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FUNDAMENTALS OF CHEMISTRY AND APPLICATIONS



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FUNDAMENTALS OF CHEMISTRY AND APPLICATIONS

Chosen from inorganic, organic, and biochemistry, with applications in physiology, microbiology, nutrition, and everyday concerns

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FOURTH EDITION

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PREFACE TO FOURTH EDITION

This textbook is written for students who do not expect to become chemists but who have chosen vocations such as nursing, home economics, or health education for which a functional knowledge of chemistry is required. A study of chemistry which is directed toward the interests of the students and which helps them to see that chemical reactions operate in the world around them, as well as in the laboratory, can contribute to both professional competence and general education.

Recent advances in chemistry have affected many areas included in this text. The impact of atomic science on our modern world means that a better understanding of radioactive elements and their associated radiations is important for the general public. It is of special importance for students of nursing whose daily work may bring them in contact with such elements. Active research in the field of biochemistry has resulted in new knowledge and better understanding of reactions within living cells. This, in turn, has focused attention on the importance of enzymes and has identified the roles of certain of the vitamins. It is beginning to become evident why these vitamins are indispensable foods. These and other developments in chemistry have been considered in this revision.

The fourth edition of *Fundamentals of Chemistry and Applications* is similar to the earlier editions in scope and selection of content. However, the text has been thoroughly revised with the introduction of new material, changes in emphasis, and, in some sections, considerable reorganization. About 20 new figures and diagrams are used. The introduction to valence now appears in the chapter on chemical shorthand, while the explanation of valence is associated with the discussion of ionic compounds and covalent molecules. Radioactive elements have been given a separate chapter. Reorganization of the chapters on acids, bases, salts, and water has enabled the study of metals to appear as a separate unit. The chapter on oxidation-reduction reactions has been rewritten with more attention to modern concepts.

Throughout the material on organic and physiological chemistry, various changes have been made to keep the content up to date. The placement of the chapter on cyclic compounds before the study

of carbohydrates, fats, and proteins should facilitate the transition from study of organic compounds to physiological chemistry. A chapter on enzymes now precedes the studies of digestion and the fates of carbohydrates, fats, and proteins in the cells. The final chapter deals with blood and its components. Blood is treated as a living tissue, the medium for transportation between tissues and organs throughout the body. With this emphasis it is appropriate to include in the same chapter the oxygen–carbon dioxide exchange and the functioning of the kidneys in maintaining homeostasis. For students whose interest is in the response of the body to changes in health and disease, this is a more helpful approach than that of the analytical study of blood. Outlines for laboratory studies of both blood and urine are included in the manual which has been prepared to accompany this text.

This book should be useful to students not only as a textbook for a chemistry course but also as a reference throughout their studies of physiology, microbiology, and nutrition. These applied sciences are using an increasing amount of material from the field of chemistry, and students will find it to their advantage to keep the fundamentals of chemistry in review.

We are happy to express our appreciation to other teachers for their suggestions and criticisms. We are grateful to the students in the general chemistry courses at Teachers College who stimulate the continued search for that chemistry which will be most valuable to them in their professional work. We are indebted to Miss Frances Russel for help in developing new figures and diagrams. Other acknowledgments will be found in the text.

May, 1956 THE AUTHORS

PREFACE TO FIRST EDITION

This book has been written as the result of numerous requests made by many people during a period of years. It is intended for use in connection with a brief course in chemistry for the purpose of helping to make more meaningful applied sciences and arts such as physiology, cookery and nutrition, bacteriology, materia medica, and nursing practice.

The usual one-year course in high-school chemistry and the usual first-year course in college—the former an abbreviated replica of the latter—are devoted almost exclusively to inorganic chemistry and are chiefly designed to prepare students for further study of chemistry in the traditional manner—high-school students for chemistry in college, college students for further courses in chemistry. And, naturally, textbooks for these courses are patterned accordingly. This scheme serves admirably for students who are to become chemists in one line or another, but it does not serve at all well for the multitude of other students.

Among the latter are those whose curriculum requirements in certain specialized schools, including all schools of nursing and some schools in home economics, call for a half year of chemistry—or at most one year—as a service course for the applied sciences and arts mentioned above. A course planned for such purpose should include content selected not only from inorganic chemistry but from organic and biochemistry as well; but since each of these fields is extensive in itself, it follows that for such an abbreviated and inclusive course the content selection must be highly limited and carefully made, and the manner of treatment should be consistent with the purpose.

It is for such a course in chemistry and with these intents continuously in mind that this book has been written.

The general plan and the content selection are much the same as are recommended for a course in chemistry in the *Curriculum Guide for Schools of Nursing*, of recent publication.[1]

Somewhat more than one half of the book is devoted to the presentation of fundamentals which of necessity must comprise a part of any first course in chemistry, but the manner of presentation

[1] *Curriculum Guide for Schools of Nursing*, National League of Nursing Education, 1937.

is more detailed than is usual with chemistry texts for the reason that the more condensed the chemistry course, the greater must be the proportion of assistance provided for the students by either teacher or text; and teachers in such schools as have been mentioned are quite commonly overburdened with a number of subjects and many hours of teaching load.

Other features of this text are as follows. Oxygen is the only simple substance that is studied in detail, and the chief emphasis is centered around the fact that its vital physiological use and its use in man's external concerns are due to its being a reservoir of an enormous amount of energy. One chapter is devoted solely to energy transformations that accompany matter transformations in many chemical reactions. More than the usual amount of emphasis is given to the study of water—its physical and chemical properties and the bearing of these properties on the affairs of man.

The text material involving molecular weights and atomic weights as unit weights for measurable quantities of substances and elements, also molecules and atoms as theoretical ultimates of substances and elements, is presented in greater detail than is customary. Valences of atomic weights versus valences of atoms are treated in like detail. Many students confuse these issues, and adequate help is not usually provided in textbooks for clarifying these concepts. The use of symbols and formulas as abbreviations of the written names for elements and substances is discouraged, as is the use of the formula equation as a convenient substitute for the word equation. It is through such practices on the part of beginning students in chemistry that these shorthand devices lose their quantitative significance.

Included in the chapter with solution is more material appertaining to colloidal solutions and emulsions than is likely to appear in beginning texts on chemistry. This has seemed necessary because some information in regard to the properties of colloidal solutions in comparison with those of true solutions has become essential to the better understanding of many phenomena with which applied sciences are concerned.

The theory of partial ionization on the part of electrolytes originally conceived by Arrhenius is presented rather than the Debye-Huckel theory of complete ionization, since the former provides all that is necessary for the sort of course for which this text is intended. Special attention is given to water as an ultrapoor electrolyte and to the concentration relationship that must be met on the part of

hydrogen ions and hydroxyl ions when water as an electrolyte attains equilibrium This emphasis is due chiefly to the increasing tendency in the applied sciences to present these concentrations quantitatively in terms of *c*H and *c*OH, or in terms of their power *p*H and *p*OH notations, as factors to be reckoned with in various phenomena. The discussion of this quantitative relationship has been carried only as far as the negative-power-of-ten values, no attempt having been made to deal with the reciprocal relationships. Neither the mathematical equipment of most students of beginning chemistry nor the scope of this text would seem to justify this latter step.

The organic chemistry and biochemistry are integrated, the chief purpose of the organic chemistry being to provide service information for the better understanding of carbohydrates, fats, and proteins, the digestive reactions, and such metabolic reactions as are discussed. Portions of the chapter on cyclics and derivatives are developed with the intent of placing especial emphasis on the theoretical accounting for similarities and differences among members of some classes of drugs.

The final chapter on the physiological functioning of salts deals with such studies as reactions through which salts aid indirectly in obtaining optimum hydrogen-ion concentrations for digestive reactions, and in maintaining the hydrogen-ion–hydroxide-ion-concentration relationship within the blood, lymph, and cells within the exceedingly limited normal range. It deals, too, with reactions involving salts which are contributing mechanisms toward effecting carbon dioxide and oxygen exchange in reverse manner at the lungs and cells.

This book is not intended as a substitute for an inorganic text, an organic text, or a biochemistry text. Students who seek something more comprehensive in these lines must look to other courses and other texts. It is intended, as has been repeatedly stated, for students who are chiefly interested in applied sciences and arts and who wish to have but one brief course in chemistry for the purpose of making these studies somewhat more meaningful. The entire content of this text and the manner of treatment of this content have been selected and shaped toward such end. However, while patterned for specific groups of students, the thought does persist that the type of chemistry course which this text aims to serve may, after all, be the type of course that, with some elaboration, really

should be given as a first course in undergraduate college chemistry and in a modified form in the high school.

Our profound gratitude goes out to many students of many years whose manifold expressions of appreciation have been chiefly responsible for our yielding to persuasions to attempt to put some of our ideas between the covers of a book.

May, 1939 THE AUTHORS

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FUNDAMENTALS OF CHEMISTRY AND APPLICATIONS

CHAPTER 1

SUBSTANCES AND HOW THEY ARE RECOGNIZED. MIXTURES

Substance. *A chemical change always involves the destruction of one or more substances and the simultaneous making of a new substance or substances.* It becomes evident, therefore, that substances are a primary concern in the study of chemistry; also, that it is essential to have a clear idea as to what constitutes a substance and how matter specimens so designated can be recognized.

In general usage the word *substance* appears with a variety of meanings, but for the chemist this word has a very specific use. For example, the *substance* water is colorless, tasteless, and odorless, a volatile liquid at ordinary temperatures, and a solvent for many other substances. The *substance* iron is a gray, magnetic solid which rusts on exposure to moist air. Moreover, whether encountered alone or in a mixture, each substance exhibits its own characteristic properties. Granite, by contrast, is not a substance but a *specimen of matter composed of several different substances.* One of these is quartz, a white solid with a characteristic crystalline structure; another is mica, a translucent material laid down in easily separable layers; mixed with these is a dark solid known as feldspar. Thus, at least three easily distinguishable *substances* contribute to the material called granite.

The foregoing statements illustrate the chemist's use of the term *substance,* namely, to designate *specimens of matter all particles of which exhibit the same set of properties.*

Specific properties of a substance. Every substance has its own specific set of properties whereby it can be recognized and distinguished from all other substances. Some of these properties are

simply helpful in recognizing the substance; others serve to identify it. Thus, by listing a group of its properties, a given substance can be described and distinguished from other substances which have somewhat different properties. For example:

Water	*Cane sugar*	*Iron (substance)*	*Chromium (substance)*
colorless	colorless	gray	gray
odorless	odorless	solid	solid
tasteless	sweet	soft	hard
liquid	solid	magnetic	nonmagnetic
volatile	soluble in water	rusts	resists corrosion
solvent for many substances	less soluble in alcohol		

In general, properties such as *color*, *odor*, and *taste*—which are more or less easily ascertained—should be considered when they are conspicuous. But, although *helpful* in recognition of a substance, these properties are not identifying. For example, to find that a given substance is white, solid, and odorless constitutes three helpful steps toward discovering what it is, but these properties are *not identifying* because many substances—starch, sugar, and sodium bicarbonate among them—are white, solid, and odorless. Again, to note that the material under investigation is solid, gray, and malleable is helpful, but more data are needed for actual identification because a number of substances—for example, silver, nickel, and aluminum—have these properties.

Some significant but not identifying physical properties

- Color
- Odor
- Taste
- Physical state—solid, liquid, gas
- Solubilities—in water or other specified solvent
- Crystalline or not (if solid)
- Hardness (if solid)
- Malleability (if solid)
- Ductility (if solid)
- Volatility—if liquid

However, there are certain properties that are so characteristic of a given substance that, although skilled technic is required for their exact determination, they can be used to identify it. These include its exact *density*, *boiling point*, and *freezing point*—as defined under standard conditions.

Density is the weight of a given volume of a substance at a given temperature and, if gaseous, under a given pressure. Whereas the density of a substance does differ at different temperatures, it is

always the same when the substance is at the same temperature, and, if gaseous, at the same pressure.

Boiling point (B.P.) is the temperature at which the pressure of the vapor leaving the surface of a pure substance in the liquid state is equal to the pressure exerted by a column of mercury 760 mm high (called standard pressure).

Freezing point (F.P.) is the temperature at which the *solid* and *liquid* phases of a substance *remain in the presence of each other without change in temperature* on the part of either phase.

Examples. *Density an identifying property.* One milliliter of water weighs exactly 1 gm when water is at 4° C and exactly 0.9982 gm when at 20° C. These are two density figures for water, and 1 ml of no other substance at these temperatures has these specific weights. One milliliter of grain alcohol weighs 0.806 gm when at 0° C and 0.789 gm at 20° C, and no other substance has these densities at these temperatures.

Freezing point an identifying property. If some pure water, as ice, below 0° C is dropped into liquid water, the temperature of the ice will rise gradually to 0° and that of the liquid water will lower gradually to 0°. From then on—whether the ice melts or the liquid water freezes—as long as *both* solid and liquid water are present, they will remain at 0° C. Hence, by definition, 0° C is the constant freezing point (also the melting point) of water, and no other substance has this same freezing point. When both solid and liquid phases of grain alcohol, in continuous contact, attain a temperature of −117.3° C, they remain at this temperature as long as both phases are present. Therefore, again, according to definition, −117.3° C is the freezing point (also the melting point) for grain alcohol, and no other substance has this same freezing point.

Boiling point an identifying property. When in an open container, water vaporizes at its surface. The quantity of vapor formed (hence its upward, or vapor, pressure) increases as the temperature of the water increases. Moreover, this vapor pressure is a constant value for water at each specific temperature. Thus, water at 20° C has a vapor pressure equal to the pressure of a column of mercury 17.4 mm high; water at 35° C has a vapor pressure equal to 41.8 mm of mercury; at 100° C the vapor pressure is equal to 760 mm of mercury. Grain alcohol is more volatile than water, and the temperature at which sufficient alcohol vapor is formed to produce a pressure equal to the pressure of 760 mm of mercury is 78.5° C, or lower than that for water.

Identifying properties

Water	*Grain alcohol*	*Copper*	*Iron*
1 ml at 4° C weighs 1 gm	1 ml at 20° C weighs 0.789 gm	1 cc at 20° C weighs 8.9 gm	1 cc at 20° C weighs 7.86 gm
Freezing point is 0° C	Freezing point is −117.3° C	Freezing point is 1083° C	Freezing point is 1530° C
Boiling point is 100° C	Boiling point is 78.5° C	Boiling point is 2310° C	Boiling point is 2735° C

Therefore, according to this definition for boiling point, which makes this property a fixed value, 100° C is the boiling point of water whereas 78.5° C is the boiling point of grain alcohol. Since no other substance has either of these boiling points, they become identifying properties for water and grain alcohol, respectively.

These standard definitions for freezing point and boiling point should not be confused with the definitions in common use; namely, *freezing point as the temperature at which a liquid freezes, boiling point as the temperature at which a liquid boils.* These definitions also have an accepted usage, but they make the boiling point and the freezing point of a substance *variables.* This fact is generally known in regard to water, the boiling point of which, according to this latter definition, varies with atmospheric pressure.

Physical and chemical properties. Most of the properties already mentioned in relation to the various substances described fall into the classification of *physical properties.* The color of a substance, its odor and taste, its physical state, whether it is malleable or ductile, its boiling point, and its freezing point are all *physical properties because, in exhibiting them, the substance is not destroyed.*

Some substances and their properties

***Sulfur,** the substance*

solid (at ordinary temperatures) yellow odorless insoluble in water soluble in carbon bisulfide	These are physical properties of sulfur because in exhibiting them sulfur, the substance, does not go out of existence.
it burns with oxygen it burns with iron	These are chemical properties of sulfur because in exhibiting them sulfur, the substance, ceases to exist.

Cane sugar

solid white crystalline soluble in water soluble in alcohol sweet	These are physical properties of cane sugar because in exhibiting them this substance does not go out of existence.
it chars at a high temperature it reacts with water to make glucose and fructose	These are chemical properties because in charring and in reacting with water cane sugar goes out of existence.

Chemical properties, on the other hand, *are those properties which are exhibited by the substance only as it goes out of existence in the course of a chemical change.* For example, copper "tarnishes," but in

doing so that portion of the copper which has been affected is destroyed as it contributes its building material to the making of a green substance, copper tarnish.[1] Consequently, the fact that copper tarnishes is one of its chemical properties. Iron rusts and silver tarnishes, but the portions of the substances iron and silver that have rusted or tarnished go out of existence during the reactions designated. The abilities of iron to rust and silver to tarnish are, accordingly, chemical properties of these substances.

Mixtures. A mixture is material composed of two or more substances each of which exhibits its own set of properties although in proximity to other substances. Thus, in the mixture *air*, oxygen occurs in association with nitrogen, carbon dioxide, water, and traces of other substances. However, the oxygen becomes a party to burning reactions in spite of this association whereas nitrogen is characteristically indifferent to most of the substances with which it comes in contact. Or, in *steel* mixtures, the iron is magnetic and subject to rusting regardless of the presence of chromium and other substances.

The term applied to substances that contribute to a mixture is *components*, meaning placed together without loss of identity. Thus, iron is the major component of steel, and oxygen is a component of air.

Substances may be assembled in mixtures in a purely accidental and helter-skelter manner, or the mixture may be so planned as to provide each component in exact proportions for some particular use. For example, a commercial baking powder mixture is not only a convenience for the housekeeper but it also assures her a more accurately measured mixture than she would be likely to obtain from the use of approximate household measures for the assembly of the components.

Many of the reagents used in the laboratory carry a designation indicating that they are *chemically pure* (CP). This means that they conform to certain standards agreed upon by chemists. Labels on their containers may provide more specific information as to other substances which have been determined to be present, usually in mere traces, in the material. Such substances are referred to as *impurities*. As a rule such impurities have no significant effect on the properties exhibited by the material as a whole, although for some purposes even a trace of a given impurity may be undesirable because of possible inter-

[1] There are several copper tarnishes—sometimes one appears, sometimes another. The most conspicuous tarnish is green and is a complex copper carbonate; two others are both black—one is a copper oxide, the other a copper sulfide.

ference with a reaction under study. When technical-quality material is used, it is not unusual to encounter impurities which give rise to confusing side actions. Under these conditions, the experienced laboratory instructor may say to the student, "Ignore this, it is due to an impurity" and will redirect the attention to really significant observations.

Separation of a substance from a mixture. Nature throws substances together either in conglomerate mixtures, as in the earth's crust, or else in a more ordered manner, as in plants and animals. Consequently, when the chemist or the manufacturer goes to nature for a substance—for gold or for sodium chloride from the earth's crust, or for sucrose from an appropriate plant, or for lactose from milk—he finds it in a mixture with few or many other substances. Or, in making a substance in the laboratory, it must inevitably be separated from other substances which were used in its manufacture or made along with it. Consequently, it becomes necessary to devise means whereby desired substances can be separated from other substances with which they are associated. Any method used to effect such separation must take advantage of some property of the substance which is significantly different from those of the associated substance or substances. Preferably the separation will be brought about by *physical means*, that is, methods which do not bring about the destruction of the desired substances. The following procedures are among those frequently used.

Evaporation can be used when one substance is easily evaporated and the other component substances are not. Sugar can be separated from a sugar-water solution by evaporating the water; also, iodine can be separated from an iodine-alcohol solution by evaporating the alcohol.

Solution, filtration, and evaporation, used successively, serve as means for the separation of a substance which is soluble in some selected solvent whereas the associated substances are not. Given a mixture of sand and sugar, the sugar is soluble in water, but the sand is not; hence, the mixture can be treated with water with which the sugar forms a solution. This solution can be separated from the sand by filtration. Finally, the sugar can be separated from the water by evaporation of the latter. Ether used as a solvent can separate fat from meat mixtures. The fat dissolves in the ether, and the fat-ether solution is separated from the meat residue by filtration, after which the fat is precipitated by evaporation of the ether.

Distillation can be employed for the separation of two or more

liquid substances by taking advantage of their differing boiling points, that is, of their differing temperatures of maximum volatility. Alcohol and water can be separated by such means.

Decantation is frequently used for separation of an insoluble, precipitated solid from a superimposed liquid. Pouring water off from raw starch that has settled to the bottom of the container is an example of decantation.

Melting and draining can be used when the desired substance within the mixture has an easily obtained melting point and the other substances have higher melting points. In this manner sulfur, with its comparatively low melting temperature, is easily separated from other substances with which it is found mixed in the crust of the earth.

Frequently, the separation of a desired substance from all save a very small percentage of other substances, with which it was originally in mixture, is a problem that taxes the ingenuity of the most capable and careful operators.

QUESTIONS

1. Sodium chloride, the major component of table salt, is a substance. Give reason. Why is ether a substance? Why is carbon (a component of coal) a substance?

2. Silver is a white, solid substance capable of a high polish; it can be hammered into various shapes and can be drawn out into a fine wire; upon contact with egg it tarnishes; it has a melting point of 955° C; 1 cc of silver at 20° C weighs 10.5 gm.
   a. Which of these properties are physical and why?
   b. Which are chemical properties of silver and why?
   c. Which are identifying properties and why?

3. Why are density values for water other than those given on page 3 possible? Criticize the accuracy of the statement that "1 ml of water weighs 1 gm."

4. a. Why is −116.2° C the freezing point of ether?
   b. Why is 34.5° C the boiling point of this substance?
   c. Why are these identifying properties of ether?

5. What are the characteristics by which a mixture is recognized? Classify the following as to whether they are substances or mixtures and in each instance provide convincing evidence to support your claim: granite, sodium bicarbonate, air, milk, mercury, baking powder.

6. How would you proceed to separate alcohol from an alcohol-water mixture? Salt from a sand-salt mixture? In each instance, what knowledge of the properties of the components of the mixture must you consider in planning the separation?

CHAPTER 2

PHYSICAL AND CHEMICAL CHANGE

Substances undergo changes, some of which are physical in nature and others which are chemical. Our chief interest lies in chemical changes but it is impossible to understand the characteristic behavior of substances without considering physical changes as well.

