tannic acid. In the vegetable kingdom, it has been found in beet juice. It is prepared by oxidizing uric acid with either $PbO_2$, $MnO_2$, alkaline $KMnO_4$, or potassium ferrocyanide; synthetically, it has been obtained by heating for 10 hours 1 part of glyoxalic acid with 2 parts of urea, as is seen from the following equation:

$$\underset{\text{glyoxalic acid}}{C_2H_2O_3} + \underset{\text{urea}}{2(CH_4N_2O)} = \underset{\text{allantoin}}{C_4H_6N_4O_3} + 2H_2O$$

From this synthesis it may be assumed that allantoin is derived from two molecules of urea and that allantoin is a diureide of glyoxalic acid. Allantoin crystallizes in glistening, colorless needles, is insoluble in ether, sparingly soluble in cold water, and readily soluble in hot water and alcohol. Allantoin has a neutral reaction, but dissolves in alkalies, forming salts.

**123. Parabanic Acid.**—Parabanic acid $C_3H_2N_2O_3$, which is known as oxalyl urea, is, as its graphical formula  $CO\begin{cases}NH\cdot CO\\ \qquad\;|\\ NH\cdot CO\end{cases}$ shows, a ureide of oxalic acid. It is formed by the action of an excess of nitric acid on alloxan, which then gives up the elements of carbon dioxide:

$$\underset{\text{alloxan}}{C_4H_2N_2O_4} + O = \underset{\text{parabanic acid}}{C_3H_2N_2O_3} + CO_2$$

Parabanic acid forms thin, transparent prisms that are soluble in water and alcohol, but insoluble in ether. It has a strongly acid character. When boiled with dilute acids, parabanic acid yields urea and oxalic acid. When heated with ammonia, *ammonium oxalurate* is formed, which separates in fine needles. In this case the parabanic acid is converted into oxaluric acid by directly combining with the elements of water, as may be seen from the following equation:

$$\underset{\text{parabanic acid}}{C_3H_2N_2O_3} + H_2O = \underset{\text{oxaluric acid}}{C_3H_4N_2O_4}$$

It is seen that oxaluric acid is related to parabanic acid, as alloxanic acid is to alloxan.

**124. Guanine.**—Guanine $C_5H_5N_5O$ occurs in guano, the excrement of sea fowls, from which it is extracted by boiling with water and lime, and boiling the undissolved residue with soda, which dissolves the guanine and uric acid; these are precipitated by acetic acid, and the guanine is dissolved out by hydrochloric acid, and precipitated by ammonia. Guanine is amorphous, is insoluble in water and alcohol, and acts as a weak acid as well as a base, and is very nearly related to uric acid $C_5H_4N_4O_3$. When evaporated with nitric acid, guanine leaves a yellow residue that becomes purple-red with soda, but oxidized by potassium chlorate and hydrochloric acid, it yields $CO_2$, parabanic acid, and guanidine, as is seen from the following equation:

$$\underset{\text{guanine}}{C_5H_5N_5O} + O_3 + H_2O = CO_2 + \underset{\substack{\text{parabanic}\\ \text{acid}}}{C_3H_2N_2O_3} + \underset{\text{guanidine}}{C(NH)(NH_2)_2}$$

Guanine is also found in the pancreas of the horse, in gouty deposits in pigs, in the excrements of spiders, etc., being also formed, together with xanthine and sarcine, when yeast is allowed to decompose in water at 35°.

**125. Xanthine.**—Xanthine $C_5H_4N_4O_2$ is prepared by the action of nitrous acid on guanine, as is seen from the equation:

$$\underset{\text{guanine}}{C_5H_5N_5O} + HNO_2 = \underset{\text{xanthine}}{C_5H_4N_4O_2} + H_2O + N_2$$

Xanthine forms minute, white crystals, that are sparingly soluble in water, insoluble in alcohol, dissolved by alkalies, and reprecipitated by acids. Evaporated with nitric acid, it leaves a yellow residue, becoming violet when heated with potassium-hydrate solution. It yields crystalline salts with acids, but they are decomposed by water. Its ammoniacal solution yields, with silver nitrate, a gelatinous precipitate containing $C_5H_2Ag_2N_4O_2 \cdot H_2O$, which, when treated with methyl iodide, yields theobromine.

**126. Sarcine.**—Sarcine $C_5H_4N_4O$, or hypoxanthine, is found in extract of meat, which contains about .6 per cent. of it. It may be precipitated from the mother liquor of the extraction of creatine (described in a preceding Section) by boiling with cupric acetate. The brown precipitate is dissolved in nitric acid and precipitated by silver nitrate, which forms an insoluble compound from which the sarcine may be extracted by decomposing with $H_2S$ and boiling with much water. It crystallizes in minute needles, and is more soluble than xanthine, though it forms a less soluble hydrochloride. Sarcine is generally found with xanthine, and occurs in many parts of the animal body, especially in marrow; it is feebly basic and acid, and nitric acid oxidizes it to xanthine.

**127. Carnine** $C_7H_8N_4O_3$ is found in the extract of meat, and resembles xanthine and sarcine. Nitric acid or bromine water oxidizes carnine to sarcine. *Tetanine* $C_5H_{11}N$ has been obtained from the putrefying beef extract used for cultivating a microbe *Bacillus tetani*, alleged to be the cause of tetanus (lockjaw) in animals. Tetanine is a volatile liquid, boils at about 100°, and produces symptoms of tetanus when injected under the skin.

### ALKALOIDS

**128.** The term *alkaloids* is generally applied to nitrogenous organic substances occurring in plants, frequently constituting those parts of the plants that are most active when taken into the animal body, hence they are sometimes called the *active principle* of the plants. Many of these substances are used in medicine, and all of them are more or less poisonous. As regards their chemical character, they are basic in the sense that ammonia is basic; they contain nitrogen, and form salts just as ammonia does, i. e., by direct addition of the acids. These and other facts lead to the belief that the alkaloids are related to ammonia—that they are substituted ammonias. Recently it has been shown that several of the alkaloids are related to pyridine and quinoline. They do not represent a very sharply defined group of compounds, and it has become customary, in the absence of a more precise and scientific classification, to divide them into two classes, the first of which includes those which are free from oxygen, and volatile, and the second which embraces those that are decomposed by distillation. They all contain nitrogen, but rarely more than 1 or 2 atoms in a molecule, though there may be 20 or 30 carbon atoms; all alkaloids with the exception of conine, nicotine, and sparteine contain oxygen.

The alkaloids, as a whole, are sparingly soluble in water, but dissolve readily in alcohol, ether, benzene, chloroform, etc.; their solutions are mostly alkaline and have a bitter taste.

**129. Conine.**—Conine $C_8H_{17}N$ is extracted from the seeds of hemlock (*Conium maculatum*) by crushing them and distilling with a weak potash solution. The distillate, which contains ammonia and conine, is neutralized with sulphuric acid, concentrated by evaporation, and mixed with alcohol to precipitate the ammonium sulphate. On evaporating the filtrate and distilling with strong potash, conine distils over, together with water, upon the surface of which it floats. It is distilled with dried potassium carbonate, to remove water, and the portion distilling at 168° is collected separately. Conine has been synthesized by heating $\alpha$-picoline with aldehyde, and subjecting the thus obtained $\alpha$-allyl pyridine to the action of nascent hydrogen:

$$\underset{\alpha\text{-picoline}}{C_5H_4(CH_3)N} + \underset{\text{aldehyde}}{CH_3\cdot COH} = \underset{\text{allyl pyridine}}{C_5H_4(C_3H_5)N} + H_2O$$

Conine exists in three stereoisomeric modifications. Natural conine is dextrorotary, and the synthetic conine, which is optically inactive, can be readily broken up into two active varieties. Conine is a limpid, oily liquid, with a strong odor of mice; its specific gravity is .89, it boils at 168°, and is sparingly soluble in cold water, the solution becoming cloudy on being heated, owing to the fact that the compound is more soluble in cold water than in hot water. Conine readily dissolves in alcohol and ether, and when exposed to air for some time it becomes brown and evolves ammonia; it also has a strongly alkaline reaction, immediately restoring the blue color to reddened litmus paper. Conine is often mixed with *methyl conine* $NCH_3(C_8H_{16})$, a compound existing in the hemlock, and which is derived by the substitution of a methyl group $CH_3$ for an atom of hydrogen, and formed artificially by the action of methyl iodide on conine. From the flowers and seeds of the hemlock a solid crystalline alkaloid, *conhydrine* $C_{18}H_{17}NO$, has also been obtained.