PHYSICAL CHANGE

Defined. *When a substance undergoes a change during which the substance itself is not destroyed, the change is physical in nature.* The following are typical examples.

Molding of clay. A lump of clay on the potter's wheel swiftly undergoes a change from a crude lump into a vase of definite shape. *Before the change* the lump of clay was gray, solid, and smooth; *after the change* the substance constituting the vase is still gray, solid, and smooth. The reshaping of the clay did not result in making a different substance; therefore, this change is *physical* in nature.

Heating a platinum wire. The platinum, *before heating,* is a silvery gray, ductile solid. *During the heating,* it becomes glowing red and hot to touch. *Withdrawn from the flame* and cooled to room temperature, the material is a silvery gray, ductile solid. These are properties of platinum; therefore, this is a physical change.

Vaporizing alcohol. The substance *before the change* is colorless and liquid and has a pleasant, characteristic odor. *During vaporization* the substance, although gaseous, is colorless and has the same characteristic, pleasant odor. Conclusion: the same odor provides evidence that the liquid substance and the gaseous substance are the same; hence, the *change* involved *is physical* in nature.

The conclusion that the observed change was physical in nature rests on evidence that the substance involved was not destroyed

during the change. With changing conditions, properties may become evident that were not observable under the original conditions; but, under the same conditions, the material always exhibits the same properties, indicating that it is the same substance.

Changes in physical state. The changes which a substance undergoes in the transition from solid to liquid to gas, and the reverse, are physical changes. In the solid state, the substance has definite form and occupies a definite volume. *On raising the temperature*, the heat imparts increased energy to the individual particles comprising the mass and the material expands. When a sufficiently high temperature is reached, the more active particles begin to flow away from the solid and tumble over one another as a liquid. Some of the active particles at the edge of the mass escape into the surrounding air in gaseous form. These particles diffuse freely throughout the air and, if in a confined space, will soon be found in even distribution throughout the container. *On lowering the temperature*, the energy of the individual particles is decreased and the particles come closer together, first in liquid, then in solid form.

These changes are familiar to all who work with substances; they are the usual happenings. Some substances are capable, under ordinary temperature conditions, of changing directly from solid to gas with no apparent liquid state. This is known as *sublimation*. Moreover, the process may be reversed; the gas, on coming in contact with a cool surface, may be observed to condense directly to solid with no intervening liquid state.

A familiar example of this phenomenon is encountered in the change of *solid carbon dioxide (dry ice) directly to gaseous carbon dioxide* at room temperature. Considerable heat must be absorbed from the atmosphere to effect this change; hence, the associated cooling in the immediate environment. Another example is the *sublimation of naphthalene* as when moth balls, packed away with the woolens, disappear but the lingering odor provides unmistakable evidence that naphthalene is still present. The change directly from gas to solid can be observed with the substance water; it accounts for the beautiful frost crystals that form on the cold windowpane in freezing weather when the gaseous water in the air condenses directly to ice as it hits the cold surface.

CHEMICAL CHANGE

Defined. *When a substance undergoes a change during which it is destroyed as another substance or substances are made, the change is chemical in nature.*

How to recognize. The evidence of such a change is obvious: if a substance is gone, its properties disappear along with it; as another substance is made, its presence is indicated by the appearance of its properties.

For example, the rusting of iron is a typical chemical change since iron substance (gray, magnetic, and tenacious) is destroyed as a different substance (reddish brown, crumbly, and nonmagnetic), commonly called iron rust, is made. Other commonly experienced changes which are chemical in nature are tarnishing of silver, corroding of copper, and burning of the carbon component of charcoal or coal.[1] Or, turning to laboratory experiences, water can be decomposed to make the two substances, oxygen and hydrogen, by passing an electric current through it (Fig. 7, p. 15).

Let us gather convincing *evidence* that these phenomena do indeed involve chemical changes.

The tarnishing of silver. *Before the change,* the substance is silvery gray, shiny, and solid. *During the change,* this substance is destroyed as a new substance appears which is black, dull, and solid. Conclusion: a different substance is made during the change, as evidenced by the appearance of a different set of properties; hence, *the change is chemical.* (This tarnishing can continue until there is no more silver.)

The burning of carbon. *Before the change,* the substance is black, solid, and burnable. *During the change,* a different substance is made which is colorless, gaseous, and nonburnable. Conclusion: a different set of properties gives evidence of a *different substance;* hence, *the change is chemical* in nature.

Decomposition of water. *Before the change,* the substance is colorless, liquid, nonburnable. *During the change,* one substance is made which is colorless, gaseous, and burnable, and another substance is made which is colorless, gaseous, and will cause a wood splint, which is burning with glowing speed in air, to burn with a flame. Conclusion: the two resulting substances, with their different sets of properties, must be *different substances* from those before the change; hence, *the change is chemical* in nature.

In considering the foregoing chemical changes, not all of the substances have been named. Nor is it necessary always to know the whole story of the reaction to be sure that a chemical change has occurred. Frequently, changes encountered in nature are complex and involve a series of reactions. For instance, in the rusting of iron, the reaction of iron with oxygen is only part of the process. But, evidence of the making of even one new substance, or the destruction

[1] Charcoal and coal are mixtures of carbon with nonburnable substances. Since the latter take no part in the burning reaction, they are left behind in the mixture called *ash.*

of even one substance, provides ample proof that chemical change has taken place.

The word equation. When all of the substances involved in a chemical reaction are known, it is possible to summarize this information in an expression known as a "*word equation.*" For example:

1. ***For the tarnishing of silver***

$$\text{Silver} + \text{Hydrogen sulfide} \rightarrow \underset{\text{(silver sulfide)}}{\text{Silver tarnish}} + \text{Hydrogen}$$

Interpreted. Silver reacts with hydrogen sulfide to make silver tarnish, or silver sulfide, and hydrogen.

2. ***For the burning of carbon***

$$\text{Carbon} + \text{Oxygen} \rightarrow \text{Carbon dioxide}$$

Interpreted. Carbon reacts with oxygen to make carbon dioxide.

3. ***For the decomposition of water***

$$\text{Water} \rightarrow \text{Hydrogen} + \text{Oxygen}$$

Interpreted. Water decomposes to make the substances hydrogen and oxygen.

The so-called "word equation" provides only limited information concerning a chemical reaction. It mentions (1) the substance or substances that exist before the reaction, and (2) the substance or substances that result therefrom. It is not really an equation because no equality of materials before and after the reaction is indicated; that there is such an equality we shall see later (p. 105), but the word equation does not register this fact. Nor does this expression commonly represent conditions which make the reaction possible, such as whether the substances must be heated or exposed to light; nor, again, does it commonly tell of any accompanying phenomenon, such as whether heat or light or electricity is made along with the matter products, although such information may be introduced if desired.

Incidental items to begin to think about. 1. *Substances and building materials.* The building materials of which substances are made are known as the *elements.* When a substance is composed of only one building material, or element, throughout, it is customary for the substance to carry the name of the element of which it is composed. Thus, silver substance is built from only the element silver; carbon substance contains only the element carbon.

2. *During a chemical change* a given substance or substances are destroyed as another substance or substances are made, but the building materials within these substances, that is, the elements, are not destroyed. During the reaction

the elements form new combinations and consequently new substances. For example:

Hydrogen sulfide + Silver → Silver sulfide + Hydrogen

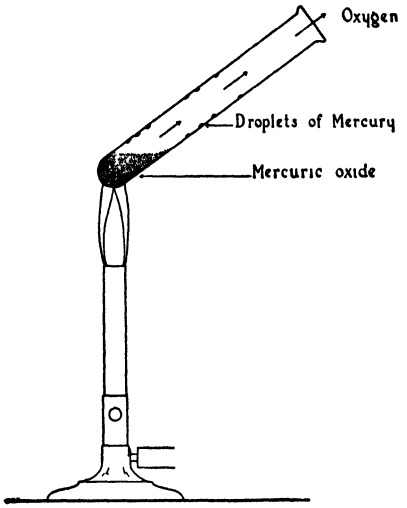
3. *The ending ide* is used in the names of substances that are built of only two elements. Thus, silver sulf*ide* indicates that this substance contains only the two building materials silver and sulfur. Similarly, hydrogen sulf*ide* is composed of two elements, hydrogen and sulfur. The *hydroxides*, of which sodium hydroxide is an example, form an exception to this rule. *The ending ate* usually signifies the presence of *oxygen as a third element* within the substance.

Types of chemical change. *Direct combination.* It is helpful in the study of chemistry to be able to classify chemical changes from the standpoint of similarities. For example, the reactions which take place in the rusting of iron with oxygen, the burning of carbon with oxygen, and the burning of sulfur with iron (p. 68) are of the same type because during the reaction, in each case, *two substances go out of existence whereas only one substance is made. This type of reaction is known as direct combination*, and many reactions are of this variety. Word equations for these reactions are as follows:

Iron + Oxygen → Iron oxide
Carbon + Oxygen → Carbon dioxide
Sulfur + Iron → Iron sulfide

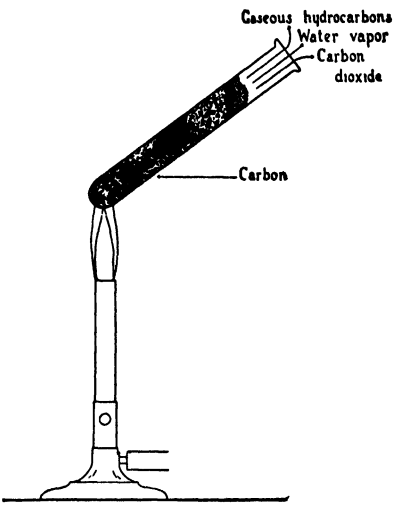
Decomposition. There are other reactions, such as the decomposition of water (p. 10), in which only one substance exists before the reaction whereas two substances and sometimes more than two substances are made. Another reaction of this type is involved when mercuric oxide is heated until it *decomposes* to make the substances mercury and oxygen (Fig. 1). Still another reaction of this type occurs when cane sugar is heated in a test tube or, more familiarly, when the pie boils over in the oven. The cane sugar, if it is kept at a sufficiently high temperature, *decomposes* during such heating to make a number of substances, some of which are mentioned in the pictured representation of this phenomenon in Figure 2. *Reactions of this type, in which one substance goes out of existence as two or more substances are made, are called decomposition reactions.*

A caution: Decomposition is a term that is frequently used carelessly for reactions that are not of the type described. For example, meat spoilage is often referred to as decomposition. Actually, during spoilage a series of reactions occur, some of which may be decompositions whereas others are different types of reactions.



Mercuric oxide → Mercury + Oxygen

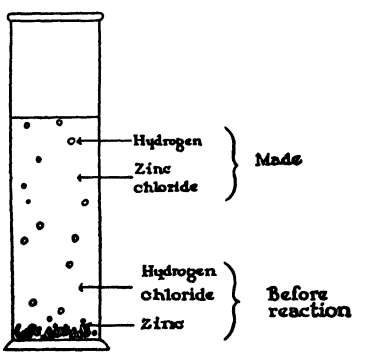
Fig. 1. Decomposition of mercuric oxide.



Cane sugar → Carbon + Hydrocarbons + Water + Carbon dioxide + Many other substances

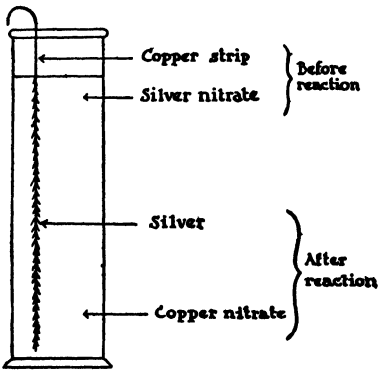
Fig. 2. Decomposition of cane sugar.

Displacement. Another type of reaction is exemplified by the tarnishing of silver. During this reaction, silver building material from silver substance displaces hydrogen from hydrogen sulfide to make black silver sulfide. At the same time the hydrogen thus dis-



Zinc + Hydrogen chloride → Hydrogen + Zinc chloride

Fig. 3. Reaction of zinc with hydrogen chloride.



Copper + Silver nitrate → Silver + Copper nitrate

Fig. 4. Reaction of copper with silver nitrate.

placed builds itself into the gaseous substance hydrogen (p. 10). Reactions of this type occur also when zinc is in contact with hydrogen chloride (Fig. 3), and when copper is in contact with silver nitrate (Fig. 4). *Such reactions, that is, the displacement of one element by another element in the substances concerned, are called displacement reactions.*

Double decomposition. The fourth type of chemical reaction takes place between two substances each of which is composed of two parts in more or less loose combination. When substances of this

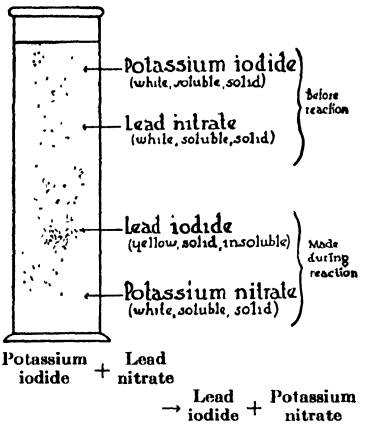


Fig. 5. Reaction of potassium iodide with lead nitrate.

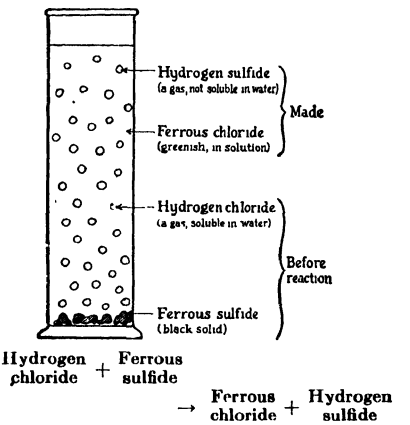


Fig. 6. Reaction of hydrogen chloride with ferrous sulfide.

variety, such as potassium iodide and lead nitrate, are in contact with each other in water solution, a "change in partner" reaction takes place, as is suggested by the following word equation.

$$\text{Potassium iodide} + \text{Lead nitrate} \rightarrow \text{Potassium nitrate} + \text{Lead iodide}$$

Another such reaction occurs when a solution of hydrogen chloride comes in contact with iron sulfide. These reactions are described in Figures 5 and 6.

Hundreds of reactions of this type occur, and the term generally applied to them is *double decomposition.* This is an unfortunate term, in a way, because such reactions have no relationship to the decomposition reactions of previous discussion.

There are other types of reactions, some of which will be encoun-

tered later; also, there are many reactions which are individualistic in that they follow no specific type.

FUNDAMENTAL FACTS IN REGARD TO CHEMICAL CHANGE

Ever since the beginnings of chemistry science, chemists have been studying reactions from various aspects in a continual search for factual information concerning them. Their findings, obtained many times as the result of a tremendous amount of very careful laboratory investigations, constitute a large part of our science heritage.

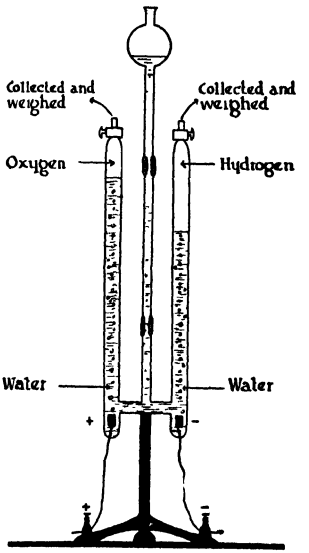


Fig. 7. Decomposition of water by electrolysis.

Quantities of substances before and after reaction. The early chemists observed, even as we have seen for ourselves, that always as one or more substances go out of existence during a chemical change one or more different substances are made. But what of the total quantity of matter—does it increase, or decrease, or remain the same? To answer these questions involved repeated careful weighing, first of the substances entering into the reaction, then of the products of the reaction. Obviously, this necessitated great care that not one iota of the beginning substances or of the products was lost. Let us consider the measured findings for a typical example, in this instance the decomposition of water (Fig. 7).

If 12 oz is the weight of the water to begin with, and if its decomposition is continued until no water is left, the inclusive weight of hydrogen and oxygen obtained will be found to be exactly 12 oz. Thus, the inclusive weight of the two substances, hydrogen and oxygen, that result from this reaction is identical with the weight quantity of the original water.

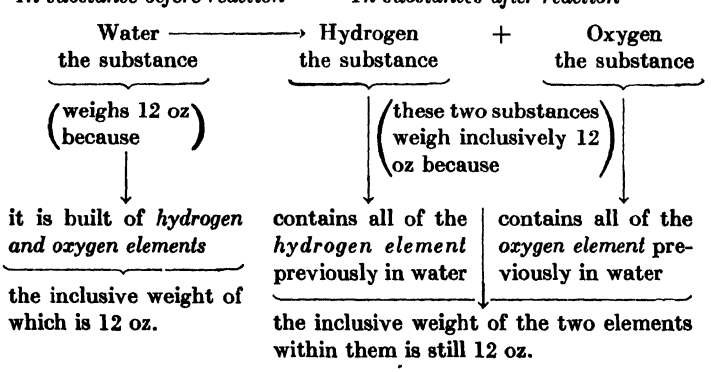
These quantitative findings are in accordance with all that have been made in respect to chemical reactions: namely, *the inclusive weight of* ***substances*** *mutually involved before a reaction is exactly*

equal to the inclusive weight of the ***substances*** *that result from said reaction.* The term that has come to be applied to this fact is the *Law of Conservation of Mass.*

This fact was first stated by the great French scientist Lavoisier in 1785. It has stood the test of repeated measurings from that time to the present and has come to be regarded as one of the fundamental facts of the science. Nevertheless, this law, once believed to be absolute in its operation, is now regarded as relative. Recent experimental findings substantiate the concept that matter can go out of existence with the production of energy and vice versa. However, as it affects the quantities of substances involved in the ordinary chemical change,[2] the weight of matter thus lost or made is negligible.

Quantitative findings of elements in substances. The explanation for the equality in weight of substances before and after a reaction is found in the fact that the ***elements,*** *the building materials for substances, neither lose nor gain in weight as they pass from the beginning substance or substances to another substance or substances during a chemical change.* This fundamental fact of chemistry is called the *Law of Chemical Change.* It is applied to the reaction studied previously (p. 15) as follows:

In the decomposition of water to make hydrogen and oxygen:



These two fundamental laws, or facts, must not be confused. *The fact of conservation of mass refers to substances,* which are respectively destroyed and made; *the fact of chemical change looks within substances to their building materials or elements,* which are not destroyed

[2] The term *ordinary chemical change* is exclusive of nuclear reactions.

but are taken from the beginning substance or substances for making the resulting substance or substances.

That these two facts have always been consistently observed by nature in the operation of chemical reactions is undoubtedly true, but man's discovery of them is of comparatively recent date. And it is certain that these discoveries, and the accompanying understanding of their quantitative significance, have contributed enormously during the past 150 years both to the progress of scientific study and to the progress of industrial concerns. Nutritionists and animal and plant physiologists now know that, for every reaction that takes place in the cells of animals and plants, the inclusive weight of substances entering a reaction must be equal to the inclusive weight of substances made. They know, too, that any given element—iron, oxygen, iodine, or nitrogen—remains constant in quantity as it passes from substance to substance in any sequence of reactions within the cells of plants and animals. In industry, the knowledge of the quantitative involvement of substances and their constituent elements has played a fundamental part in placing modern manufacturing on a known calculated basis with assurance in regard to the quantitative outcome of products. Before these quantitative relations were known, manufacturers were obliged to depend on handed-down recipes which were the development of years or even centuries of trial-and-error procedures!

Speed of chemical reactions. There are various factors that determine the speed with which a chemical reaction takes place.

A most important speed factor lies in the *tendency of the substance or substances to engage in reaction.* The greater their tendency to react the greater the speed of reaction and vice versa. For example:

1. When the same quantities of cane sugar and mercuric oxide (p. 13) of the same degree of fineness are put into separate test tubes and heated to exactly the same temperature, the cane sugar will decompose more rapidly than the mercuric oxide because of the fact that, of these two compounds, cane sugar has the greater tendency to decompose.

2. Again, both magnesium and zinc react with hydrochloric acid to make hydrogen as one product. But—provided the magnesium and zinc present the same surface areas to the acid and the acid is of the same concentration—reaction between magnesium and hydrochloric acid takes place more rapidly than between zinc and this acid (Fig. 57, p. 167). And, the reason is that magnesium and hydrochloric acid have a greater tendency to engage in reaction than have zinc and this acid.

A second speed factor, and the one that is most familiar, is

the temperature of the substance. The higher the temperature of the substance or substances concerned the greater is the speed of reaction and vice versa. Thus:

1. Magnesium and oxygen react with each other only slowly at ordinary temperatures, but the reaction increases in speed with increasing temperatures, as long as the magnesium and oxygen are kept in contact.
2. All reactions that are responsible for food spoilage take place more rapidly on warm days than on cold ones and less rapidly in the refrigerator than on the pantry shelf.
3. Of vital significance is the fact that metabolic reactions take place more rapidly in the cells when body temperatures are above normal, hence during the prevalence of fever temperatures. Evidence of this fact is the continual decrease in weight of the body under such conditions.

A third speed factor is in reference to the *area of the substance that is presented to the reaction.* The greater the area of contact between the two or more substances mutually concerned in the reaction (or the greater the area of the one substance presented to the reaction, provided only one is involved before the reaction), the greater the speed of the reaction. Conversely, the less the area of contact, the less the speed of reaction. Examples are as follows:

1. It is common knowledge that oxygen and wood shavings react more speedily than oxygen and the more compact stick of wood. The obvious reason is that the shavings present a greater area of burnable substances for contact with oxygen than does the stick of wood.
2. Finely powdered mercuric oxide (Fig. 1, p. 13) decomposes more rapidly than mercuric oxide in coarse grains or in lumps when at the same temperature level.
3. The speed of reaction of zinc with hydrochloric acid depends both upon the area of zinc presented to the reaction and upon the concentration of the acid in the solution. The greater the area of the zinc the speedier the reaction and vice versa. Or, given the same areas of zinc, there will be more rapid reaction with concentrated hydrochloric acid than with dilute acid.
4. Iron is commonly covered with various coatings—tin, nickel, a plastic, or paint—in order to protect the iron from reaction with oxygen. It follows, then, that this coating should be treated with care. Wherever it is rubbed off, cracked, or chipped, rusting sets in, and the greater the number of worn spots, chips, or cracks, the greater the rusting reaction between the exposed iron and oxygen.