**130. Nicotine.**—Nicotine $C_{10}H_{14}N_2$ is found in the seeds and leaves of the tobacco plant. Nicotine is extracted from tobacco leaves by digesting them with very dilute sulphuric acid, evaporating to a very small bulk, and distilling with an excess of potash. The distillate is shaken with ether, which collects the nicotine and rises to the surface; the ethereal layer is drawn off, the ether distilled, and the nicotine placed in contact with quicklime to remove the water, and distilled in a current of hydrogen, since it is decomposed when distilled in air at ordinary pressure. Nicotine, when freshly prepared, is a colorless liquid, which, however, soon assumes a brownish color when exposed to the atmosphere. It has an offensive, penetrating odor, its specific gravity is 1.048, and it boils at 247°, undergoing a partial decomposition; it is soluble in water, alcohol, and ether. Nicotine is optically active, rotating the plane of polarization to the right; it has a strongly alkaline reaction, and perfectly neutralizes the acids, and precipitates the metallic oxides from solutions of their salts; it is also a very violently acting poison.

**131. Piperine.**—Piperine $C_{17}H_{19}NO_3$ occurs in various species of pepper, particularly in black pepper, from which it may be extracted by alcohol. It crystallizes in prisms, which melt at 128°, and which are insoluble in water, but soluble in ether. The alcoholic solution has the hot taste that is peculiar to pepper. Its reaction is neutral, and its salts are not very well defined. Sulphuric acid dissolves it, producing a dark-red solution. When boiled with potash, piperine yields piperidine, and with potassium it yields piperate.

**132.** *Piperidine*, or *hexahydro-pyridine*, $C_5H_{11}N$ is a liquid secondary monamine, boiling at 106°, and smelling of pepper and ammonia; it is soluble in water, forms crystalline salts, and behaves like other secondary amines in yielding tertiary amines and ammonia bases. When heated to 300° with strong sulphuric acid, piperidine yields pyridine

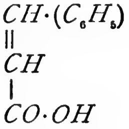
$C_5H_5N$, which may be reconverted into piperidine by nascent hydrogen, furnished by the action of hydrochloric acid on tin.

**133. Atropine.**—Atropine $C_{17}H_{23}NO_3$, also known as *daturine*, is found in the deadly nightshade (*Atropa Belladonna*) and thorn apple (*Datura Stramonium*), plants of the same order as the tobacco plant. It appears, however, that atropine does not exist readily formed in these plants, but is formed during extraction from an isomeric alkaloid, *hyoscyamine*, which, together with another alkaloid, *hyoscine*, exists naturally in the plants. Atropine is obtained by pressing the sap from the flowers of belladonna, heating the sap to 90° to coagulate the albumin, filtering, adding potash to liberate the base, and shaking with chloroform, which collects the atropine and sinks to the bottom. The chloroform is distilled off, and the atropine recrystallized from alcohol in small needles that are fusible at 115°. Atropine dissolves with difficulty in cold water, somewhat more easily in boiling water. It is easily soluble in alcohol, more difficultly in ether. The aqueous solution has an alkaline reaction. Atropine salts dissolve easily in water and alcohol. Atropine has a burning, bitter taste, and a very poisonous action, with the characteristic effect of enlarging the pupil of the eye, and thus it finds wide employment in the treatment of diseases of the eye. A solution of bromine in aqueous hydrobromic acid precipitates from solutions of atropine a yellow amorphous mass that soon becomes converted into characteristic crystals. Heated with baryta water or hydrochloric acid, atropine breaks up into tropine and tropic acid, as is seen from the following equation:

$$\underset{\text{atropine}}{C_{17}H_{23}NO_3} + H_2O = \underset{\text{tropic acid}}{C_9H_{10}O_3} + \underset{\text{tropine}}{C_8H_{15}NO}$$

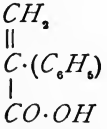
**134.** *Tropine* $C_8H_{15}NO$ is an active base, soluble in water, alcohol, and ether, and crystallizing from the last solvent in tables that fuse at 61°.

*Tropic acid* $C_9H_{10}O_3$ forms small crystals that fuse at 117°. By long boiling with either baryta water or hydrochloric acid, tropic acid is converted into *atropic acid* $C_9H_8O_2$ by losing the elements of 1 molecule of water. Atropic acid is isomeric with cinnamic acid, as will be readily seen by comparing the two formulas:



$$\begin{array}{l} CH\cdot(C_6H_5) \\ \| \\ CH \\ | \\ CO\cdot OH \end{array}$$

cinnamic acid



$$\begin{array}{l} CH_2 \\ \| \\ C\cdot(C_6H_5) \\ | \\ CO\cdot OH \end{array}$$

atropic acid

Tropic acid and tropine combine to form a salt known as *tropine tropate* $C_8H_{15}NO\cdot C_9H_{10}O_3$, and if this is heated for some time with hydrochloric acid, it loses the elements of water and is converted into atropine, as is seen from the equation:

$$\underset{\text{tropine tropate}}{C_8H_{15}NO\cdot C_9H_{10}O_3} = \underset{\text{atropine}}{C_{17}H_{23}NO_3} + H_2O$$

**135. Cocaine.**—Cocaine $C_{17}H_{21}NO_4$ is extracted from the leaves of *Erythroxylon Coca*, a Peruvian stimulant. It is prepared by exhausting the coca leaves with water at a temperature between 60° and 80°; the solution is precipitated by lead acetate, and filtered. The filtrate is freed from the excess of lead acetate by precipitation with sodium sulphate, again filtered, and the filtrate evaporated. Sodium carbonate is then added until a state of faint alkalinity is reached; then the liquid is shaken up with ether, which takes up the cocaine, and the ethereal solution is evaporated, whereby the cocaine is deposited. Cocaine crystallizes in colorless, odorless prisms that fuse at about 98°. Cocaine is only slightly soluble in cold water, more readily in alcohol, and quite freely in ether; it has a bitter taste, a slightly alkaline reaction, and for the last few years has been widely used in surgery as a local anesthetic. Heated with hydrochloric acid, cocaine absorbs 2 molecules of water and decomposes into methyl alcohol, benzoic acid, and ecgonine, a crystallizable alkaloid, thus:

$$\underset{\text{cocaine}}{C_{17}H_{21}NO_4} + 2H_2O = \underset{\text{ecgonine}}{C_9H_{15}NO_3} + \underset{\text{methyl alcohol}}{CH_4O} + \underset{\text{benzoic acid}}{C_7H_6O_2}$$

Cocaine has been synthesized by introducing successively the methyl and benzoyl groups into ecgonine.

### ALKALOIDS OF CINCHONA

**136.** The various cinchona barks owe their prominence as antifever remedies to several alkaloids they contain, the best known of which are *quinine* and *cinchonine*. Besides these, quinidine, isomeric with quinine, and cinchonidine, isomeric with cinchonine, have been isolated. When the sulphates of quinidine and cinchonidine are heated with sulphuric acid, they are converted into two new isomerides, quinicine and cinchonicine. Hence the following six alkaloids of cinchona are known:

cinchonine, cinchonidine, cinchonicine $C_{19}H_{22}N_2O$
quinine, quinidine, quinicine $C_{20}H_{24}N_2O_2$

The different species of cinchona yield a bark containing these alkaloids in different proportions. The yellow bark yields from 2 to 3 per cent. of quinine, and only .2 to .3 per cent. of cinchonine; the red bark yields about 2 per cent. of quinine and 1 per cent. of cinchonine; the pale, or gray, bark yields about .8 per cent. of quinine and 2 per cent. cinchonine. The alkaloids exist in combination with *quinic acid* and with a variety of tannin known as *quinotannic acid.*

**137. Quinine.**—Quinine is obtained by boiling the cinchona bark with dilute hydrochloric acid and adding to the filtered solution sufficient lime water to make it distinctly alkaline, and to precipitate the quinine, cinchonine, and vegetable coloring matter contained in the acid extraction. This is filtered off, and boiled with alcohol, which dissolves the alkaloids, leaving any excess of lime undissolved. The solution is then partly distilled, to recover part of the alcohol, and the solution, which is still alkaline, neutralized with sulphuric acid, then boiled with charcoal until entirely decolorized, and filtered. On standing, quinine sulphate crystallizes out, while the cinchonine sulphate remains in solution. The quinine sulphate crystals are dissolved in water, and ammonia is added, whereby the quinine sulphate is decomposed and quinine precipitated. Quinine crystallizes in prisms with 3 molecules of water, and these crystals require 2,266 parts of cold water and 760 parts of hot water for their solution; they dissolve quite readily in alcohol, ether, and chloroform. Quinine, like the other alkaloids, is an optically active compound, turning the plane of polarization to the left. Quinine has a decided alkaline reaction, and an extremely bitter taste; it appears to be a tertiary amine, because, when heated with the iodides of alcohol radicals, it yields iodides that furnish ammonium bases when decomposed by moist silver oxide; thus, methyl iodides give, with quinine, a compound having the formula $C_{20}H_{24}N_2O_2 \cdot CH_3I$, which, when acted on by the moist silver oxide, yields an alkaline hydrate $C_{20}H_{24}N_2O_2 \cdot CH_3 \cdot OH$.