Finally, there are instances of reactions that are accelerated by the presence of specifically selected substances called *catalytic agents.* But the study of this phenomenon will be left until later (Chap. 5).

QUESTIONS

1. What distinguishes a chemical change from a physical change?
2. Which of the following changes are physical and which are chemical in nature? Give convincing reasoning in each instance.
   a. The corroding of copper
   b. The disappearance of moth balls shut up with stored clothing
   c. The burning of the celluloses of wood
   d. The preparation of French dressing
   e. The burning of a candle
   f. The heating of an iron
3. What information regarding a chemical reaction is provided by the *word equation?* Interpret the following: Mercury + Iodine → Mercury iodide.
4. Interpret the word equations given on page 12.
5. Assemble word equations for all reactions studied in this chapter for which sufficient information is provided and classify these reactions, when possible, as to the four types of chemical change studied.
6. What building materials are contained in the substance water? What becomes of these building materials when water decomposes?
7. State the Law of Conservation of Mass and illustrate with reference to:
   a. The decomposition of mercuric oxide
   b. The burning of carbon
   c. The tarnishing of silver
8. State the Law of Chemical Change and illustrate with reference to:
   a. The burning of sulfur
   b. The reaction of zinc with hydrogen chloride
9. In respect to each of the following, tell which will weigh more, and give the reason.
   a. A silver spoon before or after tarnishing
   b. A gram of mercuric oxide or the mercury resulting from its decomposition
   c. The potassium iodide and lead nitrate before a reaction or the resulting potassium nitrate and lead iodide
10. Name four factors that affect the speed of a chemical reaction, telling how each functions. Give specific examples.
11. How does refrigeration function in respect to food spoilage? Give examples.
12. Explain why cutting potatoes into small pieces can be used to facilitate their cooking.
13. Why is concentrated hydrochloric acid (37 per cent) more rapidly destructive to tissue than a 10 per cent solution of this acid?

CHAPTER 3

SIMPLE SUBSTANCES. COMPOUNDS. ELEMENTS

Having had an introduction to *substances*, what they are and how to recognize them, and to certain characteristics of *chemical change*, let us proceed to further study of substances. This will lead naturally to further study of the *elements*, earth's *building materials* for substances.

Kinds of substances. The number of substances that are possible may be endless. Hundreds exist already made in earth's crust. Various gaseous substances are always present in earth's atmosphere. Earth's waters hold in solution and in suspension many salts, most of which have been washed out of earth's solid crust. Plants and animals are composed of numerous substances. Finally, from materials provided by nature, man has made thousands of substances, many of which had never been in existence until their birth in a laboratory. Although many thousands of substances are possible, they fall into *two* main groups: namely, *simple substances* and *compound substances*, or *compounds*.[1]

[1] The term *simple substance* is used here in contrast to *compound* to designate a substance that is composed of one element throughout. This differentiation was first suggested by Robert Boyle in the *Skeptical Chymist*, published in 1666. He used the word element to designate substances that could neither be decomposed nor made by direct combination from other substances. However, he also suggested that elements are the building materials from which compounds are made. This double meaning for the term *element* persists in common usage and creates confusion for the beginning student of chemistry. Many teachers of beginning chemistry have recognized this and have attempted to clarify the situation by using descriptive terms with reference to the substance, such as *free element*, *elementary substance*, and *simple substance*. Of these frequently used terms, our preference is *simple substance*. When the word element

SIMPLE SUBSTANCES

Introduction. Among simple substances of common occurrence are the following:

Copper—reddish brown, solid, subject to tarnishing
Iron—gray, magnetic, solid, subject to rusting
Aluminum—gray, nonmagnetic, solid
Carbon—black, solid, burns with oxygen

These are classed as simple substances because, up to the present time, no one has been able (1) to make the substance copper, or the substances iron and aluminum, or the substance carbon by the direct combination of two or more other substances; or (2) to decompose any one of these substances into two or more other substances. Of course, the substances copper and iron can be made, and have been made for hundreds of years. So, also, aluminum can be made, and has been for about a hundred years. Carbon is made every time wood or sugar chars. However, not one of these substances has ever been made by direct combination between other substances.

Incidentally, the following word equations, which represent reactions whereby these substances can be made, indicate that the reactions are not of the direct-combination type:

Copper oxide + Hydrogen → Copper + Water
Iron oxide + Carbon → Iron + Carbon dioxide
Aluminum oxide + Silicon → Aluminum + Silicon dioxide
Sugar → Carbon + many other substances

Defined. A *simple substance*, then, is a substance which *can neither be made by the direct combination of, nor be decomposed into, two or more other substances.* Further investigation of simple substances reveals that they are invariably *composed of only one element throughout.* As a rule, the simple substance carries the name of the element of which it is built.

How many simple substances are there? The number of simple substances is limited. Generally, although not always, nature seems to build but one simple substance from any one given building material or element. Accordingly, there is one iron substance built of only iron element; one copper substance built of only copper

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is used without specific differentiation, the student must look to the context to discover the meaning which the author has attached to this word.

element. If, therefore, this situation held right straight through, only as many simple substances would be possible as there are building materials (p. 31). But, there are exceptions—two or more simple substances being built of the same element. For example:

Oxygen—gaseous and odorless *Ozone*—gaseous, with a fresh odor	are two simple substances made of the same element, namely, oxygen.
Carbon—black, dull, solid *Graphite*—black, lustrous, solid *Diamond*—colorless, crystalline, hard	are three simple substances made of the same element, namely, carbon.
Yellow phosphorus—solid, active chemically *Red phosphorus*—solid, inactive chemically	are two simple substances made of the same element, namely, phosphorus.

How many are commonly known? How many *simple substances* are encountered so commonly as to render personal and conscious acquaintance with them unavoidable? Certainly such a list would include most of the following:

Aluminum	Iron	Oxygen
Carbon	Lead	Platinum
Chromium	Mercury	Silver
Copper	Nickel	Tin
Gold	Nitrogen	Zinc

Most simple substances—including hydrogen, which is gaseous and burns with oxygen, and sulfur, which is yellow, solid, and burns with both oxygen and iron—are met with only by workers in laboratories or in industries in which they are used. Consequently, acquaintance with them is the exceptional rather than the usual experience.

Physical state. About ten simple substances—oxygen, nitrogen, hydrogen, chlorine, and helium among them—are *gaseous* at ordinary temperatures but can be obtained in liquid and solid states at sufficiently low temperatures. (See accompanying table.) Two simple substances are *liquid:* the well-known silvery liquid mercury and the less well-known bromine, which is reddish brown, liquid, very volatile, and dangerously caustic. All other simple substances are *solid* at ordinary temperatures. Some of these solid substances, including phosphorus and sulfur, can be obtained in the liquid and gaseous states at easily reached elevated temperatures; others, such as aluminum, copper, nickel, and iron, remain solid up to very high temperatures.

	Solid below	*Liquid below*	*Gaseous*
Oxygen	−219° C	−183° C	
Nitrogen	−210° C	−196° C	at ordinary
Hydrogen	−260° C	−253° C	temperatures
Helium	−273° C	−269° C	

	Solid below	*Liquid*	*Gaseous above*
Bromine	− 8° C	at ordinary	59° C
Mercury	−39° C	temperatures	357° C

	Solid	*Liquid above*	*Gaseous above*
Sulfur		113° C	445° C
Aluminum	at ordinary	660° C	1800° C
Copper	temperatures	1083° C	2300° C
Iron		1535° C	3000° C

Classification. The differentiating terms *metals* and *nonmetals*, when used in reference to substances, apply only to simple substances.

The original and ancient use of the term *metals*, with reference to the few such substances as were known long ago, chiefly iron, copper, silver, lead, and tin, was of purely *physical* significance. This group included, and still includes, those substances which are capable of high polish, are good conductors of heat and electricity, and, when solid, are malleable and ductile. Nonmetal substances, as a rule, do not exhibit these properties.

*These are **metal** substances*

Potassium—bluish gray, shiny, soft, solid
Sodium—gray, shiny, soft, solid
Barium—yellowish, shiny, solid
Calcium—silvery gray, hard, solid
Magnesium—shiny, gray, solid
Aluminum
Zinc
Chromium
Iron
Nickel
Tin
Lead
Copper
Mercury
Silver
Platinum
Gold

*These are **nonmetal** substances*

Sulfur—yellow, solid
Phosphorus—yellowish white, solid
Carbon—black, lusterless, solid
Fluorine—greenish yellow, gas
Chlorine—green, gas
Bromine—reddish brown, volatile, liquid
Iodine—purplish black, volatile, solid
Nitrogen—colorless, gas
Helium—colorless, gas

But, aside from this purely physical implication in the line-up of substances as metals or nonmetals, it has been discovered that the substances classed as *metals react chemically in characteristically similar ways*, quite unlike the chemical behaviors of substances classed as nonmetals. As a result, this classification of simple substances has a *chemical significance* which, although not entirely satisfactory, is helpful to the student of chemistry.

Chemical activity. The expressions *very active*, *active*, and *inactive*, when referring to the chemical behavior of substances, have doubtless come to stay as part of the language of chemistry. It is essential, therefore, to make these expressions as meaningful as possible as we use them, at this time in respect to the chemical behavior of simple substances, and later in respect to compounds.

Of metal substances. In the accompanying list of substances, metals are arranged according to their chemical activities. *Potassium*, *sodium*, and *calcium are very active chemically* since they react very readily, even at ordinary temperatures, with many other substances, including water, oxygen, and acids. These substances are seldom encountered outside of laboratories; even there they must be used with due caution and supplies not in use stored with great care. *Aluminum*, *zinc*, and *iron* are less active as evidenced by the fact that, at ordinary temperatures, they react very slowly with water and oxygen and less readily with acids than do potassium, sodium, and calcium. These metals have many everyday uses. *Silver*, *platinum*, and *gold* are relatively inactive metals because they react appreciably with only a few substances, and, with many of these, reaction is slow. If platinum were as abundant as aluminum and iron are, it would make extremely durable cooking utensils and other metal containers. It would be excellent for metal fittings and structures of all sorts. Silver and gold, even if plentiful, would not be practical for some of these uses. Gold, although inactive, is very soft. Silver is likewise soft and, although generally inactive, it does react with one commonly occurring substance, namely, hydrogen sulfide (p. 11).

Of nonmetal substances. *Yellow phosphorus is chemically very active* because it reacts readily with a number of substances, including oxygen. *Sulfur*, *oxygen*, *and hydrogen are relatively inactive* at ordinary temperatures but *active* at elevated temperatures since they react with other substances either slowly or inappreciably at ordinary temperatures but rapidly at elevated temperatures. *Fluorine*, *chlorine*, *bromine*, and *iodine* are inert with respect to oxygen but

chemically active with metals. Fluorine and chlorine give appreciable reaction even with silver, platinum, and gold. Bromine is less active than chlorine and iodine less active than bromine.

A chemical family. Fluorine, chlorine, bromine, and iodine, because of their marked similarity in physical properties and chemical reactions, constitute a chemical family. They are known as the *halogens*, meaning the salt formers.

Some uses and cautions. Because of the reaction of chlorine with metals, the persistent presence of chlorine in water for disinfecting purposes will, in time, result in appreciable wearing away of metal fittings in plumbing. Also, when chlorine is used for bleaching, it may react appreciably with surface layers of any silver, gold, or platinum jewelry that may be at hand.

The tendency of these halogens to react with proteins is responsible for the effectiveness of chlorine and iodine as disinfectants since they react readily with the proteins of bacterial cells. At the same time, their reactions with proteins lead to severe tissue injury when iodine is used lavishly or when bromine is spilled on skin areas. Bromine is also an effective disinfectant, but it is more hazardous to handle than either chlorine or iodine.

There are a few simple substances that are the *extreme of chemical inactivity*. Among these are *helium*, *argon*, and *neon* which are colorless, odorless gases and comprise a very small proportion of earth's atmosphere. These are known as the *inert gases* because they do not react with other substances.

Uses of inert gases. Helium has a number of commercial uses. It can be substituted for the very inactive nitrogen in air to make an oxygen-helium mixture. This mixture is used by deep-sea divers to prevent caisson disease. At times helium is used with oxygen in the treatment of asthma; because helium is less dense than nitrogen, the oxygen-helium mixture requires less effort in breathing than does ordinary air. Neon and argon are both used in electric lights.

A summary of chemical activities. 1. A chemically *active substance* means one which reacts fairly speedily with quite a selection of other substances, not by any means with all substances.

2. An *inactive substance* means one which reacts appreciably with a very limited number of substances.

3. *Temperature* is an *important factor* because a given substance may be inactive at ordinary temperatures but active at higher temperature levels.

4. A *few substances are chemically inert*—they react either with great difficulty or not at all with other substances.

COMPOUND SUBSTANCES OR COMPOUNDS

Differentiation. In contrast with a simple substance (p. 21), *a compound substance is a substance which either can be made by the direct combination of two or more substances or can be decomposed into two or more substances* by ordinary chemical means, that is, by the use of such agents as heat, electricity, or light. For example, *carbon dioxide* is a compound substance because it can be made by direct combination of the two substances carbon and oxygen (p. 12). *Iron sulfide* is a compound because it can be made by direct combination of the two substances sulfur and iron (p. 12). *Cane sugar* is a compound because, when heated sufficiently (oxygen excluded), it decomposes to make carbon, water, and many other substances (p. 13).

Composition of compounds. In contrast with a simple substance, *a compound is built of two or more elements (building materials)*. A given compound is nonetheless a single substance with a single set of properties that are characteristic of it, the elements within the compound having no separate individuality. *Cane sugar*, for example, is composed of the three elements carbon, hydrogen, and oxygen, but these elements exhibit no properties whereby one can see or become aware of their presence. It is the cane sugar which makes itself known as a single entity with a distinctive set of properties; the carbon, hydrogen, and oxygen are the constituent elements whereas the cane sugar is the substance. Again, *sodium chloride* is composed of the two elements sodium and chlorine, which in no way indicate their presence. It is the sodium chloride which has the personality features—white, solid, salty taste, and soluble. Hence, it is the sodium chloride which is the substance; the sodium and chlorine are its constituent building materials.

Many compounds contain but two elements; many more are built of three elements, in which case oxygen is usually one of them; fewer compounds are composed of four elements; and occasionally there are compounds built of more than four elements. For example:

The compound	*contains the two elements*
Water or Hydrogen oxide	hydrogen and oxygen
Iron oxide	iron and oxygen
Silver sulfide or silver tarnish	silver and sulfur
Sodium chloride	sodium and chlorine
Any hydrocarbon	hydrogen and carbon

The compound	*contains the three elements*
Potassium chlorate	potassium, chlorine, and oxygen
Potassium chlorite	potassium, chlorine, and oxygen
Copper sulfate	copper, sulfur, and oxygen
Silver nitrate	silver, nitrogen, and oxygen
Any carbohydrate	carbon, hydrogen, and oxygen

Quantitative composition. In the quantitative make-up of compounds, nature builds in a very fixed and definite manner. Not only is a given compound composed of a definite selection of elements, but in all specimens of the compound the given elements are always present in the same definite weight proportions. Thus:

Within all specimens of *sodium chloride* the constituent elements sodium and chlorine are present in weight proportions of 39.34 to 60.66 (Fig. 8).



Within 1 oz of sodium chloride

weight of sodium : weight of chlorine
as
39.34 : 60.66

Within 10 oz of sodium chloride

weight of sodium : weight of chlorine
as
39.34 : 60.66

Fig. 8

Within *cane sugar* the constituent elements hydrogen, carbon, and oxygen are present in a weight proportion of 42.10 to 6.48 to 51.42; therefore, within any mass whatsoever of cane sugar—whether 1 oz or 6 oz, 1 gm or 50 gm, 8 tons or 25 tons—42.10 per cent of the total weight is the element carbon, 6.48 per cent is the element hydrogen, and 51.42 per cent is the element oxygen (Fig. 9).



Within 1 gm of cane sugar

weight of carbon : weight of hydrogen : weight of oxygen
as
42.10 : 6.48 : 51.42

Within 12 gm of cane sugar

weight of carbon : weight of hydrogen : weight of oxygen
as
42.10 : 6.48 : 51.42

Fig. 9

The same condition holds for every compound in existence: *Every specimen of a given compound substance is composed of the same constituent elements, always in the same definite weight proportions—both to one another and to the compound as a whole.* This fact has come to be called the *Law of Definite Weight Proportions.*

It follows that, if ever the same selection of elements should be found in combination in two, three, or several differing weight proportions, then two, three, or several different compounds are involved. *Carbon dioxide* and *carbon monoxide*, for example, are composed of the same elements, yet they are totally different substances, as everyone very well knows. Carbon dioxide is harmless physiologically; indeed, it is a product of plant and animal living, and it will not burn. Carbon monoxide is poisonous, and after sufficient intake of it, an animal will die; carbon monoxide will burn. These two compounds are different substances chiefly because of the differing weight proportions between the carbon and oxygen elements within them. So also, are *water* and *hydrogen peroxide* two different substances although they are made of the same constituent elements. Water is odorless and tasteless as to physical properties and chemically stable. Hydrogen peroxide has an odor and taste and is unstable. The reason that these two compounds are different substances is largely because the weight proportion between the hydrogen and the oxygen in water is 11.19 to 88.81 whereas in hydrogen peroxide it is 5.93 to 94.07.

Carbon dioxide	***Carbon monoxide***
27.29 to 72.71	42.88 to 57.12
parts by weight of carbon — parts by weight of oxygen	parts by weight of carbon — parts by weight of oxygen
Hydrogen oxide (*Water*)	***Hydrogen peroxide***
11.19 to 88.81	5.93 to 94.07
Carbohydrate (*Cane sugar*)	***Carbohydrate*** (*Glucose*)
42.10 to 6.48 to 51.42	40 to 6.71 to 53.29

Chemical behavior. The chemical behavior of compounds can be considered under two headings: their *chemical activity* and their *chemical stability.*

Chemical activity of compounds, as well as of simple substances, refers to the tendency of the substances to react with other sub-

stances. If a compound substance reacts with many other substances fairly speedily, it is called chemically *active;* if it reacts with only a few substances and then usually quite slowly, it is *inactive.* As with all substances, *temperature* is an activity factor.

Acids and bases have a range of activities. Some, including hydrochloric and sulfuric acids, sodium and potassium hydroxides, react readily with many substances even at ordinary temperatures. Others, including acetic acid and ammonium hydroxide, are much less active.

Chemical stability refers to the *tendency of the compound to decompose to make two or more other substances.* For example, *water* is a very stable compound because it requires a very high temperature (about 2000° C) for its decomposition to become appreciable. *Mercuric oxide* is stable at ordinary temperatures but unstable at elevated temperatures (p. 13). *Hydrogen peroxide* is unstable even at ordinary temperatures and more so in the presence of sunlight. Hence, it is advisable to keep a reserve supply in a dark bottle and in a cool place.

It should be noted that chemical *stability* applies only to compounds, never to simple substances (p. 21).

In the main, compounds met with in everyday concerns—water, carbon dioxide, those comprising the crust of the earth, and those used daily for various purposes—are stable at ordinary temperatures.

Classification. Since hundreds of thousands of compounds are already known and millions probably are possible, it becomes a matter of considerable importance that they fall into relatively few classes from a chemical viewpoint. That is, compounds may be classified on a basis of similar reacting tendencies. So it is that:

Of the thousands of compounds known:

↓	↓	↓	↓	↓	↓	↓	↓
Many are ***Acids*** which behave alike in chemical ways	Many are ***Bases*** which exhibit common chemical behavior	Very many are ***Salts*** with similar chemical behavior	A few are ***Metal oxides***	A few are ***Nonmetal oxides***	Many are ***Hydrocarbons***	Many are ***Alcohols***	And so on for ***other classes of compounds*** some of which will be studied eventually

Thus, the task of the chemistry student is greatly simplified. Through the study of the common chemical behavior of a few compounds which belong to the same class, one may study the behavior of all compounds within this class.

Naming of compounds. Many of the compounds used today in everyday concerns, both medicinally and in the industries, carry handed-down names. These names, adopted by people living centuries ago, are not at all suggestive of the contributing building materials. Some such names are mentioned below. But, since the beginnings of chemistry science, chemists have aimed at devising a system of nomenclature for compounds which will suggest their element composition. For example:

The common or handed-down name	*The chemist's name*
Calomel	Mercur*ous* chlor*ide*
Corrosive sublimate	Mercur*ic* chlor*ide*
Common salt	Sodium chlor*ide*
Galena	Lead sulf*ide*
Litharge	Lead ox*ide*
Quicklime	Calcium ox*ide*
Slaked lime	Calcium *hydrox*ide
Chalk, Limestone	Calcium carbon*ate*
Borax	Sodium bor*ate*
Washing soda	Sodium carbon*ate*
Baking soda	Sodium hydrogen carbon*ate*
Saltpeter	Potassium nitr*ate*
Chile saltpeter	Sodium nitr*ate*
Lunar caustic	Silver nitr*ate*
Burnt alum	Potassium aluminum sulf*ate*

Significant name endings. The following are preliminary suggestions in regard to some *name endings* which have significance in chemistry nomenclature.

ide ending usually means that the compound is composed of *two elements.* An exception occurs in the naming of hydroxides such as sodium hydroxide and calcium hydroxide.

ate and *ite* as name endings signify the *presence of oxygen as one of three, or sometimes more, elements.* In a pair of compounds of the same three elements, with oxygen as one of them, the *ate compound* is the usually occurring one and it always contains a *larger weight proportion of oxygen* than does the corresponding *ite compound.* For example:

Sodium sulf*ate*	Sodium sulf*ite*
45.05% oxygen	38.08% oxygen
Potassium phosph*ate*	Potassium phosph*ite*
30.14% oxygen	24.45% oxygen

ic and *ous* are associated endings attached to the name of the first-mentioned element. The *ic compound* always contains a *higher weight proportion* of the

second element, or group of elements, than does the corresponding *ous compound.* Thus:

Mercur*ic* chloride	Mercur*ous* chloride
26.11% chlorine	15% chlorine
Ferr*ic* sulfate	Ferr*ous* sulfate
72.07% sulfate	63.24% sulfate

ELEMENTS

Where are they? Since elements are the building materials for all substances, both simple and compound, they must be present wherever substances are located.

In particular, earth's supply of *oxygen* element is distributed in oxygen substance and in carbon dioxide, both of which are found chiefly in earth's atmosphere; oxygen is a constituent element of water, and also of most of the compounds in earth's solid crust. Oxygen is also a constituent of most of the compounds that compose plants and animals.

Hydrogen element is found in water and in many compounds within plant and animal cells, but comparatively little hydrogen is present in the compounds that contribute to the crust of the earth. The elements *sodium*, *potassium*, *calcium*, *magnesium*, and *chlorine* occur in compounds distributed in earth's crust and in solution in sea water. They are also found in compounds within the cells of plants and animals.

Carbon is found in the simple substance carbon, the major component of coke, charcoal, and coal. It contributes to the compounds in plant and animal tissues.

Earth's supplies of the elements *gold*, *silver*, and *platinum* are almost entirely within the substances gold, silver, and platinum.

How many elements? For building earth's innumerable substances, 102 different elements are now recognized. Of these 90 have been found in natural sources; the others have been produced in the laboratory and may, or may not, exist as yet undiscovered in nature. (A table of elements can be found on the back cover of the text.)

Relative quantities. To undertake an exact survey of the relative quantities of the various elements possessed by earth—how much oxygen, iron, carbon, nitrogen, hydrogen, gold, etc.—would be a colossal undertaking and perhaps impossible ever to achieve.

Scientists can calculate the relative quantities of elements provided within substances that make up the atmosphere, plant and animal mixtures, and earth's water. However, up to the present time it has not been possible to ascertain the comparative element supply provided inclusively within substances throughout earth's tremendous ball of solid matters. Man's diggings, excavations, and minings have made but the merest scratches in earth's crust. The solid matters thus revealed are only pigmy portions of that mixture of substances which has been buried for eons and will continue to lie buried and hidden from man's investigations for more centuries, perhaps forever. Therefore, exact proportionate figures are out of the question.

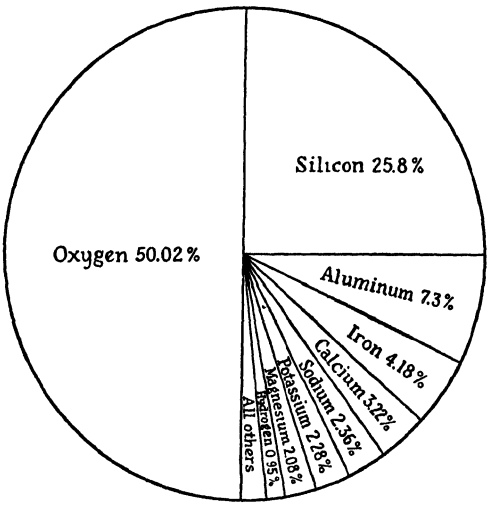


Fig. 10. The approximate composition of earth's crust, its oceans, and atmosphere. (Clarke.)

Estimates, however, are possible and have been made of the proportions of various elements provided inclusively within water and within the substances that make up the atmosphere and the outer layers of earth's crust. Comparative quantities, as computed for the most abundant elements, are represented diagrammatically in Figure 10.

It is rather significant that such an overwhelming portion of earth's building materials is the one element oxygen. However, this being true, it would seem to be the element most in demand by nature for building substances. And, in fact, most substances found already made in nature, and most that are made by man, do contain oxygen as one constituent element. It may be a surprise to find that there is so much silicon when we commonly hear so little mention of it. The reason for this is that the names which are used today for compounds containing silicon are the ones that have been used for centuries, having been given to them long before there was any

knowledge of or interest in the element make-up of substances. Thus, quartz is the handed-down name for one widely distributed compound which contains silicon; clay is another such compound; feldspar another; and mica is still another. Asbestos is also a silicate, and there are great quantities of these silicon compounds in earth's solid crust. Chemists have devised names for these substances which do specify the presence of this element silicon, but these are not the names used by people commonly.

Common names	*Chemist's names*
Quartz	Silicon dioxide
Clay	Aluminum hydrogen silicate
Feldspar	Potassium aluminum silicate
Mica	Potassium aluminum hydrogen silicate
Asbestos	Magnesium calcium silicate

Elements in substances essential to the human body. The elements that are necessary to the human body, and their relative quantities, have been computed as follows:

The elements	*Approximate percentages by weight*
Oxygen	65.0
Carbon	18.0
Hydrogen	10.0
Nitrogen	3.0
Calcium	1.5–2.2
Phosphorus	0.8–1.2
Potassium	0.35
Sulfur	0.25
Sodium	0.15
Chlorine	0.15
Magnesium	0.05
Iron	0.004
Manganese	0.0003
Copper	0.00015
Iodine	0.00004
Cobalt, zinc, and other elements	Very small amounts

(Sherman, Henry C.: *Chemistry of Food and Nutrition*, 8th ed. The Macmillan Company, New York, 1952, p. 227.)

Accordingly, the sum total supply of some elements for distribution within various requisite body compounds is relatively large, whereas that of other elements is exceedingly small. But, the fact that some elements, notably iron and iodine, are required in such small quantities does not mean that substances containing them are not important. They are, in fact, of great importance and quite as essential as those substances which, since they are made in relatively large quantities, obviously require their constituent elements in correspondingly large quantities. For example, the very *life* of the animal is dependent upon the presence of certain *iron* and *iodine* compounds, and its *health* is dependent upon the presence of these compounds in right quantities, small though these quantities are.

Must be in foods. All elements required by the living, healthy body must be distributed in the various food substances that compose the food intake. For most elements, including *hydrogen*, *oxygen*, and *carbon*, it is not necessary to take thought as to whether one is or is not getting them in the daily food rations. The average food mixture, selected even carelessly and without heed to body needs, contains these elements in more than sufficient amounts for the building in various cells of necessary quantities of required compounds. With some elements, however, there is more uncertainty. For example, the *calcium* content of compounds of the food mixture, unintelligently or carelessly selected for the average daily portion, can easily be inadequate to make sufficient calcium phosphate for bones and teeth and other calcium compounds for other essential uses. *Iron*, too, may be present in insufficient quantities in compounds of an unconsidered diet, thus limiting the building of hemoglobin.

Classification of elements. Elements may be classified, on the basis of the types of compounds to which they contribute, as metal elements and nonmetal elements. (The elements hydrogen and oxygen are set aside and not classified in this connection as either metal or nonmetal elements.)[2]

Metal elements. If an element to be classified can be found in combination with hydrogen and oxygen and if the compound concerned is a base, *the element is a metal element.*

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[2] Classification of elements in the manner about to be considered is not entirely satisfactory, but it is helpful.

Potassium
Sodium
Barium
Calcium
Magnesium
Aluminum
Zinc
Iron
Nickel
Tin
Lead
Copper
Mercury
Silver
Platinum
Gold

are all *metal elements* because they occur in combination with oxygen and hydrogen *in compounds which are bases* (see p. 146).

Nonmetal elements. But if a given element is found in combination (1) with hydrogen or (2) with hydrogen and oxygen and if the compound thus involved is an acid, *the element is a nonmetal.*

Chlorine
Bromine
Iodine
Sulfur
Nitrogen
Phosphorus
Carbon

are *nonmetal elements* because they occur in combination either with hydrogen or with hydrogen and oxygen *in compounds which are acids* (see p. 147).

Exceptions. Compounds composed of hydrogen and *nitrogen* or of hydrogen and *phosphorus* are not acids; neither are the many compounds of hydrogen and *carbon.* However, we are claiming for this classification only *some* degree of *helpfulness,* not exceptionless situations.

Metal and nonmetal elements versus metal and nonmetal substances. The student may be puzzled over the use of the same terms, metal and nonmetal, formerly for the differentiation of simple substances and now for elements. However, the relationship is really a simple one because metal substances are composed of the corresponding metal elements whereas nonmetal substances are built of corresponding nonmetal elements.

QUESTIONS

1. What is the experimental basis for the classification of substances as simple substances or compounds?

2. In reference to each of the following substances, tell whether you believe it to be a simple substance or a compound, and give convincing reasoning: nitrogen, mercuric oxide, water, platinum, iron rust.

3. Make a list of ten simple substances with which you are familiar outside of the laboratory. Give evidence of this familiarity. List several simple substances of your acquaintance not commonly encountered outside of laboratories. Describe them.

4. List some properties of the 12 metal substances that are tabulated on page 23 for which properties are not already given.

5. To what does the term *physical state* refer? Should it be possible to obtain all simple substances in all three physical states? Give reason. Is it possible to obtain all compounds in all three physical states? Give examples.

6. State the Law of Definite Weight Proportions. Give several examples. How is it possible to have two or more compounds that are composed of the same constituent elements? Give examples.

7. What differences in the composition of compounds within each of the following groups is indicated by their names?

a. Hydrogen sulfide, hydrogen sulfate, and hydrogen sulfite

b. Mercurous chloride, mercuric chloride, and mercuric chlorate

c. Cupric oxide, cuprous oxide, and cupric hydroxide

8. How many elements does earth possess? Account for the fact that there are more simple substances than elements, and illustrate by reference to specific examples.

9. What elements normally contribute to the composition of substances within the human body? Name at least ten of these elements in order of the relative weight proportions necessary for contributing to adequate quantities of substances for body needs. Of these elements, which are ordinarily supplied in adequate quantities within substances of the usual mixed diet? Which elements need to receive some special consideration in the selection of foods to ensure adequate quantities for making adequate amounts of substances containing them?

CHAPTER 4

OXYGEN THE ELEMENT. OXYGEN THE SUBSTANCE

OXYGEN ELEMENT

The element oxygen contributes to many substances. It is one of the elements in all oxygen compounds. It is the only element in the substances oxygen and ozone. In all, about one half of earth's available supply of building materials for substances consists of oxygen element.

OXYGEN SUBSTANCE

Occurrence. Since oxygen, the substance, is gaseous not only at ordinary temperatures but even at the very low temperatures that prevail in earth's coldest regions, *nearly all* of earth's supply of this substance is found where all substances that are gaseous are chiefly located, namely, in the air. About 21 per cent of the atmosphere's total volume is the substance oxygen. This proportion remains fairly constant owing to the fact that, while oxygen is being removed continuously from the atmosphere both for the respiration of animals and for various burning reactions, it is being made continuously, and as rapidly, in green plants, whence it passes into the atmosphere. The stirring and mixing by breezes and air currents, and the natural tendency of gases to diffuse, keep it in remarkably even distribution. Some of the reactions that take place are as follows:

Oxygen removed from air

Hydrocarbons (of fuel-oil mixtures) + Oxygen → Carbon dioxide + Water
Carbon (of coal mixture) + Oxygen → Carbon dioxide
Glucose (within animal cells) + Oxygen → Carbon dioxide + Water

Oxygen returned to air (from chlorophyll cells of plants)

Carbon dioxide + Water → Oxygen + Plant carbohydrates

Because oxygen is slightly soluble in water, a *small portion of* earth's supply of this substance is in solution in the water of streams, ponds, lakes, and oceans. This is fortunate since fish must have oxygen substance for living needs just as land animals must. The oxygen element which is combined within water itself is of no more use to fish for respiration purposes than it is to land animals; in fact, fish "drown" in water which has an inadequate supply of dissolved oxygen.

How long has it been known? Strange as it may seem, considering its vital importance and the fact that it is around us everywhere, conscious acquaintance with oxygen dates back to only a little over a century and a half ago. Historical records do show that longer ago than this two or three isolated men in their respective centuries had obtained knowledge of it, but what information they acquired in regard to this substance died with them.

From the writings of Leonardo da Vinci (1452–1519) it seems probable that he was aware of the gaseous substance, in earth's atmosphere, which we now call oxygen. John Mayow (1645–1697), an English physician, also recognized the presence of such a substance in the air but did not isolate it. So it came about that the discovery which was to bring the knowledge of oxygen to the world to stay and to grow to present-day magnitude was left for fairly recent accomplishment.

The final birthday of this substance—if one can thus label the time when something that has existed for eons became known to man—is definitely known to be August 1, 1774. It was on this day that Joseph Priestley—an Englishman, a dissenting preacher, and a more or less skillful scientist—happened to be heating what was then called *mercurius calcinatus per se* (now called mercuric oxide). He obtained a gaseous substance which to his great surprise caused a candle which he chanced to thrust into it to "burn with a remarkably brilliant flame."[1] Thus did Priestley happen upon this substance which he felt convinced was different from all other gaseous substances known at that time.

Later it became known that a Swedish contemporary, Karl Wilhelm Scheele (1742–1786), had really made this substance by three

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[1] An interesting account of this discovery of oxygen is to be found in Moore, F. J.: *History of Chemistry*. McGraw-Hill Book Company, Inc., New York, 1939, p. 77.

or four different methods prior to its independent discovery by Priestley, but the latter was the first to publish his findings.

Among others who became interested in this substance was Antoine Lavoisier, a distinguished French scientist, who, through his experiments with Priestley's "dephlogisticated air,"[2] accomplished more toward revealing its true nature than did Priestley himself. It was Lavoisier who discovered that the "new" gaseous substance really comprises 21 per cent of the atmosphere and who first demonstrated its relationship to burning phenomena and to animal respiration. Lavoisier gave this newly discovered substance the name *oxygen*, which means *acid producer*, because he believed the element material therein to be essential to all acids. Later findings proved that he was mistaken because it is hydrogen element, not oxygen, that is thus essential. But the name *oxygen*, misnomer though it is, has persisted down through the years to designate this illusive but important simple substance.

Securing concentrated supplies of oxygen. The dilute oxygen of the atmosphere is entirely sufficient for the everyday uses of people for respiration and burning. But, when it comes to packing oxygen into tubes for man to take along as indispensable baggage for under-sea and upper-air investigations, as well as for other uses, highly concentrated oxygen is essential. Chemists and manufacturers, also, need more concentrated supplies of oxygen than that of the air for their uses. Thus, the business of securing commercial supplies of oxygen has become one of the important industries of modern times.

For commercial uses. In obtaining concentrated and relatively pure oxygen in large quantities for commercial purposes, cost is obviously an important factor. But inasmuch as there is an already made oxygen supply in the atmosphere, the expense of obtaining it undiluted from this source lies solely in the process. This involves separating oxygen from its association with other substances in the air, chiefly nitrogen, carbon dioxide, and water.

Without going into mechanical details of the process by which this is accomplished, the main procedures are as follows. The air is first treated with certain chemicals for the removal of carbon dioxide and water. Next, the remaining gaseous mixture of nitrogen and

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[2] The name that Priestley gave to this newly discovered gaseous substance was *dephlogisticated air.*

oxygen is subjected to increasingly high pressures and lower temperatures until eventually (below −196° C) *liquid air* is obtained—namely, a mixture of liquid oxygen and liquid nitrogen (Fig. 11). Then, since the lower-boiling-point liquid nitrogen is more volatile than the higher-boiling-point oxygen, a slight raising of the temperature of the liquid air causes a more rapid evaporation of nitrogen which, in the gaseous state, is lifted up away from the oxygen. This nitrogen gas, mixed with small quantities of oxygen, is pumped into

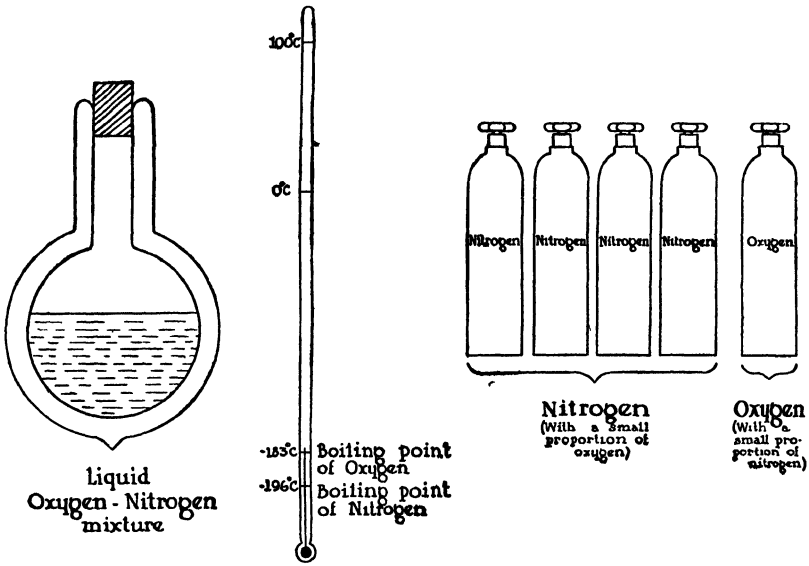


Fig. 11. **Commercial supplies of oxygen obtained from air.**

metal cylinders, packed there under pressure, sealed, and eventually marketed for making ammonia (p. 50). The temperature of the remaining liquid air is now raised slightly until the oxygen, now about 99.5 per cent pure, evaporates. Finally, the oxygen is collected in heavy metal containers, under pressure, as was the nitrogen.[3]

Some of the uses for commercial supplies of oxygen will receive attention in a later chapter (pp. 63 to 65).

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[3] At the temperature of a warm room, 70° F or 39° C, in a full tank of commercial oxygen, the gas is under a pressure of approximately 2000 lb per sq in. For more specific information see: *Oxygen Therapy Handbook*, The Linde Air Products Company, New York, 1949.

Other sources of oxygen. Since oxygen of air mixture is the only supply of this substance already made, to obtain it from other sources necessitates making it from oxygen element provided in oxygen-containing compounds. There are thousands of oxygen compounds, and all of them can be considered as potential sources for the production of oxygen substance. Actually, however, many compounds, including carbon dioxide, carbohydrates, and calcium carbonate, do not yield up their oxygen element toward this end. But, there are other oxygen-containing compounds from which oxygen substance can be made more or less readily. *Water* would seem to be the obvious first choice for this purpose. It is true that when an electric current is passed through water, to which a little acid has been added, the water does decompose making the two simple substances oxygen and hydrogen (Fig. 12).

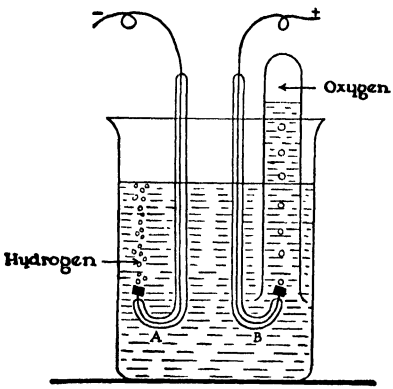


Fig. 12. Oxygen made by decomposition of water.

$$\text{Water} \rightarrow \text{Oxygen} + \text{Hydrogen}$$

This would seem to be a feasible method for making commercial supplies of oxygen; however, unless there is a cheap source of electricity and a market for hydrogen, this method is too expensive to compete with the air reduction method.

We have already learned that Priestley made oxygen by decomposing *mercurius calcinatus per se*, now called *mercuric oxide*. The reaction is easily accomplished as follows:

A small quantity of *mercuric oxide* is put into a test tube and heated (Fig. 1, p. 13). When its temperature is high enough, decomposition of the mercuric oxide begins to take place *very slowly*, as evidenced by the gradual appearance (1) of mercury substance which, although gaseous at the high temperature at which it is made, presently condenses to liquid mercury on cool portions of the tube, where it collects in characteristic silvery droplets; (2) of oxygen whose presence, while not sensed directly, can be detected by thrusting into it a "glowing" wood splint which, though it burns only with "glowing speed" with the dilute oxygen of the air, springs into vigorous burning when sur-

rounded by the greater concentration of oxygen within the tube. The word equation which represents this reaction is as follows.

Mercuric oxide → Oxygen + Mercury

But, this method for making oxygen is of more interest historically than from a practical viewpoint since mercuric oxide is expensive and the yield per pound is comparatively small (p. 43).

We might consider several other compounds which yield oxygen readily, but we shall satisfy ourselves with only two. These are selected because of their classic significance and their adaptability to making easily the small quantities of oxygen commonly needed for laboratory study. These two compounds are *potassium chlorate* and *manganese dioxide*, and the procedures for making oxygen from them are described in some detail as follows.

Oxygen made from potassium chlorate. When this compound—white, crystalline, solid—is put into a test tube and heated (Fig. 13) it melts (at about 368° C) before decomposition becomes appreciable. But, as heating is continued and the liquid potassium chlorate boils (about 400° C) reaction begins to take place so rapidly that there is need for *very careful control* of oxygen production through intelligent adjustment of the heat applied. With uncontrolled technic the reaction can easily become uncomfortably, even dangerously, violent. The other product of the reaction is potassium chloride, a colorless compound which is liquid at the high temperatures at which it is made but solid at ordinary temperatures.

Potassium chlorate → Oxygen + Potassium chloride

Oxygen made from manganese dioxide. Manganese dioxide, a black solid, can be made to decompose by using the same procedure as that used with potassium chlorate. But, making oxygen from this compound is more difficult than from potassium chlorate because manganese dioxide must be at a much higher temperature (about 535° C) before it begins to give up appreciable quantities of its oxygen element. Even then it gives it up very sluggishly and only part of it at that. Along with oxygen, there is made another manganese oxide—brown in color—which contains a lower percentage of oxygen element than does the initial black manganese dioxide.