Quinine is characterized by exhibiting a blue fluorescence when dissolved in dilute sulphuric acid, and by producing a green color when its dilute acid solutions are mixed with either chlorine or bromine water, and afterwards some ammonia added. This green color is due to the formation of a compound known as thalleiochin, which is formed by the reaction:

$$\underset{\text{quinine}}{C_{20}H_{24}N_2O_2} + NH_3 + O_4 = \underset{\text{thalleiochin}}{C_{20}H_{27}N_3O_6}$$

Quinine is a diacid base, but it sometimes forms salts in which it is monacid; there are two hydrochlorides; $C_{20}H_{24}N_2O_2 2HCl$ is converted by water into $C_{20}H_{24}N_2O_2HCl$, which crystallizes in needles of the formula

$$2(C_{20}H_{24}N_2O_2HCl), 3Aq$$

**138.** *Normal quinine sulphate* $C_{20}H_{24}N_2O_2 \cdot H_2SO_4, 7H_2O$ is soluble in 11 parts of cold water, but the *basic sulphate* $(C_{20}H_{24}N_2O_2)_2H_2SO_4, 8Aq$ is much less soluble and requires 780 parts of cold water for its solution. This is the quinine salt generally used in medicine; it forms very light, silky needles that dissolve readily in dilute sulphuric acid, forming the *acid sulphate* $C_{20}H_{24}N_2O_2(H_2SO_4)_2, 7Aq$, which is quite freely soluble. When tincture of iodine is added to a solution of quinine sulphate in hot acetic acid, the liquid in a few hours deposits large, thin plates of iodo-quinine sulphate $C_{20}H_{24}N_2O_2I_2SO_4H_2, 5H_2O$. These crystals, which are known as *herapathite*, or *artificial tourmaline*, appear bronze-green by reflected light, and are almost colorless by transmitted light. When two of these crystals are crossed, the portions that are superposed almost entirely intercept the passage of light. In this respect, iodo-quinine sulphate acts as a polarizer like tourmaline, hence its name. Quinine sulphate possesses valuable medical properties; it is employed as an antifever remedy, and generally in the treatment of diseases of an intermittent type. It is successfully administered in such diseases as acute articular rheumatism, gout, neuralgia, etc.

**139.** *Quinidine*, or *conquinine*, $C_{20}H_{24}N_2O_2$ is, as has been already stated, isomeric with quinine, and is extracted from a brown substance called quinoidine or amorphous quinine, which is obtained from the mother liquors of quinine sulphate, and is sold as a cheap substitute for quinine. It is also obtained in quantity from some of the inferior varieties of cinchona, such as *cinchona cordifolia*, which yields the Carthagena bark. Quinidine forms larger prismatic crystals than quinine, and these contain only 2 molecules of water of crystallization. Its salts are more soluble than those of quinine, and they are strongly dextrorotary. *Quinicine*, also isomeric with quinine, is formed by heating quinine or quinidine with dilute sulphuric acid to 130°. It is resinous, but its salts are crystalline, and its solutions are feebly dextrorotary.

**140. Cinchonine.**—Cinchonine $C_{19}H_{22}N_2O$ is a by-product in the manufacture of quinine. It is almost insoluble in water and ether, and only very sparingly soluble in alcohol and chloroform. From a hot solution of the former it crystallizes in anhydrous prisms. Cinchonine is an optically active compound, its alcoholic solution turning the plane of polarization to the right. Cinchonine has an alkaline reaction, a bitter taste, melts at 257°, and, when cautiously heated in the bottom of a closed tube, sublimes in very light, delicate crystals. The salts of cinchonine are more soluble than those of quinine, and give a much more voluminous precipitate with ammonia, which is insoluble in large excess, and is not cleared up by shaking with ether, as in the case of quinine. *Cinchonine sulphate* $(C_{19}H_{22}N_2O)_2H_2SO_4,2H_2O$ fuses when heated, evolving an aromatic odor and assuming a red color. A solution of cinchonine sulphate is less strongly fluorescent than one of quinine sulphate.

*Cinchonidine* and *cinchonicine* are isomeric with cinchonine, the first named compound being strongly levorotary.

### STRYCHNOS ALKALOIDS

**141.** The two alkaloids *strychnine* and *brucine* were discovered by Pelletier and Caventon. They are obtained from *nux vomica*, the seeds of the tropical plant, *Strychnos nux vomica*, from *false Angostura bark* of the same tree, and from *Ignatia amara*, or *St. Ignatius' bean.* Nux vomica, or crow fig, contains about 1 per cent. of strychnine and 1 per cent. of brucine. These two alkaloids, to which *igasurine* has recently been added, appear to be combined in the strychnos plant with an acid called *igasuric acid*, of which, however, little is known so far.

**142. Strychnine.**—Strychnine $C_{21}H_{22}N_2O_2$ is extracted from the crushed seeds of nux vomica by boiling them with very dilute hydrochloric acid. The solution is mixed with milk of lime, and the precipitate filtered off and boiled with alcohol, which dissolves the strychnine and brucine, and deposits the strychnine in crystals mixed with brucine when evaporated. The two alkaloids are separated by converting them into nitrates, which are made to crystallize; the strychnine nitrate, being less soluble than the brucine nitrate, deposits in needles, and the concentrated solution afterwards deposits voluminous crystals of brucine nitrate. To isolate the alkaloids, the corresponding nitrates are precipitated by ammonia, and the alkaloid dissolved in boiling alcohol, which, on cooling, deposits the strychnine in crystals. Pure strychnine crystallizes, under favorable conditions, in small, but exceedingly brilliant, octahedral crystals that are transparent and colorless; it is insoluble in ether and absolute alcohol, but dissolves in dilute alcohol, also dissolving very readily in chloroform and the volatile oils. The alcoholic solution of strychnine is optically active, turning the plane of polarization to the left, and having a remarkably bitter and somewhat metallic taste (1 part in 1,000,000,000 parts of water is still perceptible). Strychnine is one of the most active poisons known, giving rise to tetanic convulsions even in very small, dilute quantities. The smallest particle of strychnine or its salts may be identified by dissolving it in strong sulphuric acid and adding a minute fragment of potassium dichromate, which produces a blue color changing to red, and finally reddish yellow. The alcoholic solution of strychnine is alkaline, and it is a monacid tertiary base, combining with methyl iodide to form *strychnine methylium iodide* $N_2C_{21}H_{22}O_2 \cdot CH_3I$, which yields the corresponding hydroxide base when decomposed with moist silver oxide. But this ammonium base is not bitter nor poisonous unless injected under the skin, when it produces paralysis.

**143. Brucine.**—Brucine $C_{23}H_{26}N_2O_4$ is precipitated by potash from the solution of brucine nitrate obtained in the extraction of strychnine, is more soluble in water and alcohol than strychnine, and crystallizes with 4 molecules of water of crystallization, into oblique rhombic prisms that are often of considerable size, but rapidly effloresce in the air. Brucine solutions are strongly alkaline, intensely bitter, and optically active, turning the plane of polarization to the left. If brucine is moistened with nitric acid, it immediately assumes a red color, and, by the aid of a gentle heat, disengages carbon dioxide and vapors that contain methyl nitrite. The red color produced by adding nitric acid to brucine is turned to violet by the addition of stannous chloride.

## ALKALOIDS OF OPIUM

**144. Opium.**—Opium is the thickened juice of the capsules of the white poppy (*Papaver somniferum*) cultivated in Turkey, Egypt, India, and other Oriental countries. A few days after the poppy flower has fallen, incisions are made in these capsules, which remain on the stem of the plant, from base to summit, when a milky juice exudes. After 24 hours, this becomes a soft, brown, solid mass, and is scraped off, pressed together, and fashioned in variously formed masses for the market. The basic nature of morphine, one of the crystallizable principles of opium, was first recognized in 1806 by Sertürner. Besides this, opium contains a considerable number of alkaloids combined with several acids. Among these are lactic acid $C_3H_6O_3$ and meconic acid $C_7H_4O_7$. The latter is one of the most important constituents of opium; it possesses the characteristic property of producing a blood-red color with ferric salts. Opium also contains a gummy matter, about 25 per cent. soluble in water, and a brown, insoluble, resinous matter that remains in the mass when opium is exhausted with water. The aqueous solution of opium has a dirty, brown color. Opium further contains a large number of alkaloids in variable proportions, of which morphine, narcotine, and narceine are the most abundant. Some of these have been imperfectly studied, but they are mentioned in the following list:

| | | | |
|---|---|---|---|
| Hydrocotarnine | $C_{12}H_{15}NO_3$ | Papaverine | $C_{20}H_{21}NO_4$ |
| Morphine | $C_{17}H_{19}NO_3$ | Meconidine | $C_{21}H_{23}NO_4$ |
| Oxymorphine | $C_{17}H_{19}NO_4$ | Laudanosine | $C_{21}H_{27}NO_4$ |
| Codeine | $C_{18}H_{21}NO_3$ | Rhœadine | $C_{21}H_{21}NO_6$ |
| Thebaine | $C_{19}H_{21}NO_3$ | Cryptopine | $C_{21}H_{23}NO_5$ |
| Codamine | $C_{20}H_{25}NO_4$ | Narcotine | $C_{22}H_{23}NO_7$ |
| Laudanine | | Lanthopine | $C_{23}H_{25}NO_4$ |
| Protopine | $C_{20}H_{19}NO_5$ | Narceine | $C_{23}H_{29}NO_9$ |

**145. Morphine.**—Morphine $C_{17}H_{19}NO_3$ is extracted from opium by steeping it in warm water, which dissolves the meconate and sulphate of morphine, straining, and adding calcium chloride, which precipitates calcium meconate. The filtered solution is evaporated to a small bulk and set aside, when the hydrochlorides of morphine, codeine, and oxymorphine crystallize out. They are dissolved in water, and the morphine precipitated by adding ammonia. The precipitate is collected on a filter and redissolved in boiling alcohol, from which the morphine crystallizes on cooling. Morphine crystallizes in small, colorless, right-rhombic prisms that have a bitter taste and are almost insoluble in water, requiring 10,000 parts of cold and 500 parts of boiling water for their solution; it is nearly insoluble in ether and chloroform, both of which dissolve more or less nearly all other alkaloids; it is soluble in ethyl acetate and in amyl alcohol; the alcoholic solution of morphine is optically active and turns the plane of polarization to the left. Morphine differs from most other alkaloids by being very soluble in potassium hydrate; if a drop of weak potash is stirred with solution of a salt of morphine, the alkaloid is precipitated, but it is readily redissolved by adding a little more potash solution. Morphine crystallizes with 1 molecule of water of crystallization, and does not lose this water until heated to 120°, when it fuses, and becomes a crystalline anhydrous mass on cooling. When more strongly heated, a little sublimes, but the greater part carbonizes and evolves alkaline vapors. The proportion of morphine in opium varies from 6 to 15 per cent.

**146.** *Morphine hydrochloride* $C_{17}H_{19}NO_3 \cdot HCl$, or *muriate of morphia*, is the chief form in which morphine is used in medicine. It crystallizes with 3 molecules of water of crystallization in silky needles that are soluble in 1 part of boiling and 16 to 20 parts of cold water, and which are also very soluble in alcohol. Platinic chloride forms a yellow precipitate of a double chloride in an aqueous solution of morphine hydrochloride which has the formula $(C_{17}H_{19}NO_3 \cdot HCl)_2PtCl_4$. When a solution of morphine hydrochloride is heated to 60° with silver nitrite, the base is oxidized and converted into oxymorphine $C_{17}H_{19}NO_4$.

**147.** *Apomorphine* $C_{17}H_{19}NO_2$ is formed when morphine is heated for some hours at 150° with a large excess of concentrate hydrochloric acid. From the hydrochloride first obtained, sodium carbonate precipitates apomorphine as an amorphous powder, rapidly turning green in the air, and then dissolving in ether with a pink color. This base possesses special therapeutic properties. When administered by hypodermic injection or swallowed, it acts as an emetic.

**148.** *Morphine periodide* $C_{17}H_{19}NO_3I_4$ is obtained as a brown precipitate when solution of iodine in potassium iodide is added to morphine hydrochloride.

**149. Codeine.**—Codeine $C_{18}H_{21}NO_3$, or $C_{17}H_{18}(CH_3)NO_3$, is methyl morphine, and is obtained from the ammoniacal mother liquor from which the morphine is deposited in the preparation of the latter body. For this purpose, the mother liquor is concentrated, and potash or soda is added, precipitating the codeine, which is collected, dissolved in hydrochloric acid, the solution decolorized with animal charcoal, and the codeine again precipitated with potash or soda. Lastly the precipitate is dissolved in ordinary ether, which deposits the codeine in voluminous crystals by spontaneous evaporation. Codeine is easy soluble in hot water, alcohol, and ether, crystallizing from ether in anhydrous octahedra, and from hot water in rhombic prisms that contain 1 molecule of water of crystallization. The alcoholic solution of codeine is optically active, turning the plane of polarization to the left; it is a narcotic poison, though less powerful than morphine, and has been employed quite extensively in medicine for some years. If bromine water is poured upon finely powdered codeine, the latter dissolves and is converted into hydrobromide of monobromo codeine. By continued addition of bromine water, a yellow precipitate is formed, consisting of hydrobromide of tribromo codeine, that is, codeine in which 3 atoms of hydrogen have been replaced by 3 atoms of bromine.

**150. Narcotine.** — Narcotine $C_{22}H_{23}NO_7$, or $C_{19}H_{14}(CH_3)_3NO_7$, may be extracted from the residue of opium that has been exhausted by water. This is treated with hydrochloric acid, filtered, and the filtrate precipitated by sodium carbonate. The precipitate is dissolved in alcohol, and the alcoholic solution decolorized by animal charcoal. The narcotine crystallizes, on cooling, in small, colorless, brilliant prisms. Narcotine, like morphine, is almost insoluble in water, but, unlike that base, dissolves in ether, which will extract it from powdered opium, leaving the morphine. Narcotine is sparingly soluble in alcohol; both the ethereal as well as the alcoholic solution have a bitter taste, and are optically active, turning the plane of polarization to the left. Narcotine is insoluble in potash, is a weak base, not alkaline, dissolving in acids, but not forming well defined salts. If a few crystals of narcotine are moistened with a little sulphuric acid containing a trace of nitric acid, an intense blood-red color is produced. Narcotine has a narcotic effect, but is not nearly so poisonous as morphine. Opium contains usually about 1 per cent. of narcotine, and the presence of opium is more easily detected by testing for narcotine than for morphine itself, on account of the solubility of the former in ether. The material to be tested is extracted with ether, the latter evaporated, the residue dissolved in dilute hydrochloric acid and a little euchlorine water (made by adding strong hydrochloric acid to a weak solution of potassium chlorate till it has a bright-yellow color, and adding water till it is pale yellow); this produces, with narcotine, a yellow color in the cold, becoming pink on boiling, and adding more of the euchlorine water. By the action of oxidizing agents, narcotine is decomposed into opianic acid and cotarnine, another alkaloid, as is seen from the following equation:

$$\underset{\text{narcotine}}{C_{22}H_{23}NO_7} + O = \underset{\text{opianic acid}}{C_{10}H_{10}O_5} + \underset{\text{cotarnine}}{C_{12}H_{13}NO_3}$$

**151.** *Cotarnine* forms a yellow or colorless crystalline mass, very soluble, of bitter taste, and feebly alkaline reactions. When narcotine is heated with water, it breaks up into *cotarnine* and *meconine*, which latter compound is also present in opium:

$$\underset{\text{narcotine}}{C_{22}H_{23}NO_7} = \underset{\text{meconine}}{C_{10}H_{10}O_4} + \underset{\text{cotarnine}}{C_{12}H_{13}NO_8}$$

When subjected to the action of hydriodic acid, narcotine loses successively three methyl groups, and yields hydriodides of three new bases. One of them contains $C_{19}H_{17}NO_7$ and has been designated as *nornacotine* or *normal narcotine;* it is formed according to the equation:

$$\underset{\text{narcotine}}{C_{22}H_{23}NO_7} + 3HI = \underset{\text{nornacotine}}{C_{19}H_{17}NO_7} + \underset{\substack{\text{methyl}\\\text{iodide}}}{3CH_3I}$$