A comparison. Of the last three means presented for making oxygen from compounds, that from potassium chlorate is obviously the most feasible. First, this compound decomposes appreciably at a lower, hence a more easily obtained, temperature than does either mercuric oxide or manganese dioxide; second, relatively larger quantities of oxygen are made from it.

From 1 lb	*Oxygen made*
Mercuric oxide	0.074 lb
Potassium chlorate	0.393 lb
Manganese dioxide	0 122 lb

Now for an experimental venture which has come to be a classic: namely, that of mixing potassium chlorate and manganese dioxide and heating this mixture.

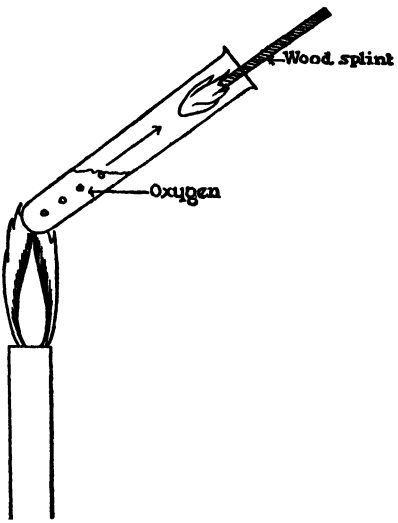


Fig. 13. Oxygen made by decomposition of potassium chlorate.

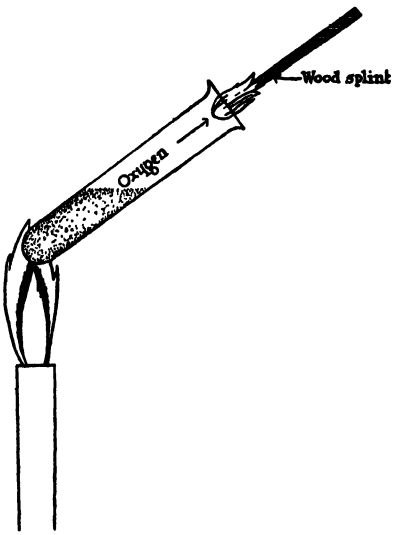


Fig. 14. Oxygen from potassium chlorate–manganese dioxide mixture.

Take some *potassium chlorate*, mix a little *manganese dioxide* with it quite thoroughly, put the mixture into a test tube, and heat it (Fig. 14). Almost right away, certainly at a much, much lower temperature than that at which manganese dioxide decomposes, even considerably below that at which potassium chlorate melts, oxygen begins to be made and so rapidly that the heat supply must be very carefully controlled in order to avoid too violent delivery of this gaseous substance.

Certainly this is a surprising happening—that oxygen should be thus made at a temperature far below that at which it can be made from either one of these compounds alone. It is not surprising, however, that this mixture has come to have an important place in general laboratory student practice as a source of small and easily obtainable supplies of oxygen.

But thinking students will wonder: Is the oxygen made from potassium chlorate, or from manganese dioxide, or from both? An answer to this question has come as a result of many experimental studies of this phenomenon from a quantitative angle. Always, when such studies have been made with painstaking accuracy, it has been found that in the test tube, when reaction is complete, the substances left are potassium chlor*ide* and *manganese dioxide.* Also, the quantity of manganese dioxide is *exactly equal* to the quantity present before any reaction began (Fig. 15).

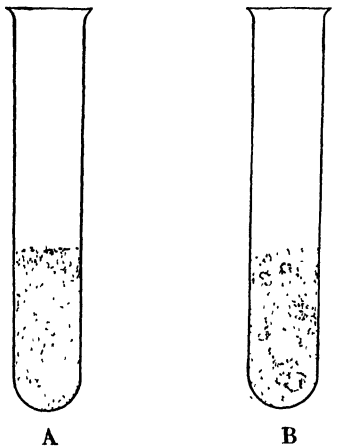


Fig. 15. *A.* If in the beginning the mixture contains 5 gm of potassium chor*ate*, 2 gm of manganese dioxide.

B. When the reaction is complete, there will be left within the test tube 3.04 gm of potassium chlor*ide*, 2 gm of manganese dioxide.

It appears evident, then, that under these circumstances oxygen is made from the potassium chlorate. The manganese dioxide does not seem to enter into the reaction at all.

What, then, is the function of the manganese dioxide? The answer to this question leads to one of the most interesting and least understood of chemical phenomena: that *the speed of a chemical reaction can be influenced by the mere presence of some selected substance which in itself is seemingly not part of the reaction.* Such substances have received various labels—*catalytic agents*, or *catalysts*, or *contact agents.* Manganese dioxide, then, functions as a catalyst for the decomposition of potassium chlorate because, in its presence, this reaction takes place more speedily. One method for representing the presence of this catalyst is as follows.

$$\text{Potassium chlorate} \xrightarrow{\text{manganese dioxide}} \text{Oxygen} + \text{Potassium chloride}$$

QUESTIONS

1. Make a statement in which you differentiate clearly between oxygen the element and oxygen the substance.
2. Where is oxygen element located? About how much does earth possess, comparatively speaking? Where is oxygen substance to be found in earth's matter possessions?

3. How long has the substance oxygen been known? What famous scientists were associated with (a) the final discovery and (b) the later study of oxygen?

4. From what source are commercial supplies of oxygen obtained and by what method? Is the involved process physical or chemical? Why?

5. Explain the sudden rush of gas that accompanies the first opening of a commercial tank of oxygen.

6. How is the pressure of a gas within a tightly closed tank of oxygen affected by removal from a cool to a warm room? Explain.

7. What substances, in general, can be considered as potential sources from which oxygen substance can be made? Name at least three compounds from which oxygen can be made in the laboratory. Assemble word equations for the reactions concerned. Which of the methods studied appears to you to be the most practical for securing such quantities of oxygen as are needed for laboratory use? Give reasons for your selection.

8. When potassium chlorate and manganese dioxide mixture is used for obtaining oxygen: (a) What is the function of the potassium chlorate? (b) What is the function of the manganese dioxide? (c) What name is given to a substance which functions as manganese dioxide does with reference to this reaction?

CHAPTER 5

CATALYTIC AGENTS

The functioning of catalysts is a subject that merits further attention and, for this purpose, we shall interrupt the study of oxygen.

Catalytic agents. *A catalyst can be defined as a substance which affects the speed of a chemical reaction without, seemingly, being part of the reaction.* The catalyst can be recovered when the reaction is over; hence, it is not used up in the process.

Ever since the early 1800's there has been some knowledge of specific substances that functioned to increase the speeds of selected chemical reactions. However, it was not until about 1900 that chemists became seriously interested in the investigation of this extraordinary speed factor. Today, catalysis is one of the major fields of chemical investigation. Studies of this phenomenon have invaded many areas of human interest bringing better understanding of time-honored reactions, opening up new developments in industry and in reactions of physiological importance.

Catalysts included in recipes for food preparations. It is known now that since ancient times people have included substances, which function as catalysts for reactions concerned, as part of recipe procedures. The following are examples.

In making leavened bread. For centuries, recipes for leavened bread have called for the inclusion of yeast and for keeping the dough mass in a warm place. But, no one knew in the long-ago days—most people do not know now—either why yeast is necessary or why the bread dough must be kept warm. They simply knew that if these directions were observed bread dough would "rise"; if not, the dough would not "rise." So it was left for chemists to find out that in leavening bread several reactions take place:

1. *Starch* (component of flour) reacts with *water* to make *maltose.*
2. *Maltose* reacts with *water* to make *glucose.*
3. *Glucose* decomposes to make *carbon dioxide* and *grain alcohol.*

However, none of these reactions proceeds with appreciable speed until (1) the dough is warmed, at which time a catalyst known as *diastase*—an amylase associated with the flour—begins to speed up the first reaction and (2) bread yeast is introduced, bringing with it the catalysts known as *maltase* and *zymase*[1] which accelerate the other two reactions.

$$\text{Starch} + \text{Water} \xrightarrow{\text{amylase}} \text{Maltose}$$

$$\text{Maltose} + \text{Water} \xrightarrow{\text{maltase}} \text{Glucose}$$

$$\text{Glucose} \xrightarrow{\text{zymase}} \text{Carbon dioxide} + \text{Grain alcohol}$$

It is the making of carbon dioxide, together with the expansion of warm imprisioned air, that leavens the dough mass. When the desired "lightness" is attained, the dough is moulded into loaves and, presently, the catalysts are destroyed by the heat of the oven.

In cheese making. Among the recipes handed down through centuries of usage is one for making cheese from cow's milk. In olden days this called for adding to the milk the ground lining of a calf's stomach. So ancient is this recipe that its origin is ledgendary, but actual knowledge of the reactions concerned is a matter of less than a century. It is now known that in the process of cheese making one of the proteins of milk, known as caseinogen, reacts with water to make casein, the protein of cheese. However, the speed of this reaction is negligible save in the presence of a functioning catalyst. *Rennin,* which is made in abundance in the mucosa of the calf's stomach functions in this capacity

$$\text{Caseinogen} + \text{Water} \xrightarrow{\text{rennin}} \text{Casein}$$

With modern methods for extracting the rennin, the old recipe has been changed and the extract, rather than the entire mucosa, is used in the process.

Investigation of these inherited recipes is interesting, and there are other recipes of long usage, an analysis of which would show that

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[1] *Zymase* is not a single substance but a group of catalysts that function to favor a series of reactions with carbon dioxide and grain alcohol as end products.

catalysts have always been included among essential components for securing desired products.

Catalysts and modern industries. The tremendous progress that has been made during the current century in the field of manufacturing has, to a surprising degree, become possible through the agency of catalysts. Some industries have been born, others have been revolutionized because of the discovery of catalysts for speeding up key reactions. The following are specific instances.

Sulfuric acid manufacture. Sulfuric acid is the most important chemical of industry because, in one way or another, it is used in the manufacture of more useful materials—fertilizers, explosives, rayon, artificial leathers and woods, lacquers and paints, drugs, dyes, soaps, paper, glass, steel, etc.—than any other one substance.

Now sulfuric acid has been made on a commercial scale for nearly 200 years. However, until the early 1900's it was manufactured almost entirely by a process—called the lead-chamber process—which yields an impure and dilute product. But, the manufacture of many materials, such as explosives and rayon, requires "pure" and concentrated sulfuric acid. As a result, the time came, about the beginning of the present century, when the need for a better grade of this acid became urgent. Attempts were made to purify and concentrate the product of the lead-chamber process, but they were far from successful. The alternative was to search for another method for making this essential substance.

Already a good start had been made. It had been known for nearly a hundred years that a good grade of concentrated sulfuric acid was possible from a sequence of two reactions, as follows.

$$\text{Sulfur dioxide} + \text{Oxygen} \rightarrow \text{Sulfur trioxide}$$
$$\text{Sulfur trioxide} + \text{Water} \rightarrow \text{Sulfuric acid}$$

And a catalyst—namely, platinum—had been discovered for speeding up the first of these reactions, which, without this aid, is exceedingly slow. The second reaction is in no need of such assistance. But, trouble had been encountered in the use of this catalyst. It was found that when platinum was brought in contact with sulfur dioxide and oxygen it would catalyze the reaction for a time, then would gradually become "poisoned"—meaning that, although present, for some unknown reason its function was interfered with. There the matter rested until the end of the 1800's when interested chemists resurrected these ancient findings and set themselves to the task

of discovering what was responsible for "poisoning" the platinum catalyst and how to circumvent it. Eventually, the information sought was obtained. The way was paved for the development of a rival of the lead-chamber process, which came to be called the contact process, for the production of this important acid. The product of the contact process was found to be of an excellent grade.

Of course, platinum is very costly, but it must be remembered that, as a catalyst, it is not destroyed in the reaction; hence, it can function over and over again for catalyzing reactions of large quantities of substances.

It is this more concentrated, purer, and less expensive sulfuric acid that has been one of the contributing factors in the development to present-day proportions of some of our largest modern industries.

For making nitrates. The next tale has to do with the tremendous development during the past 50 years of the production of fertilizers and high explosives, as well as numerous other useful materials which require nitric acid in their making.

The demand for *nitrate* fertilizers arises from the fact that plants depend on nitrate salts in the soil to supply nitrogen for building their essential proteins. Before the 1900's this need for nitrate had been met, partially, by various means as follows. (1) Animal manures were spread on soils; such excreta contain nitrogen compounds from which, through the agency of certain bacteria in soils, nitrates are made. (2) Guano, with its component of Chile saltpeter or sodium nitrate, was brought by shiploads from the west coast of South America. Within this compound, as the name implies, the nitrate is already present. (3) Fields were enriched by growing crops of clover and other leguminous plants whose root nodules house certain bacteria which are able to utilize gaseous nitrogen of the atmosphere, together with other substances at hand, for making nitrate—at the very roots of the needy plants.

But, despite these several sources, there was not sufficient nitrate to maintain the fertility of incessantly cultivated lands. Accordingly, by the late 1800's, certain scientists of Europe, with an eye to the future, had begun to feel some concern about the matter.

Thus, for the sake of the future food supply of the world as well as for other needs, the problem was put up to the chemist to see whether something could be done about making nitrate from the ever-ready nitrogen supply of the air.

Certain rudimentary information was already at hand. It was already known that

Nitrogen reacts with *hydrogen* to make *ammonia* (nitrogen hydride).
Ammonia reacts with *oxygen* to make *nitric acid* (or hydrogen nitrate) and water.

However, unaided, these reactions proceed very, very slowly. So researches were begun to discover ways for speeding them up sufficiently to render them useful. These investigations included a hunt for appropriate catalysts.

In due time—about 1900—a German chemist, Fritz Haber, discovered that uranium acts as a catalyst (other catalysts have been discovered since) for making ammonia by the above-mentioned reaction. About that same time another German chemist, Wilhelm Ostwald, discovered that platinum functions as a catalyst for speeding up the second reaction, the reaction whereby nitric acid can be made from ammonia. Once nitric acid is obtained, making all other nitrates is accomplished easily.

By 1915 Germany had developed this industry to such an extent that she was able to manufacture nitrates, for use as fertilizers and in making high explosives, not only in sufficient quantities to render her independent of the Chile saltpeter deposits but to sell to other countries as well.

During the years since then, manufacturers in most, if not all, other countries have learned how to make nitrates by using atmospheric nitrogen. Today nitrates made from nitric acid of synthetic origin have very largely replaced those extracted from Chile saltpeter.

Hydrogenation of fats. Fats have two world-wide uses—for food and for making soap. For both of these uses, solid fats are and always have been generally preferred. Even so, up to about 50 years ago there were not enough solid fats to meet the food requirement of the world's peoples and to make sufficient soap for cleansing purposes. This great deficiency of solid fats existed despite a considerable excess of liquid fats, such as cottonseed oil, other plant fats, and fish oils. These fats were to quite an extent utter waste.

It had long been known that solid fats contain a slightly higher proportion of hydrogen than do liquid fats. Hence, chemists became convinced that if the less desirable liquid fats could be made to combine with hydrogen, fats of the solid variety should result.

Liquid fat	+	Hydrogen	⟶	Solid fat
carbon : hydrogen : oxygen		6 parts by weight		carbon : hydrogen : oxygen
684 : 104 : 96				684 : 110 : 96

But, repeated trials to bring about this combination revealed that an exceedingly sluggish reaction was involved.

Here was another reaction of great potentiality, but where was a substance that would catalyze it? The search began, and, in 1899, a French scientist, Paul Sabatier, discovered that nickel functions in this capacity.

$$\text{Liquid fat} + \text{Hydrogen} \xrightarrow{\text{nickel}} \text{Solid fat}$$

This seems very simple, but the discovery was of tremendous importance, and Sabatier was awarded the much-coveted Nobel prize for his achievement.

Thus, the discovery of a catalyst for an otherwise useless reaction led to the creation of an entirely new industry—the so-called hydrogenation of fats. Today the better grades of vegetable oils are hydrogenated to make lard substitutes and margarine, whereas poorer grades of plant fats, as well as fish fats, are hydrogenated to make semisolid fats which are used in the manufacture of soaps (p. 327).

Many other instances of outstanding industrial developments made possible by the discovery of catalysts for important reactions might be cited. These would include new methods for making methyl and ethyl alcohol, and the development of rubber substitutes and an increasing number of modern plastics. At present, the largest single use of catalysts is claimed to be in the hydrocarbon field for the "cracking" of heavy hydrocarbons to obtain the more volatile hydrocarbon fuels required for our twentieth century engines.

Nature has always used catalysts. The study of catalysts and their functioning has called to the attention of the chemist the fact that many reactions of natural occurrence are catalyzed by substances provided in their surroundings. *Water* appears to be one of nature's catalysts. It is believed, for instance, to catalyze the reaction of iron with oxygen, in the process known as rusting.[2]

$$\text{Iron} + \text{Oxygen} \xrightarrow{\text{water}} \text{Iron oxide}$$

[2] Although water functions as a catalyst in the rusting of iron, it is also, itself, involved in the reaction; thus, iron rust, in total, is a more complex compound than just iron oxide.

Thus, *dry* iron does not rust appreciably because the catalyst for the reaction is not present.

Catalysts of vital importance. All living organisms, whether the single-celled microorganism or the more highly organized plant or animal, make within their own cells catalysts which control various reactions essential for the life of the organism. These catalysts produced within the cells of plants and animals are known as *enzymes.*

Among the best known of the enzyme-catalyzed reactions are the digestive reactions for which specific enzymes are provided along the digestive tract. These reactions, and the functioning catalysts, are as follows:

In salivary digestion

$$\text{Starches} + \text{Water} \xrightarrow{\text{ptyalin}} \text{Dextrins} + \text{Maltose}$$

In gastric digestion

$$\text{Proteins} + \text{Water} \xrightarrow{\text{pepsin}} \text{Proteoses} + \text{Peptones}$$

In intestinal digestion

$$\text{Dextrins} + \text{Water} \xrightarrow{\text{amylase}} \text{Maltose}$$

$$\text{Starches} + \text{Water} \xrightarrow{\text{amylase}} \text{Maltose}$$

$$\text{Maltose} + \text{Water} \xrightarrow{\text{maltase}} \text{Glucose}$$

$$\text{Sucrose (cane sugar)} + \text{Water} \xrightarrow{\text{sucrase}} \text{Glucose} + \text{Fructose}$$

$$\text{Lactose (milk sugar)} + \text{Water} \xrightarrow{\text{lactase}} \text{Glucose} + \text{Galactose}$$

$$\text{Proteins} + \text{Water} \xrightarrow{\text{trypsin}} \text{Peptides}$$

$$\text{Proteoses} + \text{Water} \xrightarrow{\text{trypsin}} \text{Peptides}$$

$$\text{Peptones} + \text{Water} \xrightarrow{\text{trypsin}} \text{Peptides}$$

$$\text{Peptides} + \text{Water} \xrightarrow{\text{erepsin}^3} \text{Amino acids}$$

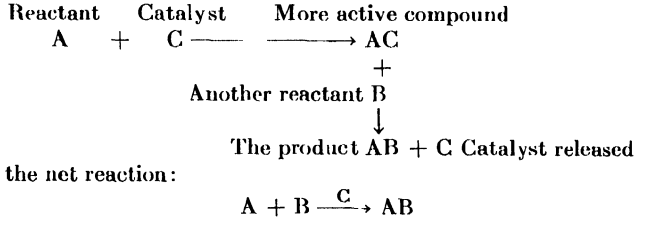
$$\text{Fats} + \text{Water} \xrightarrow[\text{pancreatic lipase}]{\text{steapsin, or}} \text{Fatty acids} + \text{Glycerol}$$

Such reactions are not peculiar to humans; they are characteristic of other animals as well. Even microorganisms produce enzymes which function in reactions whereby the organisms obtain their nutrients. In fact, it is becoming increasingly more evident that *enzymes,* functioning as catalysts, play a vitally important part in regulating the speeds of practically all of the myriads of reactions involved in the life activities of plants and animals. (See Chap. 29.)

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[3] The word *erepsin* designates a group of *peptidases;* it is no longer regarded as a single enzyme.

How do catalysts function? Although the study of catalysts and their functioning has engaged the interest of some of our most brilliant scientists, exact knowledge as to how these agents work has proved to be elusive. It seems probable that catalysts may not all function in the same manner. Contact agents, such as platinum and the finely divided solids, may adsorb the reactants at their surfaces, thus producing local areas of high concentration favorable to more rapid reaction. Other catalysts, including the enzymes, may become involved in intermediate reactions to make more active compounds which, in turn, react to produce the products—at the same time releasing the catalyst. Such a possibility is suggested in the following diagram.



Thus the net reaction:

$$A + B \xrightarrow{C} AB$$

Whatever may be the exact mechanism of catalysis, it is generally agreed that, at some stage in the reaction, the catalyst has an active role.

QUESTIONS

1. In general, what is the function of a catalyst? Illustrate by reference to a specific catalyzed reaction of your own experience.
2. What is the function of yeast when included in a recipe for breadmaking? Give details.
3. Give word equations for reactions involved in each of the following commercial processes, indicating functioning catalysts where such are necessary:
   a. Making sulfuric acid by the contact method
   b. Making of nitrate
   c. Hydrogenation of fats

Name some industrial developments which have become possible as a result of these commercial processes. Consider what, if any, effects these developments have had in relation to your concerns.

4. What precaution should be observed in the care of steel instruments or other iron equipment in order to prevent their rusting? Give reason.
5. What are enzymes? Why are they included among catalysts?
6. In regard to digestive reactions presented in this chapter, what chemical reactions are involved? Specify a functioning enzyme for each reaction. What is the function of these enzymes?

CHAPTER 6

OXYGEN THE SUBSTANCE (Continued)

Making and collecting oxygen for laboratory study. Before the subject of oxygen was set aside for that of catalytic agents, it had already been found that a feasible method for making supplies of this simple substance (p. 43) for laboratory study is through the decomposition of potassium chlorate with an admixture of manganese dioxide as a catalyst for the reaction. Apparatus for use in generating oxygen and collecting the gas by water displacement is shown in Figure 16.