From this it may be inferred that narcotine is trimethyl nornacotine, as indicated by the formula $C_{19}H_{14}(CH_3)_3NO_7$, given in Art. **150.**

**152.** *Opianic acid* $C_{10}H_{10}O_5$ is obtained, together with cotarnine, when narcotine is oxidized by manganese dioxide and sulphuric acid, or by dilute nitric acid; it crystallizes in sparingly soluble needles, and when heated with potash, yields meconine and the potassium salt of another crystalline acid, *hemipinic acid* $C_{10}H_{10}O_6$, as is seen from the following equation:

$$\underset{\text{opianic acid}}{2C_{10}H_{10}O_5} + 2KOH = \underset{\substack{\text{potassium salt}\\\text{of hemipinic acid}}}{C_{10}H_8K_2O_6} + \underset{\text{meconine}}{C_{10}H_{10}O_4} + 2H_2O$$

**153.** *Thebaine* $C_{19}H_{22}NO_3$ is contained in opium in small proportion; it remains in the solution from which the hydrochlorides of morphine and codeine have been crystallized. This solution is mixed with ammonia, which precipitates thebaine together with some narcotine; the precipitate is dissolved in a little acetic acid, and the narcotine precipitated by tribasic lead acetate. The excess of the lead is precipitated from the filtrate by dilute sulphuric acid, after which ammonia is added to precipitate the thebaine. This alkaloid, like morphine, is insoluble in water, but dissolves in alcohol and ether, from which it crystallizes in plates. Thebaine is insoluble in alkalies, and its alcoholic solution is alkaline. Thebaine gives a blood-red color with strong sulphuric acid. When heated with hydrochloric acid, it yields an isomeride, *thebenine*, which gives a blue color with sulphuric acid.

Thebaine is a very poisonous compound, producing tetanic convulsions.

**154.** *Narceine* $C_{23}H_{29}NO_9$ remains in the solution from which thebaine and narcotine have been precipitated by ammonia. This is mixed with lead acetate, to precipitate the rest of the narcotine, filtered, the excess of lead removed by sulphuric acid, the filtrate neutralized by ammonia, and evaporated, when the narceine crystallizes, leaving meconine in solution, which may be extracted by shaking with ether. Narceine crystallizes from water in prismatic crystals with 2 molecules of water of crystallization; it is soluble in alcohol, but not in ether, and it is a narcotic poison. Iodine gives a blue color to its solution.

**155.** *Papaverine* $C_{20}H_{21}NO_4$ is contained, in small proportion, in the precipitate produced by excess of potassium hydrate in the aqueous solution of opium. The precipitate is dissolved in ether, and shaken with dilute acetic acid; the lower layer then contains the acetates of narcotine, thebaine, and papaverine; these are again precipitated by potassium hydrate, and treated with oxalic acid, which leaves the acid papaverine oxalate undissolved. Papaverine is sparingly soluble in water, but dissolves in hot alcohol and ether. It gives a violet-blue solution with strong sulphuric acid. The poisonous properties of papaverine appear to be rather feeble.

**156. Aconitine.**—Aconitine $C_{33}H_{43}NO_{12}$ does not belong to the alkaloids of opium, but, lacking a better classification, will be treated here. It is extracted from the root of a plant known as monk's hood, blue rocket, and wolf's bane (*Aconitum Napellus*). The scrapings of the root are boiled with amyl alcohol, the solution thus obtained shaken with dilute sulphuric acid to extract the aconitine, and the aqueous liquid neutralized with sodium carbonate. The aconitine thus precipitated is crystallized from ether, and it may be crystallized from alcohol in plates that are anhydrous and which melt at 188°; aconitine forms well defined salts. Aconitine is one of the most poisonous alkaloids. No trustworthy chemical test to detect the presence of aconitine has been devised so far. When heated with potash, aconitine yields potassium benzoate and *aconine* $C_{26}H_{41}NO_{11}$.

**157.** *Pseudoaconitine* $C_{36}H_{49}NO_{12}$ is a poisonous alkaloid obtained from *Aconitum ferox*, an Indian plant of the same natural order. Pseudoaconitine crystallizes with 1 molecule of water of crystallization. Heated with potash, it yields pseudoaconine $C_{27}H_{41}NO_9$ and the potassium salt of dimethyl protocatechuic acid.

### ALKALOIDS RELATED TO URIC ACID

**158. Theobromine.**—The two alkaloids *theobromine* and *caffeine*, or *theine*, are closely related to uric acid. Theobromine $C_7H_8N_4O_2$ exists in the beans of the cacao tree (*Theobroma Cacao*), which are the raw material for cocoa and chocolate. In order to prepare theobromine, the cocoa beans are crushed and exhausted with water, the aqueous extract is mixed with lead acetate, and the precipitate is filtered off. The filtrate is freed from any excess of lead acetate that may be present by precipitation with hydrogen sulphide, filtered again, and evaporated to dryness. The residue is dissolved in alcohol, and the alcoholic solution concentrated, when on cooling, the theobromine crystallizes out. The theobromine is thus obtained as a crystalline powder, which has a bitter taste. It is slightly soluble in alcohol and ether. When treated with hydrochloric acid and potassium chlorate, theobromine yields dimethyl alloxantin $C_8H_2(CH_3)_2N_4O_7$, and when dissolved in ammonia and boiled with silver nitrate, a white precipitate of *silver theobromine* $C_7H_7AgN_4O_2$ is obtained; when heated with methyl iodide, it yields methyl theobromine or caffeine, as is seen from the following equation:

$$\underset{\text{silver theobromine}}{C_7H_7AgN_4O_2} + CH_3I = \underset{\text{caffeine}}{C_7H_7(CH_3)N_4O_2} + AgI$$

**159. Caffeine.**—Caffeine, or *theine*, $C_8H_{10}N_4O_2$ was first extracted from coffee in 1821 by Pelletier and others. It is contained in the seeds of the coffee tree (*Caffea Arabica*) and in the leaves of tea.

Caffeine, or theine, is generally obtained from tea. Powdered tea is boiled with water to extract all the soluble matter it contains, and which amounts to about 30 per cent., being a mixture of tannin, caffeine, aromatic oil, and other substances. The solution, after being filtered, is mixed with lead acetate to precipitate the tannin, filtered, and the excess of lead precipitated by hydrogen sulphide. The precipitate is filtered off, and the filtrate is evaporated to a small bulk, when the caffeine crystallizes out. These crystals may be purified by dissolving them in alcohol and allowing the caffeine to recrystallize therefrom.

Caffeine forms long, colorless, silky needles containing 1 molecule of water of crystallization, which is expelled at 100°. Caffeine melts at 225°, and sublimes without being decomposed; is only slightly soluble in cold water, but readily dissolves in boiling water and in alcohol; and it is only slightly soluble in ether, but freely soluble in chloroform and benzene. Caffeine is only a very weak base, its salts being decomposed by water. The hydrochloride $C_8H_{10}N_4O_2 \cdot HCl, 2H_2O$ crystallizes from strong hydrochloric acid in prisms; the sulphate $C_8H_{10}N_4O_2 \cdot H_2SO_4$ is obtained in needles by adding dilute sulphuric acid to a hot solution of caffeine. By the action of chlorine water or of nitric acid, caffeine forms methylamine, cyanogen chloride, and amalic acid $C_{12}H_{12}N_4O_7$. The latter is tetramethyl alloxantin $C_8(CH_3)_4N_4O_7$, and the reaction indicates a relationship between caffeine and the uric-acid group. Heated with baryta water, it breaks up into carbon dioxide and *caffeidine* $C_7H_{12}N_4O$. When caffeine is boiled for a few minutes with fuming nitric acid, the yellow liquid evaporated to dryness, and the residue moistened with ammonia, a purple color is obtained; this reaction serves sometimes as a test for caffeine.

# A SERIES OF QUESTIONS AND EXAMPLES

RELATING TO THE SUBJECTS
TREATED OF IN THIS VOLUME.

It will be noticed that the pages of the Examination Questions that follow have been given the same section numbers as the Instruction Papers to which they refer. No attempt should be made to answer any of the questions or to solve any of the examples until the Instruction Paper having the same section number has been carefully studied.

# ORGANIC CHEMISTRY

(PART 1)

## EXAMINATION QUESTIONS

(1) An organic compound shows the following percentage composition: carbon 40 per cent., hydrogen 6.6 per cent., oxygen 53.4 per cent. Calculate from it the empirical formula of the compound.

(2) If you were told to determine the molecular weight of a compound by the cryoscopic method, state fully how you would proceed, and describe the apparatus you would require.

(3) (*a*) Give the formula you would use to calculate the specific volume of an organic compound. (*b*) How is this formula obtained?

(4) State Van't Hoff's law of osmotic pressure.

(5) Define the term molecular formula.

(6) What do you understand by the expression "specific heat under constant pressure"?

(7) Outline the method of determining the molecular formula of a monobasic acid from its empirical formula.

(8) Define isotonic.

(9) Explain what you understand by osmotic pressure.

(10) State in your own words what you know about the kinetic theory of gases.

(11) Define organic chemistry.

(12) Define isomorphism.

(13) The freezing point of 111 grams of water was found by Beckmann's apparatus to be 0°. On dissolving 4 grams of urea in the water and again determining the freezing point, a depression of 1.148° was observed. From these data calculate the molecular weight of urea. Ans. 59.33

(14) Define isodimorphism.

(15) In determining, by the cryoscopic method, the molecular weight and molecular formula of lactic acid, it was found that by adding 3 grams of the acid the freezing point of 106 grams of water was depressed .639°. Calculate from these data the molecular weight and molecular formula. It is known that the acid has the general formula $C_nH_{2n}O_n$.

(16) State what you know about the specific heat of compounds.

(17) State Boyle's law according to the kinetic theory.

(18) Outline the method of determining the formula of a compound by means of Victor Meyer's apparatus.

(19) Describe briefly the process adopted for determining carbon and hydrogen in organic compounds.

(20) Does a direct relation exist between the specific heats and atomic weights of elements?

# ORGANIC CHEMISTRY

## (PART 2)

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## EXAMINATION QUESTIONS

(1) Define the term polymerism.

(2) Give the rational formula of acenaphthene.

(3) What do you understand by ethylenic linking?

(4) Why is the homologous series of saturated hydrocarbons, having the general formula $C_nH_{2n+2}$, known as the paraffin series of hydrocarbons?

(5) Is methane a saturated hydrocarbon? If so, state why.

(6) What are unsaturated hydrocarbons?

(7) What is the natural source of the paraffin hydrocarbons?

(8) State the general composition of the hydrocarbons.

(9) Give the rational formula for propine.

(10) Give formulas and boiling points of pentane, octane, and hexadecane.

(11) What is the general formula of the paraffin series of hydrocarbons?

(12) Explain how the alcohols are constructed?

(13) Give the formula and properties of toluene.

(14) Give the formula, preparation, and properties of benzene.

(15) Give a short account of the fractional distillation of petroleum, its products, etc.

(16) State what you know about the structure of carbohydrates.

(17) What do you understand by an homologous series?

(18) Name and give the formulas of the chlorine substitution products of methane.

(19) Give the general formula of the acetylene series of hydrocarbons.

(20) How would you express graphically the structure of methane?

(21) How many isomerides of pentane are known to exist? Name them.

# ORGANIC CHEMISTRY

## (PART 3)

## EXAMINATION QUESTIONS

(1) State by what simple chemical tests you are able to determine whether a liquid is alcohol or not.

(2) How much alcohol is needed to produce 192 grams of potassium xanthate? Ans. 55.2 grams

(3) State how isomeric alcohols are classified.

(4) What do you understand by acetic-acid fermentation?

(5) Name the compound having the formula $C_6H_4OH \cdot CHO$.

(6) What are the products of oxidation of glycols?

(7) Give formula of diethyl sulphide, and state how it is prepared.

(8) Define alcohols.

(9) Name the properties and mode of preparation of methyl alcohol.

(10) How may the three classes of alcohol, viz., primary, secondary, and tertiary, be chemically distinguished by means of certain oxidizing agents?

(11) How are aldehydes obtained?

(12) State to what class of alcohols allyl alcohol belongs, give its formula, and tell how the alcohol may be prepared.

(13) (*a*) Can ethyl alcohol be prepared synthetically? If so, state how you would proceed. (*b*) How is alcohol usually prepared in the arts?

(14) Explain how the strength of alcohol is usually determined.

(15) Describe fully how ethene alcohol is prepared.

(16) Write the equation by which mercaptan is produced from calcium sulphethylate and potassium hydrosulphide.

(17) Name the compound having the formula $CH_2 \cdot OH \cdot (CHOH)_4 \cdot CH_2OH$.

(18) What do you understand by a diatomic alcohol?

(19) Give formula and describe the preparation of acetic aldehyde.

(20) Give formula, preparation, and properties of butyl alcohol.

(21) (*a*) State what you know about the formation of the monohydric alcohols of the benzene series. (*b*) What are these alcohols called?

(22) Can oil of bitter almonds be artificially prepared? If so, state how and show the process through equations.

# ORGANIC CHEMISTRY

## (PART 4)

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## EXAMINATION QUESTIONS

(1) Give the formula and describe the preparation of normal butyric acid.

(2) You are told to prepare 228.39 grams of citric acid by synthesis; how many grams of acetone and how many liters of chlorine gas, at normal temperature and pressure, would you require to obtain the desired quantity?

(3) How is oxalic acid prepared?

(4) What is the name of a compound having the formula $CH_2Cl \cdot COOH$?

(5) What products are obtained when lactic acid is oxidized with chromic acid?

(6) Give the formula of citric acid, and state how the adulteration of this acid may be detected.

(7) How can you explain stereo-isomerism?

(8) Explain the construction of organic acids.

(9) To what class of compounds does $C_6H_3(OH)_2 \cdot CO_2H$ belong? Name this compound.

(10) Are racemic and tartaric acids related? If so, explain fully how.

(11) How many grams of potassium formate can be obtained from 500 liters of carbon monoxide?

Ans. 1,875 grams

(12) Explain what enantiomorphous means.

(13) Give the general formula of the dibasic acids obtained from olefine hydrocarbons (acids of the fumaric series).

(14) What action has sulphuric acid and heat on lactic acid?

(15) Give the formula of tartaric acid, and state how this important compound is prepared.

(16) Describe the manufacture of vinegar.

(17) Name the compound having the formula $CH_2(CO_2H)_2$, and state how it is prepared.

(18) Give the most important reaction by which the phenol acids may be obtained.

(19) In how many modifications may fumaric acid exist? Give the formula of each modification.

(20) Give the names and formulas of the known varieties of crotonic acid.

(21) Describe the continuous etherification process.

(22) What do you understand by: (*a*) plane-symmetrical, or cis, formula, and (*b*) axial-symmetrical, centri-symmetrical, or trans, formula?

(23) What are mixed ketones?

(24) How is hexa-hydroxyanthraquinone $C_{14}H_2(OH)_6O_2$ obtained?

# ORGANIC CHEMISTRY

## (PART 5)

## EXAMINATION QUESTIONS

(1) Complete the following equation:

$$C_2H_5 \cdot OH + HNO_3 = ?$$

(2) What is formed when chloroform is heated with an alcoholic solution of caustic potash?

(3) State what you understand by ketonic decomposition.

(4) How much zinc is required to prepare 194 grams of zinc ethide?

(5) State what you understand by a reversible reaction.

(6) State the properties of iodoform.

(7) What is the general method of preparing primary amines?

(8) What do you understand by a metallo-organic compound?

(9) Name the compound having the formula $(C_2H_5)_2SO_4$.

(10) Define an amido acid.

(11) Show by an equation the reaction that takes place when a reducing agent acts on nitrobenzene, and name the chief product.

(12) How is amyl nitrite prepared?

(13) What is formed when chloroform is heated with an alcholic solution of ammonia in a sealed tube?

(14) How is methyl chloride usually prepared?

(15) Define an amide.

(16) How are nitroparaffins prepared?

(17) State how ethereal salts are formed.

(18) What is the chief property of chloroform?

(19) State the most remarkable property of the cacodyl compounds.

(20) State formula, properties, and method of preparation of nitroglycerin.

(21) State how chloral may be prepared.

(22) Name some of the glycerides of the higher fatty acids.

(23) How is chloroform made?

(24) State fully how zinc ethide is usually prepared in the laboratory.

(25) Give the formulas of compounds formed when chloral is brought together with sodium hydrate.

# ORGANIC CHEMISTRY

## (PART 6)

## EXAMINATION QUESTIONS

(1) If sulphocyanic acid is added to ferric chloride, ferric thiocyanate is obtained as a blood-red solution; the same color is shown by ferric acetate, obtained by adding a neutral acetate to the solution of a ferric salt. By what simple test could you positively and quickly determine which is the ferric thiocyanate and which the ferric acetate?

(2) Name some aniline substitution-products.

(3) The formula of glycocoll $CH_2(NH_2) \cdot CO_2H$ signifies that this compound is an acid; this being the case, what is it frequently called?