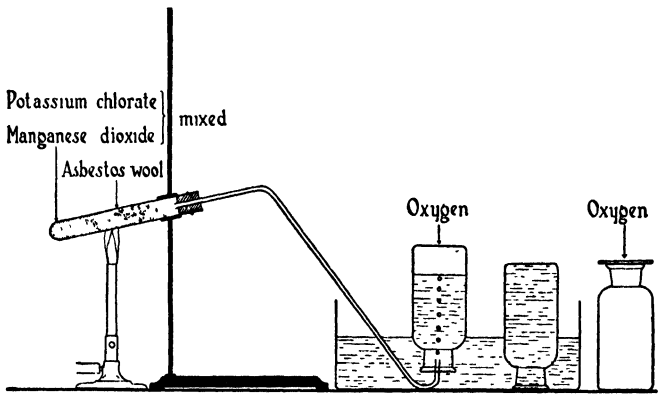


Fig. 16. Making and collecting oxygen.

$$\text{Potassium chlorate} \xrightarrow{\text{manganese dioxide}} \text{Oxygen} + \text{Potassium chloride}$$

The potassium chlorate (⅔) and manganese dioxide (⅓) are well mixed before being introduced into the test tube carrying the delivery tube. The test tube is clamped to a support in such a position as to provide easy heat control of the mixture and easy collection of the oxygen. The collecting bottles should

be made ready in advance by filling each to the brim with water, slipping a glass plate over the mouth of the bottle, and inverting it in the cistern of water.

When all is ready for the operation the mixture is heated *gently*. When sufficient oxygen has been made to displace all air in the generator and delivery tube, the latter should be inserted into the neck of the first collecting bottle. The oxygen will rise through the water and push it down out of the bottle into the cistern. (Why?) When the bottle is full of oxygen, it can be removed by slipping a glass plate down through the water and over the mouth of the bottle, which can then be removed and placed with mouth up but still covered.

When making oxygen by this method, it is advisable for the operator continuously to keep in mind the fact that *the speed of this reaction is determined by the temperature; therefore, it is under his control.*[1]

PHYSICAL PROPERTIES OF OXYGEN

It is not necessary to go into the laboratory and collect samples of oxygen in order to determine that it is *colorless*, *odorless*, *tasteless*, and *gaseous*. These properties are recognizable in the oxygen of the air. That oxygen is slightly soluble in water is obvious from the fact that fish and aquatic plants must obtain it in water to meet their respiratory needs. For other physical properties, such as its *freezing point*, *boiling point*, *density*, and the exact *solubility* in water, pure oxygen must be obtained. These important quantitative findings require careful and painstaking laboratory procedures, but once determined they serve as evidence that oxygen is indeed an individual substance, different from all other substances.

Oxygen is colorless odorless tasteless gas, at ordinary temperatures slightly soluble in water	These properties are characteristic of other gaseous substances as well as of oxygen; hence they do not serve to identify this substance.

Quantitative findings

Extent of solubility, 0.049 vol of oxygen in 1 vol of water at 0° C and standard pressure (p. 3) Its boiling point is −182.5° C freezing point is −218° C density—1 liter at 0° C and standard pressure weighs 1.429 gm	These properties are possessed exclusively by oxygen, hence identify it as a distinctive substance.

Importance. It may be that the fact that oxygen is colorless, odorless, and tasteless has no special significance. However, the fact

[1] Further details regarding this laboratory operation will be found in the manual planned to accompany *Fundamentals of Chemistry and Applications*.

that oxygen is gaseous is of vital concern because all land animals must have gaseous oxygen to meet their respiratory needs. Moreover, its low boiling point and low freezing point assure the constancy of its supply in the atmosphere because, even in the arctic regions and the very low temperatures of the upper atmosphere, oxygen neither rains nor snows out of the air. The slight solubility of oxygen in water is also of vital importance, not only for aquatic life but for land animals as well, because it must be carried in water solution across the lung membrane into the blood.

CHEMICAL PROPERTIES OF OXYGEN

The omnipresence of oxygen in the atmosphere, hence its continuous contact with other substances, makes its chemical behavior a matter of general interest.

Oxygen with other simple substances. Oxygen is the most cosmopolitan of all simple substances in its combining interests. It reacts with most of the other simple substances, more or less readily, to make oxides. For example:

Even at ordinary temperatures, fairly rapid reaction is possible between OXYGEN and	Only slow or inappreciable reaction at ordinary temperatures, but rapid reaction at elevated temperatures, can be expected from contacts between OXYGEN and	Only slow reaction, even at very high temperatures, can be commonly expected from contacts between OXYGEN and
Potassium	Magnesium	Aluminum
Sodium	Sulfur	Iron
Calcium	Carbon	Nickel
Phosphorus	Hydrogen	Tin
	and a number of other simple substances	Copper
		Nitrogen
		and some other simple substances

No reaction takes place between OXYGEN and Silver, unless the oxygen is under high pressure and at a high temperature.

No reaction takes place, even at high temperatures, between OXYGEN and

Platinum	Fluorine	Helium
Gold	Chlorine	Neon
	Bromine	Radon
	Iodine	and the other inert gases

Explanation for this varied behavior with oxygen. The clue to these observable differences in speeds of reactions with oxygen lies in *differences in the combining tendencies of the elements, making up the different simple substances, for oxygen element in oxygen substance.* Thus:

Phosphorus, potassium, and sodium elements *have a marked combining tendency for oxygen element; hence, these substances react speedily* to make oxides. Magnesium, carbon, copper, and nitrogen elements *exhibit decreasing tendencies* to form compounds with oxygen, as evidenced by *slower reactions* between the simple substances and oxygen. The *combining interests* of gold, platinum, and the halogens for oxygen are *negligible* while the inert gases evidence *no combining interest* for oxygen, nor indeed for other elements in general.

Oxygen with compound substances. The same reasoning about element behavior which accounts for differences in reaction between oxygen and other simple substances can be applied to the behavior of oxygen with compounds. In general, *the substance oxygen can be expected to react with compounds composed of elements that have combining tendencies for oxygen element.* For example:

Oxygen + Hydrocarbons* ⟶ Carbon dioxide + Water
Oxygen + Carbon bisulfide ⟶ Carbon dioxide + Sulfur dioxide
Oxygen + Iron sulfide ⟶ Iron oxide + Sulfur dioxide†

* Hydrocarbons are compounds composed of only the two elements carbon and hydrogen. There are hundreds of such compounds, methane and acetylene, for instance.

† As might be expected, this reaction takes place only at a very high temperature.

Some oxygen compounds react with oxygen. This is possible when the combining tendencies of oxygen-liking elements are only partially satisfied with the oxygen already in combination. Thus:

Oxygen + Carbon monoxide ⟶ Carbon dioxide
Oxygen + Carbohydrates ⟶ Carbon dioxide + Water
Oxygen + Ethyl alcohol ⟶ Carbon dioxide + Water

Some compounds do not react with oxygen. These include (1) *compounds composed of elements that have no combining tendency for oxygen element,* and (2) *compounds in which the combining capacities of the oxygen-combining elements are already fully satisfied.* For example:

(1) Oxygen and silver bromide do not react.
Oxygen and platinum chloride do not react.

(2) Oxygen does not react with carbon dioxide.
Oxygen does not react with magnesium silicate (asbestos).
Oxygen does not react with sodium chloride.

In fact, among the compound substances which we encounter continually in our surroundings *there are many that do not react with oxygen.* In this connection the expression "burned to the ground" is not without significance. It is a reminder that the great majority of the substances making up the crust of the earth—such as feldspar, clay, and silicon dioxide—are compounds that do not react with oxygen.

Products of reaction with oxygen. ***Matter products.*** Every reaction with oxygen must, of course, result in making new substances: these are the *matter products* of the reaction. When conditions are favorable for complete reaction, the matter products are usually oxides.

Energy products. Almost every reaction with oxygen is accompanied by an *energy product.* This usually appears as *heat,* sometimes as *heat* and *light,* and less frequently as *some other variety of energy.* This observation can be confirmed by reference to everyday experiences. Thus, for example:

	Matter products	*Energy products*
Oxygen + Carbon (of coal) ⟶	Carbon dioxide	Heat
Oxygen + Celluloses (of wood) ⟶	Carbon dioxide + Water	Heat and light
Oxygen + Hydrocarbons (of gasoline) ⟶	Carbon dioxide + Water	Heat

The production of *kinetic energy,* the energy responsible for the motion of matter, is illustrated in the reaction of oxygen with hydrocarbons in the cylinders of an automobile. Another illustration occurs within muscle cells. There, when oxygen reacts with glucose, the matter products carbon dioxide and water are made, and, at the same time, *kinetic energy* is made for the motion of body parts.

In cylinders of automobiles	*Matter products*	*Energy product*
Oxygen + Hydrocarbons (in gasoline) ⟶	Carbon dioxide + Water	Kinetic energy

In muscle cells

Oxygen + Glucose ⟶ Carbon dioxide + Water..... Kinetic energy

Source of the energy product. By this time it should be clearly understood that the matter products, that is, the substances that result from the chemical reaction, are made from the elements provided in the reacting substances. But what is the source of the energy product? First, it is believed that oxygen, and indeed every substance, contains a definite quota of hidden energy known as *chemical energy*. And, *when oxygen reacts with other substances, part of this chemical energy is transformed into other varieties of energy which appear as the energy products of the reaction.* The chemical energy not involved in the energy transformation is that portion which is required to supply chemical energy for the new substances.

1. When coal burns

The matter transformation	Oxygen	+	Carbon	⟶	Carbon dioxide			
	↑		↑		↑			
The energy transformation	Chemical energy	+	Chemical energy	⟶	Chemical energy	+	*Heat*	

Interpreted. When oxygen reacts with carbon to make carbon dioxide, part of the chemical energy in the keeping of the oxygen (and part of that which is in the keeping of the carbon) is transformed into a *heat product.* The rest of this chemical energy remains within the resulting carbon dioxide.

2. When gasoline reacts with oxygen in the kitchen stove

Oxygen	+	Hydrocarbons (of gasoline)	⟶	Carbon dioxide	+	Water		
↑		↑		↑		↑		
Chemical energy	+	Chemical energy	⟶	Chemical energy	+	Chemical energy	+	*Heat*

Some practical consequences of the chemical behavior of oxygen. The differing tendencies of different substances to react with oxygen, and the fact that such reactions are generally accompanied by an energy product, have considerable bearing on the selection of substances for various everyday uses.

It should be evident that those substances which react with oxygen at room temperatures—phosphorus, potassium, and sodium, for instance—are limited in use to particular laboratory or industrial processes. Even here their chemical activity must be kept in mind and they must be handled and stored with necessary precautions.

The selection of substances to be used in common activities of people in general must be largely from those that do not give appre-

ciable reaction with oxygen even at elevated temperatures or those which do not react with oxygen at all. Accordingly:

Carbon of coal, *celluloses* of wood and paper, *hydrocarbons* of gasoline, kerosene, and fuel oils can be safely stored if kept at ordinary temperatures, but, when so desired, they can be induced to react with oxygen for the purpose of making heat when raised to easily obtained higher temperatures.

Aluminum, iron, nickel, and *copper* are useful for making cooking utensils and any other containers that will meet with high temperatures because, among other reasons, although continuously in contact with oxygen, reactions between these metals and oxygen are slow. *Platinum* would appear to be the metal par excellence for all purposes for which metals are used. Physically, it is attractive. It is malleable and ductile as are other metal substances, and it has a very high melting point. Chemically, it does not react at all with oxygen even at the highest temperatures known, and, incidentally, it reacts with very few other substances. But the known supply of this substance is very limited.

FUNCTIONS OF OXYGEN

Oxygen is essential for living. The living body is one which is able to make within itself the *kinetic energy* that is essential for the motion of its body parts: for continual beating of the heart, for muscular control of respiratory movements, and for all other muscular contractions. The living body is also able to make its own *heat* for keeping itself warm and *other energies* required for the work of the cells. When the body has lost the ability to make these energies, it is no longer a living or "quick" body, but a dead one; it is no longer a warm body, but a cold one.

There arises, then, the significant question as to the source from which the living body obtains these energies. This brings us directly to consideration of the vital need for oxygen since *the production of energy within the animal body is dependent on chemical reactions for which oxygen is essential.*

A continuous supply of oxygen is carried by the blood to the func-

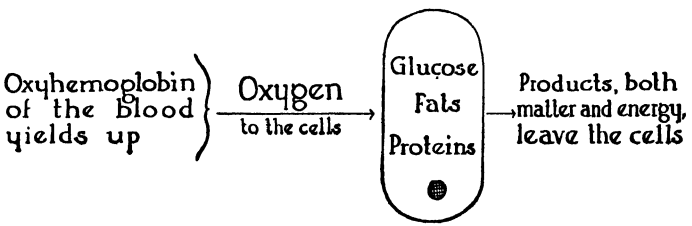


Fig. 17

tioning cells. In response to demands for the production of energy within the cells, oxygen is released from the hemoglobin of the red blood cells to become a partner with glucose,[2] fats, and proteins in reactions for production of energy within the cells (Fig. 17). The related matter and energy transformations may be summarized as follows:

1.06 gm Oxygen	+	1 gm Glucose	⟶	Carbon dioxide	+	Water				
↑ Chemical energy	+	↑ Chemical energy	⟶	↑ Chemical energy	+	↑ Chemical energy	+	3.75 Calories *Kinetic energy* or any other variety of energy needed		
2.9 gm Oxygen	+	1 gm Fats	⟶	Carbon dioxide	+	Water				
↑ Chemical energy	+	↑ Chemical energy	⟶	↑ Chemical energy	+	↑ Chemical energy	+	9.45 Calories *Kinetic energy* or another variety of energy		
1.23 gm Oxygen	+	1 gm Proteins	→	Carbon dioxide	+	Water	+	Urea		
↑ Chemical energy	+	↑ Chemical energy	→	↑ Chemical energy	+	↑ Chemical energy	+	↑ Chemical energy	+	4.35 Calories *Kinetic energy* or some other variety of energy

Note. The reactions whereby energy is produced in living cells involve many intermediate steps, some of which do not require the direct participation of oxygen. These intermediate reactions will be considered in Chapter 31.

The quantitative relations presented above provide the basis on which the nutritionist computes the quantities of carbohydrate, fat, and protein that must be supplied as partners for oxygen in the production of energy within the body.

What happens to the end products. *The matter products* from these reactions are carbon dioxide, water, and urea. These enter the blood and, subsequently, are eliminated at the lungs, kidneys, and skin, as is suggested in

[2] Glucose is referred to in this study, rather than carbohydrates in general, because, following digestion and absorption, glucose is the carbohydrate that is found in the blood and carried to the cells for the energy-producing reactions.

Figure 18. *The energy products*, having performed their functions in the cells, are transformed into heat which on its way to the outside of the body keeps the cells, lymph, blood, and all body parts warm. At the surface layers, lung and skin, a considerable portion of this heat serves to transform water from liquid to the gaseous state. This heat thereby becomes latent heat of vaporization within the exhaled water vapor (574 cal for every gram of water at 40° C changed to water vapor, likewise at 40° C). But some heat is radiated still as heat; hence, the familiar phenomenon of the warming of a room by living people or the warming of a bed in which a person is covered by heat-insulating blankets.

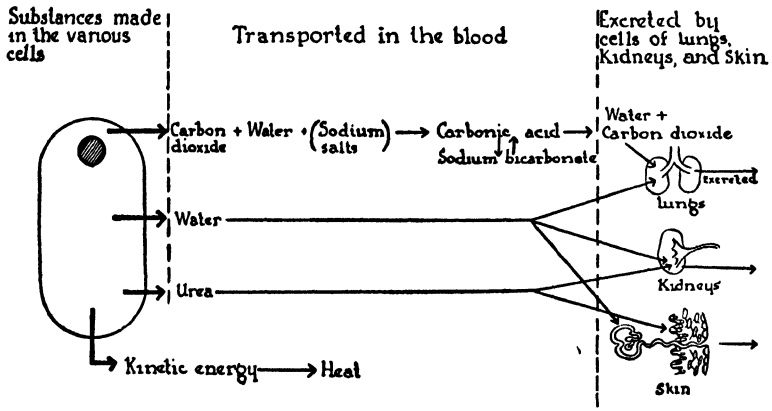


Fig. 18

Other important functionings of oxygen. In the external concerns of man *oxygen functions* (1) as a party in providing much of the world's heat for keeping buildings warm, for cooking foods, and for other purposes; (2) as a party for providing kinetic energy for moving the world's machinery. And again, oxygen is able to function thus because it holds within its keeping chemical energy, part of which—when oxygen engages in reactions with selected substances—becomes available for transformation into these desired energies. Oxygen also *functions* as *a party to getting rid of the proteins* of dead plants and animals. This is accomplished in the process commonly called decay and involves a series of many and little-understood reactions in which bacteria play an active part. These bacteria provide enzymes for speeding various reactions. With only the beginning and end substances mentioned, the following word equation tells of these reactions inclusively and briefly.

Proteins + Oxygen ⟶ Nitrogen + Carbon dioxide + Water

Proteins of dead plants and animals are thereby removed by nature, and a supply of nitrogen is thus assured for other reactions whereby proteins are remade for more living plants and animals. Also, this supply of inert nitrogen dilutes the ever-present, ever-needed, but more active oxygen.

The supply of oxygen for these uses. For everyday uses, the dilute oxygen of earth's atmosphere is adequate—a fact for which we should be devoutly thankful. For making heat, we must buy the partner substances for oxygen—carbon of coal, celluloses of wood, hydrocarbons of gasoline or illuminating gas. For making energies for living needs we must buy starches, proteins, and fats which will eventually—through digestive and assimilative processes—provide reacting partner substances for oxygen within the cells. But oxygen itself, the substance which makes available energy for transformation into heat and other energies outside the body and into vital energies within the cells, we can have for the taking and without cost.

Maintenance of this oxygen supply. Since oxygen is continuously removed from the air to meet these demands for energy production, the question arises as to how this substance is put back into the atmosphere. This brings us to consider the so-called ***photosynthesis*** reaction which goes on in the chlorophyll-containing cells of green plants. The energy for this reaction is supplied by the sun. In the plant leaf, from carbon dioxide of air and water drawn up through the roots, plant carbohydrate is made for the use of the plant. *Oxygen* is also made and escapes into the atmosphere. (See also p. 83.)

$$\text{Carbon dioxide} + \text{Water} \xrightarrow{\text{chlorophyll}} \text{Plant carbohydrate} + \textit{Oxygen}$$

COMMERCIAL SUPPLIES OF OXYGEN AND THEIR USES

Commercial supplies of oxygen have played an important role in the development of our modern civilization. Their uses fall into two main categories: (1) to meet living needs and (2) to provide high temperatures.

To meet living needs. ***In exploration and aviation.*** Whenever man goes to parts of the world where a supply of oxygen is not available, or where the oxygen concentration is low, he must take his oxygen supply with him (Fig. 19). Deep-sea diving, underwater ex-

plorations and construction, and salvaging of sunken ships have become possible only since commercial supplies of oxygen have become available to the workmen. Such supplies are also essential for life in submarines. Flights to the upper atmosphere require supplementary supplies of oxygen for the fliers as well as for the engines. Achievements in mountain climbing, such as the successful ascent of Mount Everest, necessitate the use of oxygen supplies at the higher altitudes not only for the strenuous work of climbing but even to assure restful sleep for the explorers.

Medical uses. Although a relatively small proportion of the commercially prepared oxygen goes into medical uses, these uses must be rated as important. The demand for concentrated supplies of oxygen is of daily importance in hospitals—so much so that many of the newer hospitals have oxygen piped directly to the patient's room. Less frequently, oxygen therapy is carried on in the home. Purposes for which oxygen is thus used include the following: to maintain the oxygen supply to the cells when gaseous anesthetics are used; to favor absorption of oxygen across congested lung membranes, as in pneumonia, or when fluid has invaded the air cells, as in congestive heart failure; following lung surgery, to tide the patient over the period of physiological adjustment to reduction in lung area. Oxygen is sometimes needed for resuscitation of the newborn baby and to facilitate energy production for the premature infant. In general, many of the symptoms associated with oxygen deficiency relate to impaired energy production in the cells, and a favorable response to oxygen therapy is evidenced by improved functioning of energy-producing tissues of the body.

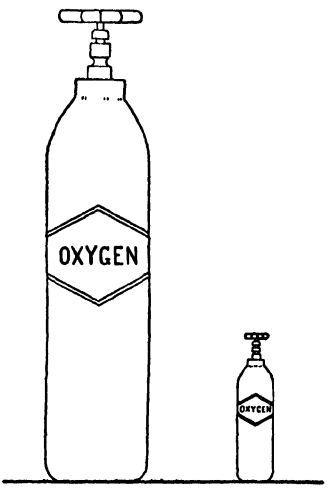


Fig. 19. Commercial supplies of oxygen.

For obtaining high temperatures. Much of the modern metal construction, as represented by automobiles, airplanes, submarines, underwater tunnels, and modern skyscrapers, calls for welding of metal parts. Welding is possible only at the high temperatures required for softening the metals (p. 23). A great deal of the com-

mercial oxygen goes into such uses. The rapid burning of almost pure oxygen with either hydrogen or acetylene provides temperatures high enough to soften metals. The oxyhydrogen torch yields temperatures as high as 2400° C, and the oxyacetylene torch can reach 3500° C. These temperatures are well above the melting points of iron, copper, platinum, and other metals used in construction.

Thus, as welding has replaced riveting and cruder methods of construction, many significant changes have taken place. Within the current century we have witnessed the passing of horse-drawn farm machinery and the man-wielded scythe with the coming of the tractor and combine. Wooden wagons and wooden ships have been replaced by automobiles, trucks, and ocean liners. The riveted locomotive with its train of heavy cars is fast being replaced by the streamlined engine with a longer train of welded lightweight metal coaches. These and many other modern developments became possible only as the required high temperatures could be attained, and the availability of commercial supplies of oxygen has been a major factor contributing to these changes.