(4) State how potassium cyanide is prepared, and illustrate the process by an equation.

(5) What class of compounds are usually called "mustard oils"?

(6) Give the formula, and state how phenyl hydrazine may be prepared.

(7) How may urea be prepared?

(8) How may mustard oil be artificially obtained?

(9) What is an auxochrome?

(10) Name the decomposition products obtained when oxamide is passed through a red-hot glass tube, and show the decomposition by an equation.

(11) What do you understand by a substantive dye?

(12) State what you know about the constitution of diazo compounds.

(13) Name some alkyl derivatives of aniline.

(14) Has hydrocyanic acid been prepared synthetically? If so, state how you would proceed.

(15) Give the equation showing the formation of diazobenzene nitrate from aniline nitrate.

(16) How is potassium ferrocyanide prepared?

(17) Give the formula of glycocoll.

(18) Give the formula for prussic acid.

(19) What is meant by a diazo reaction?

(20) How are acid derivatives of aniline obtained?

(21) Define diazo compounds.

(22) How is aniline prepared?

(23) What do you understand by an adjective dye?

(24) Name the compound having the formula $(CONH_2)_2$.

# ORGANIC CHEMISTRY

(PART 7)

## EXAMINATION QUESTIONS

(1) What is the chief coloring matter of madder?

(2) Give a short description of the preparation and refining of sugar.

(3) What is the action of yeast and dilute sulphuric acid on maltose?

(4) How is maltose obtained?

(5) How may the triphenyl-methane dyestuffs be classified?

(6) Give the formula of aseptol.

(7) Point out the chief properties of sucrose.

(8) State what you understand by a quinonoid structure, and what peculiar property compounds possess, having such a structure.

(9) State what you understand by alcoholic fermentation.

(10) How is resorcinol prepared on the large scale, and for what purposes is it used?

(11) What do you understand by "invert sugar"?

(12) Do you consider the presence of flavopurpurin and anthrapurpurin in commercial alizarine used for dyeing purposes a disadvantage?

(13) Give the formula of picric acid, and point out its properties.

(14) What is the chief physical difference between glucose and levulose ?

(15) How is chloranil prepared ?

(16) Name the most important and best known substitution derivative of phenol.

(17) (*a*) How is alizarine synthetically prepared? (*b*) What are its uses ?

(18) From what are the quinones derived ?

(19) Show by an equation how phenol is converted into picric acid by means of nitric acid.

(20) What are stereo-isomerides ?

(21) For what purpose is pyrogallol used in analytical chemistry ?

(22) Give the formula preparations and the properties of carbolic acid.

# ORGANIC CHEMISTRY

(PART 8)

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## EXAMINATION QUESTIONS

(1) Point out the chief properties of quinine, cinchonine, and their isomers.

(2) How is theobromine connected with theine?

(3) In what chemical characters do the albuminous bodies differ from other chemical compounds?

(4) Where do the pyridine bases usually occur?

(5) Can theobromine be prepared synthetically, and if so, state how?

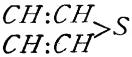
(6) Give the name of the alkaloid having the formula $C_{17}H_{19}NO_3$.

(7) Give the chief properties of uric acid, and name some of its derivatives.

(8) State the principle involved in the application of indigo as a dye.

(9) To what organic substances is the term *alkaloids* applied?

(10) (*a*) How is artificial tourmaline prepared? (*b*) What is its most characteristic property?

(11) Give name and properties of the compound to which the formula  $\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}\!>S$ has been assigned.

(12) Give the formula of cocaine, and state what particular properties this compound possesses.

(13) What is "peptonized albumin"?

(14) Give the names of the different alkaloids occurring in the different varieties of the cinchona bark.

(15) What is the most characteristic feature in cases of atropine poisoning?

(16) How may albumin be obtained?

(17) Where does nicotine for the most part occur?

(18) Give the formula and properties of indigo.

(19) How are the alkaloids usually classified?

(20) Are vegetable coloring matters, as a rule, preferable to those obtained from other sources?

(21) State the most characteristic property of the alkaloids.

(22) Where does oxyhemoglobin occur?

# A KEY

## TO ALL THE QUESTIONS AND EXAMPLES INCLUDED IN THE EXAMINATION QUESTIONS.

It will be noticed that the Keys have been given the same section numbers as occur on the headlines of Examination Questions to which they refer. All article references refer to the Instruction Paper bearing the same section number as the Key in which it occurs, unless the title of some other Instruction Paper is given in connection with the article number.

To be of the greatest benefit, the Keys should be used sparingly. They should be used much in the same manner as a pupil would go to a teacher for instruction with regard to answering some example he was unable to solve. If used in this manner, the Keys will be of great help and assistance to the student, and will be a source of encouragement to him in studying the various papers composing the Course.

# ORGANIC CHEMISTRY

## (PART 1)

(1) The percentage figures, 40, 6.6, and 53.4, divided by their atomic weights give $\frac{40}{12} = 3.3$, $\frac{6.6}{1} = 6.6$, and $\frac{53.4}{16} = 3.3$. If this ratio, 3.3 : 6.6 : 3.3, is expressed in its lowest term, it becomes 1 : 2 : 1, and the empirical formula of the compound is $CH_2O$. See Art. **59.**

(2) See Art. **49.**

(3) (*a*) $11\,m + 5.5\,n + 7.8\,p$.
(*b*) See Art. **39.**

(4) See Art. **51.**

(5) See Art. **59.**

(6) See Art. **13.**

(7) See Art. **61.**

(8) See Art. **51.**

(9) See Art. **51.**

(10) See Art. **8.**

(11) See Art. **53.**

(12) See Arts. **21, 22,** and **23.**

(13) Using the formula given in Art. **49,** $M = \frac{rp \times 100}{dg}$, and substituting the known values, we get $M = \frac{18.9 \times 4 \times 100}{1.148 \times 111} = 59.33$, a number sufficiently close to confirm the otherwise obtained molecular weight (60) of urea.

(14) See Art. **22.**

(15) Using the formula given in Art. **49,** $M = \frac{rp \times 100}{dg}$, and substituting the proper values, we get $M = \frac{18.9 \times 3 \times 100}{0.639 \times 106} = 83.71$, which is close enough to confirm the opinion that the molecular weight of lactic acid is 90, and that its formula is $C_3H_6O_3$.

(16) See Art. **20.**

(17) See Art. **10.**

(18) See Art. **5.**

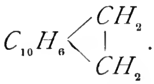
(19) See Art. **54.**

(20) See Art. **18.**

# ORGANIC CHEMISTRY

## (PART 2)

(1) See Art. **77.**

(2)  $C_{10}H_6\left<\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\right.$. See Art. **113.**

(3) See Art. **96.**

(4) See Art. **70.**

(5) See Art. **68.**

(6) See Art. **79.**

(7) See Art. **71.**

(8) See Art. **66.**

(9) $CH_3\cdot C \vdots CH$. See Art. **87.**

(10) Pentane, $C_5H_{12}$; boiling point, 37°. Octane, $C_8H_{18}$; boiling point, 125°. Hexadecane, $C_{16}H_{34}$; boiling point, 287°. See Art. **71.**

(11) $C_nH_{2n+2}$ or $H_3C\cdot C_nH_{2n}\cdot CH_3$. See Art. **70.**

(12) See Art. **66.**

(13) See Art. **102.**

(14) See Art. **91.**

(15) See Art. **71.**

(16) See Art. **66.**

(17) See Art. **70.**

(18) See Art. **73.**

(19) $C_nH_{2n-2}$. See Art. **85.**

(20) See Fig. 16, Art. **68.**

(21) See Art. **77.**

# ORGANIC CHEMISTRY

## (PART 3)

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(1) See Art. **7.**

(2) Potassium xanthate is formed according to the equation:

$$\underset{46}{C_2H_5\cdot OH} + \underset{76}{CS_2} + \underset{56}{KOH} = \underset{160}{C_2H_5\cdot O\cdot CS_2K} + \underset{18}{H_2O}$$

See Art. **32.**

Since 40 grams of alcohol produce 160 grams potassium xanthate, to produce 192 grams of potassium xanthate we will require $\frac{46\times 192}{160} = 55.2$ grams alcohol. Ans.