QUESTIONS

1. Make summary statements as to the chemical behavior of oxygen (a) with other simple substances, (b) with compounds. Illustrate by reference to specific examples.

2. What, if any, reaction would you expect to take place upon heating each of the following in contact with oxygen: carbon, platinum, tin, clay, cellulose, carbon dioxide, hydrogen sulfide? Account for the difference in tendency of these substances to react with oxygen. If a reaction is to be expected, assemble the word equation for it.

3. Why is it advisable for each student to have an asbestos mat at hand for use in the chemistry laboratory?

4. Interpret the word equations given on page 61 for the related matter and energy transformations that take place when:
   a. Oxygen reacts with glucose
   b. Oxygen reacts with a fat
   c. Oxygen reacts with protein

5. Acetylene is a hydrocarbon. Why is it able to react with oxygen? Give the word equation for this reaction.

6. Name three factors that always affect the speed of chemical reactions with oxygen, telling how each functions. Illustrate by reference to specific examples.

7. Why do fluffed-up paper and oxygen burn more rapidly than a log of wood and oxygen?

8. List several common processes whereby the oxygen supply of the atmosphere is being constantly drawn upon for reactions. How is the oxygen content

of earth's atmosphere maintained? Why is it important that atmospheric oxygen is diluted with nitrogen?

9. Why is oxygen essential for living and why can it function in this respect? Where does this vitally important functioning take place? What reacting partner substances are provided? What reactions take place? What is the source of the desired energies? What happens to the energy products? To the matter products?

10. For what therapeutic uses have commercial supplies of oxygen proved to be of value?

11. What are some of the most important uses for commercial supplies of oxygen? Cite a few of the developments of modern civilization which have become possible only through the agency of commercial supplies of oxygen.

CHAPTER 7

BURNING OR COMBUSTION

Among the reactions of everyday concern are some which are known as *burning* or *combustion*. Both of these words are familiar but let us consider their chemical meaning. Thus, *burning* or *combustion refers to a chemical reaction between two substances with heat as an energy product,* and *the speed of the reaction is such that the heat product is accompanied by light.*

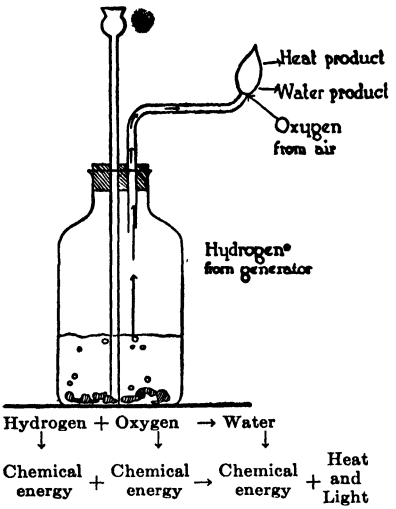


Fig. 20. Burning of hydrogen and oxygen.

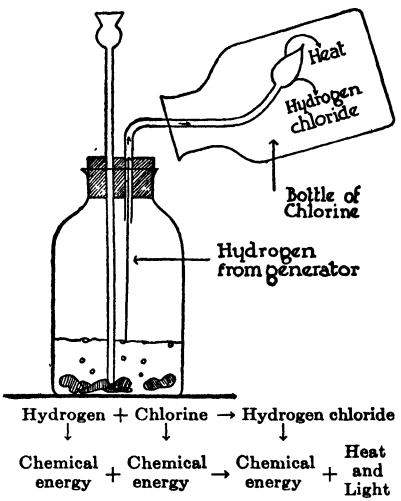


Fig. 21. Burning of hydrogen and chlorine.

* *Great caution* is necessary in the burning of hydrogen with oxygen (p. 81). Hydrogen is made from reaction between zinc and hydrochloric acid (dilute). All air must be completely displaced from the generator before the emerging jet of hydrogen is lighted.

A number of burning reactions are illustrated in the accompanying

diagrams (Figs. 20 to 23). These examples also call attention to the fact that *not all burning involves oxygen.* However, it is not surprising that many people think of oxygen as "essential to burning" since most instances of fire within the personal experience of people, in general, do involve oxygen as one of the partner substances.

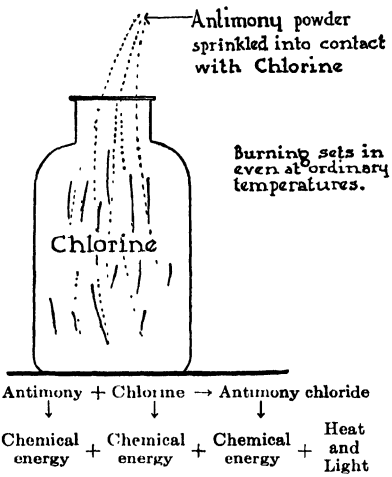


Fig. 22. Burning of antimony and chlorine.

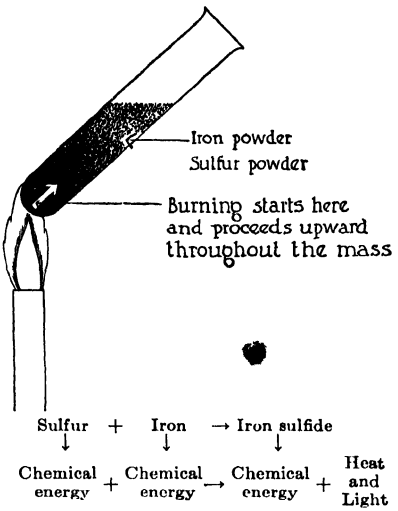


Fig. 23. Burning of iron and sulfur.

Conditions essential for burning. Before burning can occur the following conditions must be fulfilled:

1. Two substances capable of rapid reaction with heat as an energy product must be present. Usually, but not always, oxygen is one of these substances.
2. Contact must be adequate for rapid reaction to occur.
3. A temperature level at which production of heat is accompanied by production of light must be attained. This is known as *kindling temperature.*

When all of these conditions have been fulfilled, burning inevitably occurs.

BURNING WITH OXYGEN AS ONE REACTING SUBSTANCE

The continuous presence of oxygen in the atmosphere means that it is constantly available for reactions with other substances. And,

there are many substances in our surroundings that make excellent partners for reactions with oxygen. Burning, under controlled conditions, is practically indispensable to man's convenience and comfort. At the same time, the daily reports of disastrous fires, carried in our newspapers, the statistical evidence reported by insurance companies, and tragic personal experiences bear witness to the fact that many people are either ignorant or remarkably careless in relation to burning reactions. Intelligent understanding of conditions for burning with oxygen and their control is of practical importance to us all.

Suitable partners for oxygen. In general, the substances that are potential partners for oxygen in burning reactions are those composed of elements that have a marked combining tendency for the element oxygen (p. 57). The following substances are all capable of reacting with oxygen at burning speed.

In everyday concerns	*In the laboratory*
Carbon (component of coal, coke, charcoal)	Potassium
Celluloses (component of wood, paper)	Sodium
Hydrogen, Gaseous hydrocarbons, Carbon monoxide (components of illuminating gas)	Calcium
	Magnesium
	Phosphorus
Liquid hydrocarbons (components of gasoline, kerosene, fuel oils)	Sulfur
	Hydrogen
Solid hydrocarbons (components of paraffins)	Methane, Ethylene, Acetylene (hydrocarbon components of illuminating gas)
Grain alcohol	Ether
Wood alcohol	Carbon bisulfide
Fats	

Surface of contact. Contact between oxygen and suitable partner substances is obviously provided in our environment. But, it is well to keep in mind that in burning, as in all other reactions, *the greater the surface of contact between the reacting substances the greater the speed of the reaction.* And, any condition that operates to diminish surface of contact between the reactants functions to retard the reaction.

Most of the substances listed above, such as celluloses, fats, and various hydrocarbon mixtures, in the conditions under which they are usually handled in homes and institutions, have a good exposure to oxygen of air. Hence, all that is needed for burning to begin is to provide the kindling temperature. Fortunately this is usually above ordinary room temperature levels. A volatile liquid, such as ether

or gasoline, presents limited surface of contact to oxygen if kept in a tightly closed container. However, if the container is opened so that the vapor escapes freely it provides increased surface of contact with oxygen and greater fire hazard.

Kindling temperature. *Varies for different substances.* In general, the greater the tendency of the substance to react with oxygen (p. 56) the lower the kindling temperature. For example:

Given pieces of phosphorus, calcium, and carbon of identical areas of contact with dilute oxygen of the atmosphere, the kindling temperature of phosphorus and oxygen will be slightly above ordinary, of calcium and oxygen higher, and of carbon and oxygen considerably higher.

Varies with surface of contact. But the more important factor in determining kindling temperature is the surface of contact between oxygen and its partner substance. The less the area of contact the higher their kindling temperature, and the greater the area of contact between them the lower their kindling temperature. Thus:

1. Celluloses of the *same wood and the dilute oxygen of air* can have a wide range of kindling temperatures:

If compact, as in a log of wood.....kindling temperature is high.
If in kindling, loosely piled.....kindling temperature is lower.
If in loose shavings.....kindling temperature is still lower.

2. Oxygen with partner substances which are gaseous or volatile liquids have *low* kindling temperatures because of their tendencies to diffuse and thus, automatically, to get into large areas of contact. Thus:

Kerosene with dilute oxygen.....a low kindling temperature.
Gasoline with dilute oxygen.....a lower kindling temperature.
Ether with dilute oxygen.....a very low kindling temperature.
Illuminating gas with dilute oxygen.....a very low kindling temperature.

When the kindling temperature is so low that it can be attained by such means as a lighted match, a "live coal," or a smoldering cigarette, a very real fire hazard exists. *With increasingly higher concentrations of oxygen, kindling temperatures become increasingly lower.* This explains the greater fire hazards encountered in and around oxygen tents than in the dilute oxygen of normal air.

Control of burning. *Control of speed of burning* involves control of surface of contact between partner substances and oxygen. *Extinguishing fire* necessitates one of two procedures, either cutting down the contact between oxygen and the partner substance or lowering

the temperature of the burning material below the kindling temperature of the reacting parties.

Accordingly, a woolen blanket, a coat, a rug, a sheet of asbestos, or a shovelful of sand thrown over the burning masses, or a stream of nonburnable gas directed over the same are all effective in putting out fires. Their effectiveness lies in that layers of either poorly burnable or nonburnable substances are injected between oxygen and the burning partner substances. On the other hand, a continuous play of a stream of water will serve eventually to lower the temperature of the substances concerned below their kindling temperature. The same end may be accomplished by the chill produced by suddenly expanding gases released from a fire extinguisher.[1]

Fire prevention. Unfortunately, many people do not make it a habit to give careful, conscious thought to fire prevention. If they did, nine tenths or more of undesired fires would not take place. There are just *three* requirements for burning with oxygen; given all three, burning will set in whether desired or not, but *if only one of these requirements is absent there can be no burning.*

The first two requirements (oxygen with partner substance in contact with each other) are frequently provided: wood shavings, excelsior, or fluffy wastepaper in contact with oxygen; flimsy cotton draperies or clothing in contact with oxygen; dry leaves or grass in like contact. Kindling temperatures in these instances are low; therefore any means whereby these temperatures might be attained must be carefully avoided.

The first two requirements for burning are likewise obtained in an operating room whenever ether and oxygen are in contact or, more hazardous still, whenever ethylene and oxygen are in contact. Consequently, all conditions that might provide the kindling temperature must be guarded against. There must be no defective electrical switches or wiring, and sparks arising from static electricity must be carefully avoided. The same sort of hazard attends the cleansing of gloves or garments with volatile, burnable liquid substances.

The selection of fabrics for clothing and draperies also merits consideration. Some fabrics are readily flammable while others melt on heating and burn more slowly. In 1953, a law known as the *Flammable Fabrics Act* was passed by Congress. It is designed to protect the consumer in relation to wearing apparel and fabrics designed for this use by prohibiting the introduction or movement of highly flammable fabrics in interstate commerce. The accepted test, developed by the American Association of Textile Chemists and Colorists, defines a *highly flammable fabric* as one "that burns in less than four

[1] For a discussion of various types of fire extinguishers see: *Put Out That Fire,* National Fire Protection Association, Boston, Mass., 1950.

seconds when a flame the size of a match is applied for one second to a two-by-six inch swatch."[2] Although the protection thus provided to the consumer is highly desirable, it does not mean that materials passing this test can be regarded as nonburnable. But, it does remove some very hazardous material from the market.

Spontaneous combustion. Spontaneous combustion is another loosely and vaguely used expression. Frequently, when people are baffled in attempts to find a "why" for an unexpected fire outbreak they shake their heads and say mysteriously "spontaneous combustion," with the implication that in this particular fire the laws of nature have been defied, which, undoubtedly, is not the case. The offending kindling temperature has been carelessly or unwittingly provided by one or another means.

For the chemist, spontaneous combustion has a very specific significance. Sometimes oxygen and the partner substance "build up" to their kindling temperature through the accumulation of heat from their slow reaction. The instant kindling temperature level is obtained through this means, the material bursts into flames. Burnings with kindling temperatures of such origin are properly called spontaneous combustion. Here is a typical example.

A fire breaks out suddenly in a closet in which the painter has left a bunch of cotton waste carrying linseed oil which he carelessly forgets about so that it lies there for days unnoticed. Now, as it happens, *linseed oil and oxygen* react slowly at ordinary temperatures.

$$\begin{array}{ccccccccc} \text{Linseed oil} & + & \text{Oxygen} & \longrightarrow & \text{Carbon dioxide} & + & \text{Water} & & \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \\ \text{Chemical energy} & + & \text{Chemical energy} & \longrightarrow & \text{Chemical energy} & + & \text{Chemical energy} & + & \text{Heat} \end{array}$$

The *heat product* is made slowly, but, since cotton waste is a poor conductor of heat and since there is little air circulation in the closet to carry away the heat as made, it accumulates in the waste. The temperature of the waste mounts higher and higher until the linseed oil and oxygen attain their kindling temperature, and at that instant they begin to react at burning speed.

QUESTIONS

1. What three conditions must be met in order that any burning may take place? What three conditions for burning *with oxygen* must be met?

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[2] Corrigon, Faith: "Fabric Safety Act Being Criticized," *The New York Times*, Mar. 22, 1954.

2. Loose papers burn readily; books are relatively difficult to burn. Account for this difference. Kerosene and gasoline are both mixtures of liquid hydrocarbons. Explain why gasoline constitutes a greater fire hazard than kerosene.

3. When material is described as highly combustible, what should be meant? Illustrate. When a building is claimed to be of "fireproof" construction, what is meant? What conditions should be met (as far as possible) in the construction of such a building?

4. What is the hazard of cleaning gloves with gasoline?

5. Explain the function of bellows in speeding up burning of a wood fire.

6. What two conditions always encountered in the woods in a dry season are favorable to outbreak of forest fires? What one condition remains to be provided? List habits for campers that will safeguard against fire.

7. Sometimes when frying bacon a sudden burst of flame appears about the pan. Account for this happening. How would you bring such a fire under control? Explain.

8. The concentration of oxygen within an oxygen tent is frequently maintained at 50 to 90 per cent, as compared with 20 per cent in ordinary air.

   a. What effect would this have on the kindling point of oxygen with burnable substances within the tent? What burnable substances are likely to be present at all times? Occasionally?
   b. How would this affect the speed of burning should a fire accidentally occur, as compared with the speed of burning in common air? Why?
   c. What precautions in particular, therefore, should be strictly observed by all persons in or about an oxygen tent?

9. Smoking in bed is a dangerous habit. Explain in detail.

10. Explain the nature of the protection afforded the consumer by the Flammable Fabrics Act of 1953.

11. When a fire is due to "spontaneous combustion" what may have occurred?

12. Suppose you encounter burning in a wastepaper basket; what would you do to extinguish the fire? Consider two possible procedures and explain how each would function.

13. Make a list of substances and materials with which you come in frequent contact and which constitute potential fire hazards. Think over your habits in relation to these contacts and consider whether or not you are observing all necessary precautions for fire prevention.

CHAPTER 8

CHEMICAL CHANGES INVOLVE ENERGY TRANSFORMATIONS

ENERGY

Every chemical change involves both a matter and an energy transformation. Indeed, the concept of energy transformation is quite as fundamental to an understanding of chemical change as is that of making new substances. The idea of energy transformations accompanying chemical change was introduced in the study of oxygen. It is proposed now to carry this study further.

What is energy? No one really knows what energy is. People in general have a limited experience with certain varieties of energy such as heat, light, and electricity and have learned how to put them to use. Scientists have gathered an astounding amount of knowledge about all known varieties of energy. But, what energy *is* belongs still among the great mysteries of nature.

Some varieties of energy. Heat is a familiar energy manifestation. By means of specific sensory end organs, man can become aware of higher or lower temperature levels, hence the presence of more or less heat collected by the matter involved: the air of the room, water, or other heat-collecting material. The phenomenon of *light* energy is familiar within limits. Humans are equipped to sense the presence of such light energy as is responsible for colors from red to violet, but they are blind to ultraviolet and infrared light. *Kinetic energy*, or that energy which is responsible for the motion of matter, one can be made aware of in various ways: through direct impact with moving bodies; through the eyes, because of the change of position of a moving mass; or through the ears, because of the resulting

swish of the air in the wake of the rapidly moving object. On the other hand, humans are utterly blind to *electricity*. Electricity can be transformed into heat which one can feel or into light which one can see, but then it has ceased to be electricity and one must reason one's way back to it as the precursor of the heat or the light. But, one may say: "I do certainly feel electricity when I put moist fingers on two electric terminals"; however, what one really feels is the kinetic energy of quivering muscles that has been made from the electricity.

Measuring possibilities. ***For heat.*** Inasmuch as energy can be sensed only in association with matter, it follows that it can be measured only in terms of a definite measurable effect produced in the matter affected. Hence, adopted measuring units for heat, called *small calorie or gram-calorie, large calorie or kilogram-calorie,* and *British thermal unit relate to the quantities of heat that are required to produce temperature changes with water as the collecting medium.* Thus:

One ***small calorie*** (cal), or ***gram-calorie,*** is the quantity of heat which is sufficient to raise the temperature of 1 gm of water through 1° C.

One ***large calorie*** (Cal), or ***kilogram-calorie,*** is the quantity of heat which will raise the temperature of 1 kg of water through 1° C.

One ***British thermal unit*** (Btu) is the quantity of heat which will raise 1 lb of water through 1° F.

For example, 20 Cal of heat would be enough heat to increase the temperature of

1 kg of water through 20° C
5 kg of water through 4° C
10 kg of water through 2° C

For kinetic energy. There is more to the basis upon which a unit for measuring kinetic energy has been obtained than it is advisable to enter into in this study. Therefore, we shall use a unit for measuring this energy, called a *foot-pound,*[1] that has been established with reference to a related energy phenomenon. For our purposes, then, *a foot-pound shall mean the quantity of kinetic energy that is required to lift 1 lb of matter through 1 ft of distance.* Which would mean that:

[1] This really is a unit for measuring what the physicist calls *work.* The related kinetic energy unit is a foot-poundal, the basis for which involves considerations which it is not desirable to enter into in this study. But, since there is an exact relationship between this more involved foot-poundal kinetic energy unit and the foot-pound work unit (1 foot-pound = 32.174 foot-poundals), there is some justification for looking upon the more easily comprehended foot-pound as a kinetic energy unit equivalent.

1. For climbing a flight of stairs 20 ft high a person weighing 120 lb and one weighing 140 lb must make, within the cells of the muscles concerned, the following respective quantities of kinetic energy:

120 (lb) × 20 (ft) or 2400 foot-pounds of kinetic energy
140 (lb) × 20 (ft) or 2800 foot-pounds of kinetic energy

2. For carrying an automobile and load weighing 2500 lb up a hill 200 ft high from base to top, 2500 (lb) × 200 (ft) or 500,000 foot-pounds of kinetic energy must be made. This kinetic energy is made within the cylinders of the automobile from chemical energy provided within the initial substances, oxygen and hydrocarbons, parties to the reaction (pp. 80 to 81).

For measuring electricity. Electricity is made, distributed, and used on a *kilowatt-hour* measuring basis. The basis on which this measuring unit is established, of course, is known to students of electricity, but, for our purposes suffice it to say that the *kilowatt-hour of electricity* is based on definite measurable effects produced by this energy in relation to matter.

Energy transformations. ***Various possibilities.*** That some varieties of energy are easily transformed into other energies is a well-known fact. The possibility of the transformation of

$$\text{Kinetic energy} \xrightarrow{\text{into}} \text{Heat}$$

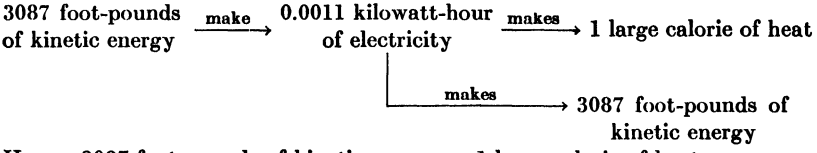
is exemplified in the familiar making of heat from the kinetic energy of parts of machinery moving against each other. And, of *vital importance* is the transformation of the kinetic energy, made within muscle cells for the motion of body parts, into the heat which keeps the body warm (pp. 60 to 62). Also of importance are the transformations of

$$\text{Kinetic energy} \xrightarrow{\text{into}} \text{Electricity}$$
$$\text{Electricity} \xrightarrow{\text{into}} \text{Kinetic energy}$$
$$\text{Electricity} \xrightarrow{\text{into}} \text{Heat}$$
$$\text{Electricity} \xrightarrow{\text{into}} \text{Light}$$

Most electricity of commerce is made from the kinetic energy of waterfalls or of expanding steam. And, in turn, large quantities of this electricity are conducted into homes, stores, manufacturing plants, and other places for transformation, as desired, into heat or into light or into kinetic energy.

Energy transformations are quantitative. A definite number

of foot-pounds of kinetic energy makes a definite number of kilowatt-hours of electricity or a definite number of large calories of heat, and vice versa. Here are actual quantitative transformation values that have been discovered as the result of numerous painstaking laboratory measurements.