(3) See Art. **11.**

(4) See Art. **5.**

(5) See Art. **59.**

(6) See Art. **35.**

(7) See Art. **27.**

(8) See Art. **2.**

(9) See Art. **10.**

(10) See Arts. **13** and **14.**

(11) See Art. **47.**

(12) A monohydric alcohol of the olefine series. See Arts. **20.** and **21.**

(13) (*a*) and (*b*) See Arts. **4.** and **5.**

(14) See Art. **9.**

(15) See Art. **36.**

(16) See Art. **26.**

(17) See Art. **43.**

(18) A diatomic or dihydric alcohol is an alcohol containing two hydroxyl ($OH$) groups. See Art. **2.**

(19) See Art. **50.**

(20) See Art. **17.**

(21) (*a*) and (*b*) See Art. **23.**

(22) See Art. **57.**

# ORGANIC CHEMISTRY

## (PART 4)

(1) See Art. **75.**

(2) From the equation showing the synthetical preparation of citric acid, given in Art. **157,** we see that 58 parts of acetone and 142 parts of chlorine are necessary to obtain 192 parts of citric acid; hence,

$$192 : 58 = 228.39 : 68.99 \text{ grams of acetone}$$
$$192 : 142 = 228.39 : 168.91 \text{ grams of chlorine}$$

As 1 liter of chlorine weighs 3.17 grams, 168.91 grams = 53.28 liters.

$$\text{Ans.} \begin{cases} 68.97 \text{ grams acetone} \\ 53.28 \text{ liters chlorine} \end{cases}$$

(3) See Art. **128.**

(4) Monochlor-acetic acid.

(5) Acetic acid $CH_3 \cdot CO_2H$; carbon dioxide $CO_2$; and water $H_2O$. See Art. **110.**

(6) See Art. **157.**

(7) See Art. **111.**

(8) See Art. **64.**

(9) Is protocatechuic acid, a phenol acid belonging to the class of monobasic hydroxy acids derived from benzene hydrocarbons. See Art. **119.**

(10) Yes; racemic acid is an isomeride of tartaric acid, it is externally compensated tartaric acid. See Arts. **147-150.**

(11) Potassium formate is obtained according to the equation:

$$\underset{28}{CO} + \underset{56}{KOH} = \underset{84}{HCO \cdot OK}$$

See Art. **66.**

1 liter $CO$ weighs 1.25 grams; therefore, 500 liters weigh 625 grams.

$$28 : 84 = 625 : 1{,}875 \text{ grams.} \quad \text{Ans.}$$

(12) See Art. **148.**

(13) $C_nH_{2n-2}(CO_2H)_2$. See Art. **133.**

(14) Decomposes it into aldehyde and formic acid, and if the sulphuric acid is of sufficient strength, this acid acts further on the formic acid, decomposing it into water and carbon monoxide. See Art. **110**

(15) See Art. **145.**

(16) See Art. **69.**

(17) Malonic acid. See Art. **130.**

(18) See Art. **116.**

(19) See Art. **133.**

(20) See Art. **87.**

(21) See Art. **163.**

(22) (*a*) and (*b*) See Art. **136.**

(23) See Art. **158.**

(24) See Art. **121.**

# ORGANIC CHEMISTRY

(PART 5)

(1) $C_2H_5 \cdot OH + HNO_3 = C_2H_5 \cdot NO_3 + H_2O$. See Art. **36.**

(2) See Art. **14.**

(3) See Art. **43.**

(4) The equation $Zn_2 + 2C_2H_5I = Zn(C_2H_5)_2 + ZnI_2$ represents the formation of zinc ethide (see Art. **61**). Taking the molecular weight of zinc as 130, and that of zinc ethide as 123, we have the proportion $130 : 123 = x : 194$. $x = 205.04$ grams of zinc. Ans.

(5) See Art. **1.**

(6) See Art. **15.**

(7) See Arts. **75** and **76.**

(8) See Art. **60.**

(9) $(C_2H_5)_2SO_4$ is ethyl sulphate. See Art. **34.**

(10) See Art. **74.**

(11) See Art. **58.** $C_6H_5NO_2 + 3H_2 = 2H_2O + C_6H_5NH_2$ (aniline).

(12) See Art. **40.**

(13) See Art. **14.**

(14) See Art. **3.**

(15) See Art. **74.**

(16) See Art. **56.**

(17) See Art. **30.**

(18) Chloroform is best known by its anesthetic property. See Art. **14.**

(19) Cacodyl compounds are extremely poisonous. See Art. **67.**

(20) See Art. **51.**

(21) See Art. **23.**

(22) See Art. **53.**

(23) See Art. **14.**

(24) See Art. **61.**

(25) $CCl_3COH + NaOH = \underset{\text{sodium formate}}{NaCHO_2} + \underset{\text{chloroform}}{CHCl_3}$. See Art. **23.**

# ORGANIC CHEMISTRY

## (PART 6)

(1) The addition of mercuric chloride destroys the red color of ferric thiocyanate, but does not change that of ferric acetate. See Art. **145.**

(2) See Art. **88.**

(3) Amido-acetic acid. See Art. **109.**

(4) See Arts. **131** and **133.**

(5) See Art. **147.**

(6) See Art. **128.**

(7) See Art. **103.**

(8) See Art. **147.**

(9) See Art. **125.**

(10) See Art. **101.**

(11) A substantive dye is one that has an affinity for the fiber and attaches itself without the aid of a mordant. See Art. **125.**

(12) See Art. **119.**

(13) See Art. **89.**

(14) See Art. **132.**

(15) $C_6H_5 \cdot NH_2HNO_3 + HNO_2 = C_6H_5 \cdot N : N \cdot NO_3 + 2H_2O$. See Art. **121.**

(16) See Art. **131.**

(17) $CH_2(NH_2)\cdot CO_2H$. See Art. **109.**

(18) See Art. **132.**

(19) See Art. **119.**

(20) See Art. **90.**

(21) See Art. **119.**

(22) See Art. **86.**

(23) An adjective dye is one that requires a mordant to fix it on the fiber. See Art. **125.**

(24) $(CONH_2)_2$ is oxamide. See Art. **101.**

# ORGANIC CHEMISTRY

## (PART 7)

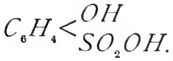
(1) See Art. **25.**

(2) See Arts. **52, 53,** and **54.**

(3) See Art. **57.**

(4) See Art. **57.**

(5) See Art. **31.**

(6) Aseptol is ortho-phenol-sulphonic acid; its formula is  $C_6H_4<\begin{matrix}OH\\SO_2OH.\end{matrix}$ See Art. **10.**

(7) See Art. **55.**

(8) See Arts. **28** and **29.**

(9) See Art. **63.**

(10) See Art. **15.**

(11) See Art. **55.**

(12) No; rather an advantage. See Art. **27.**

(13) See Arts. **7, 8,** and **9.**

(14) Glucose is dextrorotary, while levulose is levorotary. See Arts. **46** and **47.**

(15) See Art. **23.**

(16) Trinitrophenol, or picric acid. See Art. **7.**

(17) See Arts. **25** and **26.**

(18) See Art. **19.**

(19) $C_6H_5 \cdot OH + 3HNO_3 = C_6H_2(NO_2)_3OH + 3H_2O$. See Art. **7.**

(20) Stereo-isomerides are compounds having the same composition, but possessing different optical activity.

(21) An alkaline solution of pyrogallol is used in gas analysis to absorb oxygen. See Art. **17.**

(22) See Arts. **2** and **3**.

# ORGANIC CHEMISTRY

## (PART 8)

(1) See Arts. **137, 138, 139,** and **140.**

(2) See Arts. **158** and **159.**

(3) They are neither crystalline nor volatile. See Art. **91.**

(4) The pyridine bases are found in coal tar and oil extracted from bones. See Art. **108.**

(5) See Arts. **124, 125,** and **158.**

(6) Morphine. See Art. **145.**

(7) See Arts. **113, 114, 115,** and **116.**

(8) See Art. **87.**

(9) See Art. **128.**

(10) See Art. **138.**

(11) Thiophene. See Art. **104.**

(12) See Art. **135.**

(13) See Art. **95.**

(14) See Art. **136.**

(15) The enlargement of the pupil of the eye. See Art. **133.**

(16) See Art. **92.**

(17) See Art. **130.**

(18) See Art. **86.**

(19) See Art. **128.**

(20) No; most vegetable coloring matters do not resist sufficiently the decomposing action of light, air, etc., and consequently the colors fade sooner than those obtained from other sources.

(21) The alkaloids are distinguished by being more or less poisonous; they are the "active principle" of poisonous plants. See Art. **128.**

(22) See Art. **96.**

# INDEX.

NOTE.—All items in this index refer first to the section (see the Preface) and then to the page of the section. Thus, “ Combustion 5 86” means that combustion will be found on page 86 of section 5.