Hence, 3087 foot-pounds of kinetic energy $\rightleftarrows$ 1 large calorie of heat.

Consequently, making electricity can be placed on a very definite quantitative basis because the manufacturer can figure exactly how much electricity he can make from a given quantity of kinetic energy. Likewise, he can determine with great exactness how much heat, light, or kinetic energy the consumer can depend upon obtaining from every kilowatt-hour of electricity.

Units are interchangeable. Moreover, since energy transformations are quantitatively exact, it follows that it should be possible to measure any one variety of energy in terms of units established primarily for measuring other energies. Nutritionists usually measure all energies that the living animal must make in terms of the large or kilogram-calorie, even though kinetic energy constitutes the major portion of animal energy. Thus, a requirement of 2500 large calories of energy per day would be a measure of the various energies that the animal must make within its cells during a 24-hour period.

Fact of conservation of energy. These measured relationships in regard to energy transformations have led to the discovery of one of the fundamental facts of physical science; namely, that *the disappearance of a definite quantity of one variety of energy is accompanied by making a corresponding quantity of another variety of energy, or energies, inclusively.*

CHEMICAL ENERGY

Hidden within substances. Chemical energy is a variety of energy which all substances have by virtue of their composition. It is hidden, so far as human ability to sense it is concerned, and its existence becomes apparent only as energy changes take place in

the course of chemical reactions. It is believed that *every substance, gram for gram, possesses a fixed quantity of chemical energy* and that this energy is in part responsible for the nature of the substance. Oxygen, for example, is the substance that it is, with all its distinctive properties, both because it is built of oxygen element and because, gram for gram, it holds within its keeping a definite quantity of chemical energy. This would mean that if the element oxygen, within oxygen substance, were forced to become associated with a greater quantity of chemical energy—made from some other energy—then oxygen substance would have to go out of existence to make a substance possessing more chemical energy. Thus, when a charge of electricity is passed through an atmosphere of oxygen, some of the *electricity is transformed into chemical energy.* As a result, oxygen substance goes out of existence as ozone is made:

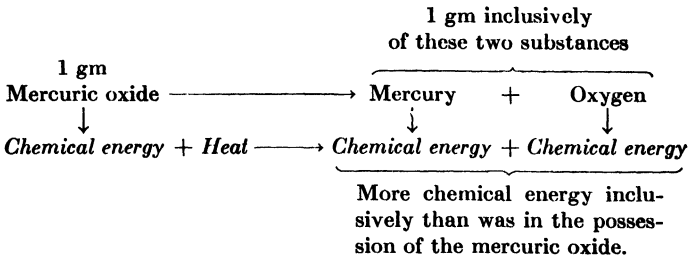
1 gm Oxygen	⟶	1 gm Ozone
↓ possessing a definite quantity of Chemical energy	+ Electricity ⟶	↓ possessing a larger quantity of Chemical energy

Again, the *substances* carbon, graphite, and diamond, gram for gram, are built of the same element, carbon; nonetheless, they are different substances, as is evidenced by their different properties. What, then, is responsible for making them different substances? The answer lies, in part, in the fact that, gram for gram, they possess different quantities of chemical energy.

Mercuric oxide is the substance that it is not only because it is composed of mercury and oxygen elements in a definite weight proportion but because, gram for gram, this substance holds within its keeping a definite quantity of chemical energy. Therefore, if more chemical energy should become associated with the elements concerned, the mercuric oxide would of necessity go out of existence to make substances in possession of a larger supply of this energy. This is what happens when mercuric oxide is heated. Some[2] of the *heat* used *is transformed into chemical energy;* consequently, the mercuric oxide decomposes to make the substances mercury and oxygen which

[2] A portion of the heat used simply raises the temperature of the substance; this portion, therefore, is still heat.

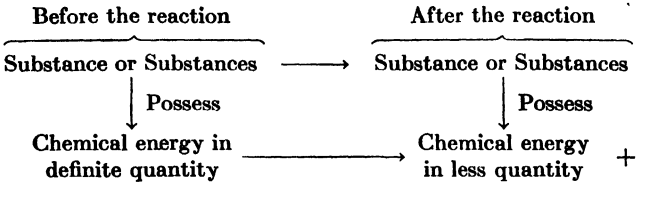
between them possess more chemical energy than did the mercuric oxide.



Subject to transformation. *Chemical energy, like other energies, is subject to transformations.* In fact, because chemical energy cannot be detected directly, evidence that such energy exists must be gathered through observation of energy transformations. Thus, to account for the appearance of heat and light in the course of a chemical reaction, one must reason back to the previous existence of energy in the reacting substances. And, because *all chemical energy is in the keeping of substances*, it follows that *any energy transformation that involves chemical energy must be accompanied by a matter transformation.* This implies that such energy transformations occur when substances go out of existence to make new substances that require either more or less chemical energy.

It should also be kept in mind that not all of the chemical energy within the substance is available for transformation; some remains as chemical energy within the substances made during the reaction.

Chemical energy transformed into other energies. When, during a chemical reaction, chemical energy undergoes a transformation into some other variety of energy, it is because the resulting substances contain less chemical energy than the previously existing ones.



Whether the energy product is heat, kinetic energy, light, or elec-

tricity depends in some instances upon the reacting substances. In other instances the energy product depends upon conditions under which the reactions take place.

Chemical energy into heat. We have already met a number of reactions (pp. 67 to 72) during which part of the chemical energy in the beginning substance or substances is transformed into heat. Here is another example.

When a jet of hydrogen is brought into contact with oxygen *a little at a time* (p. 67) and kindling temperature is obtained, as these two substances react to make water, part of the *chemical energy* within the oxygen and within the hydrogen *is transformed into heat.* The remaining chemical energy supplies the water. These related transformations, matter and energy, are represented briefly thus:

$$\begin{array}{ccccc} \text{Hydrogen} + \text{Oxygen} & & \longrightarrow & & \text{Water} \\ \downarrow & \downarrow & & & \downarrow \\ \text{Chemical energy} + \text{Chemical energy} & & \longrightarrow & \text{Heat} + & \text{Chemical energy} \end{array}$$

Chemical energy into kinetic energy. Under certain conditions nature favors the transformation of chemical energy into kinetic energy. For instance, *within muscle cells, whenever kinetic energy is required for the motion of body parts, nature makes it from chemical energy originally in the keeping of oxygen and glucose* or other energy-rich substances made in the cells.

Outside of the body, the transformation of *chemical energy into* kinetic energy occurs under certain definite conditions. In general, such transformations occur *when large quantities of gaseous products are made, all in an instant, within a confined space.* Kinetic energy is essential for the expansion of the gaseous products, and, as they force their way out against the resistance offered by the container, we become aware of the existence of this force. In certain instances, as in blasting rocks and running automobiles, man has learned to put this variety of energy transformations to his own uses. Thus:

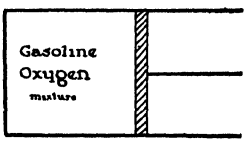
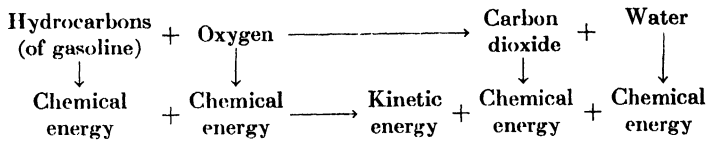


Fig. 24. Kinetic energy is the energy product.

When a spark is admitted to the *mixture* of gasoline vapor and oxygen within the cylinders of the automobile, *reaction takes place instantaneously throughout the mixture.* This means that a maximum quantity of two gaseous products, carbon dioxide and water, are made in a confined space, all in a flash of time. Along with these gases a supply of kinetic energy must also be made for their

needed expansions, and nature makes this kinetic energy from a portion of the chemical energy within the beginning oxygen substances.



And in this instance the expanding gases set into motion the piston head and the machinery connected therewith (Fig. 24).

Other instances of such energy transformations can be encountered in the home, sometimes with disastrous consequences. Many a wrecked stove has resulted from such a happening. These are the usual conditions: In the oven illuminating gas, which was admitted through a leaking or carelessly opened gas cock, mixes with oxygen of the air which is already in the enclosure. Then, the lighted match, brought for the purpose of "lighting the oven," provides the kindling temperature. All in an instant the explosive reaction occurs!

The same sort of hazard accompanies the administration of gaseous hydrocarbon anesthetics, unavoidably mixed with oxygen, in the operating room. A spark occurring at any point where the gas mixture is in just the right proportions for instantaneous reaction can result in explosive reaction. Workers in the operating room who appreciate the nature of the hazard also appreciate the importance of the meticulous precautions maintained in this area to safeguard against such accidents.[3]

Explosive reactions. Because explosive reactions do not just happen but occur only when the specific conditions for such reactions have been established, intelligent knowledge of these conditions can be used in laboratories, homes, and elsewhere to safeguard against such reactions. In general, these are the essential conditions:

1. Substances that are capable of rapid reaction with the production of an energy product.
2. Concentrations and distribution of reactants to give the great surface of contact that favors fast reaction. (Because of the tendency of gaseous substances to diffuse, mixtures of gases are especially likely to provide this condition. Gases with finely divided solids can likewise give large surface of contact.)
3. A gaseous product produced within a confined space.
4. A source of ignition.

[3] Guest, P. G.; Sikers, V. W.; and Lewis, Bernard: *Static Electricity in Hospital Operating Suites: Direct and Related Hazards and Pertinent Remedies.* Bulletin 520, Bureau of Mines, U.S. Govt. Printing Office, Washington, D. C., 1953.

Unless all of these conditions are fulfilled, the reaction will not produce an explosion.

Chemical energy into electricity. There are certain reactions during which nature can transform chemical energy into electricity. Here is an example.

When strips of zinc and copper are put into dilute sulfuric acid and connected by a conducting wire, electricity is made from chemical energy in one or both of the beginning substances (Fig. 25). The complete detail in regard to this phenomenon involves complications which, for our purpose, it is quite unnecessary to consider. The matter and energy transformations concerned are essentially as indicated in the following word equations.

$$\begin{array}{ccccccccc} \text{Zinc} & + & \text{Hydrogen sulfate} & \longrightarrow & \text{Hydrogen} & + & \text{Zinc sulfate} \\ \downarrow & & \downarrow & & \downarrow & & \downarrow \\ \text{Chemical energy} & + & \text{Chemical energy} & \longrightarrow \text{Electricity} + & \text{Chemical energy} & + & \text{Chemical energy} \end{array}$$

All battery-made electricity is made in this manner. It follows that the battery is "dead" when the beginning substances have been used up and only the products remain in the cell—new substances with less chemical energy than the original substances held.

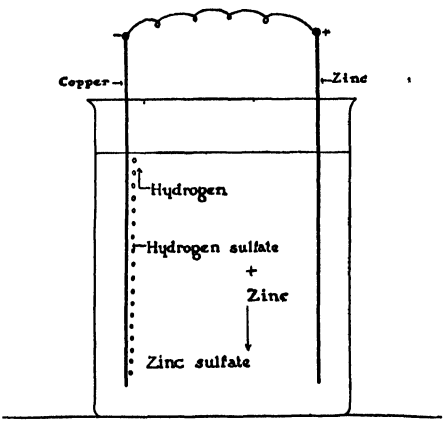
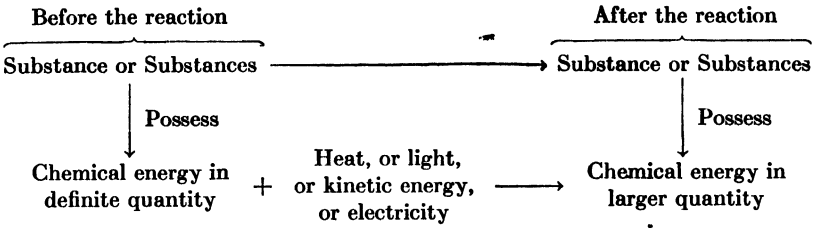


Fig. 25. Chemical energy → electricity.

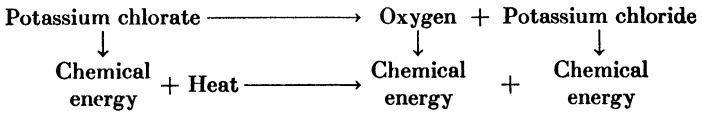
In summary. When the beginning substances contain more chemical energy than is required by the products of the reaction, chemical energy must be transformed into other varieties of energy and *an energy product appears.* Such changes are known as *exothermic reactions.*

Other energies transformed into chemical energy. There are also many reactions during which other varieties of energy—heat, light, or electricity—are transformed into chemical energy. Obviously, this must be the case when the products of the reaction are substances that possess more chemical energy than that which is provided in the beginning substances. Thus:



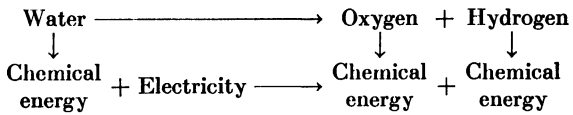
Heat transformed into chemical energy. There are numerous reactions in which nature seems to prefer to use heat for transformation into needed chemical energy. For example:

Potassium chlorate possesses *less* chemical energy than that which is essential to the oxygen and potassium chloride which can be made from it. Therefore, if this reaction is to take place (p. 42), *chemical energy must be made from some other variety of energy*, and, in this instance, nature favors *heat* for this purpose.

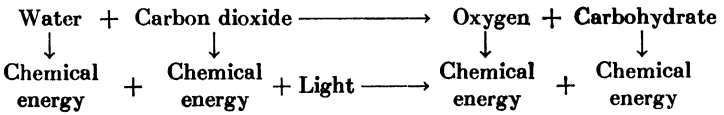


The decomposition of mercuric oxide (p. 41) provides another example of the transformation of heat into chemical energy.

Electricity into chemical energy. Frequently, electricity lends itself for transformation into the required extra chemical energy for the substances made during a reaction. Examples of such reactions are the making of ozone from oxygen (p. 78) and the decomposition of water (p. 15):



Light into chemical energy. Nature sometimes transforms light into chemical energy. One of the most important reactions of all nature, the so-called *photosynthesis* reaction, is of this variety. During this reaction, sunlight is transformed into the chemical energy which is required to make oxygen and plant carbohydrate over and above the quantity of chemical energy supplied in the water and carbon dioxide.



In this way *great quantities of energy from the sun are captured on earth and imprisoned as transformable chemical energy within oxygen and the associated carbohydrates.* This energy then becomes available for retransformation: (1) into the various energies needed by living cells as oxygen reacts with partner substances provided for this purpose, or (2) into heat and light or into kinetic energy when oxygen reacts with cellulose or other suitable substances in the environment.

In summary. In contrast to the exothermic reaction, there is no energy product from these reactions. Instead, a continuous supply of external energy must be provided for absorption into the new substances and transformation into chemical energy. These are known as *endothermic reactions.*

MEASUREMENT OF CHEMICAL ENERGY

There are three facts of primary importance in regard to the measurement of chemical energy. (1) It cannot be measured directly but must be transformed into heat or some energy which can be measured. And, quite logically, the quantity of heat or kinetic energy obtained becomes a measure of that which *was* chemical energy before the transformation took place. (2) Even then only a portion of the chemical energy of the beginning substance or substances is available for measurement because some must remain chemical energy within the resulting substances. (3) In many instances it is not possible to arrive at a measurement of the available chemical energy in one substance all by itself because the substance may yield up part of its chemical energy for transformation only in reaction with another substance. In this case one would be finding a measure for the *available chemical energy of the two substances* inclusively.

One method that is used for measuring the available chemical energy of a substance, or substances inclusively, applies when *heat* can be obtained as the energy product. The essence of the method[4] is as follows: Weighed quantities of the substance or substances concerned are made to react in a closed container which is buried in water (Fig. 26). This portion of the apparatus is, in turn, enclosed in a double-walled, heat-insulating jacket. The heat product is thereby collected in the water and can be measured, provided the

[4] Details of procedure can be obtained from any comprehensive text on nutrition.

weight quantity of the water has been previously noted and the temperature of the water was taken before the reaction began and is taken again when it is complete. This heat becomes a measure (1) of the energy product obtainable from the reaction of given quantities

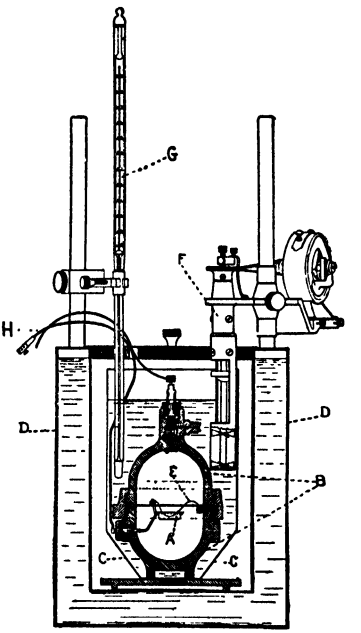


Fig. 26. Diagram of bomb calorimeter with bomb in position.

A. Platinum dish holding food sample
B. Bomb filled with pure oxygen enclosing food sample
C. Can holding water, in which bomb is submerged
D. Outer double-walled insulating jacket
E. Fuse which is ignited by an electric current
F. Motor-driven water stirrer
G. Thermometer
H. Electric wires to send current through fuse

(Rose, Mary S.: *Foundations of Nutrition.* Courtesy of the author and the Emerson Apparatus Company, Boston, Mass. By permission of The Macmillan Company, publishers.)

of the beginning substances; hence, (2) of the available chemical energy previously in the possession of these substances. For example:

It has been determined, through the agency of such a piece of apparatus, that, when *1 gm of carbon and 2.66 gm of oxygen* react to make carbon dioxide, enough heat is made to raise the temperature of 2 kg of water through 3.93° C, or 7.86 large calories. And since this is the quantity of energy product always made from this reaction between these quantities of these substances, 7.86 large calories becomes a measure of the available chemical energy possessed inclusively by 1 gm of carbon and 2.66 gm of oxygen.

Thus, in general, the quantity of energy product obtained becomes a measure of the available chemical energy previously possessed by the beginning substance or substances.

Experimental findings as to the quantities of available chemical energy possessed by oxygen and various partner substances are as follows.

1 gm of glucose and.....	1.06	gm of oxygen	3.75	large calories
1 gm of methyl alcohol and.....	1.5	gm of oxygen	5.33	large calories
1 gm of ethyl alcohol and.....	2.085	gm of oxygen	7 11	large calories
1 gm of carbon and	2.66	gm of oxygen	7 865	large calories
1 gm of stearin (a fat) and.....	2 9	gm of oxygen	9.45	large calories
1 gm of methane and.....	3.9	gm of oxygen	13.14	large calories
1 gm of hydrogen and.....	7.93	gm of oxygen	28.68	large calories

Indirect measurement of energy products. There are also indirect methods for measuring energy production. A well-known example of this is the *basal metabolism test.* The conditions for this test are that the individual shall be rested and relaxed, in a prone position, and at least 14 hours shall have elapsed after the intake of food. The temperature of the subject should be normal and the room in which the test is made at approximately 20° C (68° F). *The measurement is made in terms of the oxygen consumed* over the 6- to 10-minute period of the test. From this measurement, it is possible to compute the energy production for a 24-hour period in terms of kilogram-calories. The information thus obtained can be compared with that of other individuals tested under the same conditions. The principle on which this test is based is that, under the conditions specified, the rate of energy production within the body cells is directly related to the quantity of oxygen used for oxidation of glucose and fats during the test period. (See data, p. 61.) Studies made with many individuals show a remarkable consistency in the proportion of glucose and fat oxidized under these standard conditions; hence, the calorie yield per liter of oxygen used is relatively consistent.

Comparable methods have been developed for measuring energy production during periods of activity.

QUESTIONS

1. Cite situations within your own experience where one variety of energy is transformed into another variety of energy.
2. How much is a small calorie of heat? A large calorie? Which of these units is used by the nutritionist?
3. How much electricity must be used to raise the temperature of 1 kg of water from 20° C to 100° C?
4. How much oxygen must be used for reaction with glucose in the cells to

provide the energy required to carry a person weighing 100 lb up a flight of stairs 15 ft high? How much glucose will be used?

5. Why must there be an energy product when the celluloses of wood react with oxygen? What is the source of this energy product? Represent, by word equations, the related matter and energy transformations involved.

6. Why does the decomposition of mercuric oxide cease when heat is withdrawn?

7. What becomes of the electricity used to bring about the decomposition of water? Why was an external source of energy required for this reaction?

8. When "lighting" a gas oven it is always advisable to have the oven door open. What is the hazard involved? Explain. How does this precaution safeguard the individual?

9. A workman, after scraping a wooden floor preparatory to refinishing, disposed of the fine dust by dumping it loosely into an incinerator. An explosive reaction promptly ensued. Show how all conditions essential for an explosive reaction were fulfilled in this situation. What precaution would have prevented the explosion? Explain.

10. What is the principle on which the basal metabolism test operates? Show how variations from the standard conditions might invalidate the test.

CHAPTER 9

CHEMICAL MEASURINGS AND RELATED THEORIES

Early in the study of chemistry scientists became interested in the measurement of substances as they become involved in chemical reactions and in the weight relations of elements as they occur in combination within substances. We have already cited the findings of Lavoisier recorded in the Law of Conservation of Mass (p. 15) and the generalization known as the Law of Definite Weight Proportions (p. 28). These and other quantitative studies have made major contributions to an understanding of substances and their behavior not only from the factual standpoint but also in the development of theories fundamental to the science.

It is not possible in this brief text to enter into the experimental studies through which chemists arrived at these significant findings, but we can be introduced to some of the results of their investigations and learn how to use them in our own study.

SUBSTANCES AND CHEMICAL REACTIONS

Unit-reacting weights for substances. Substances do not participate in chemical reactions in a haphazard fashion but follow definite quantitative patterns. Quantitative studies reveal that *there are significant weights, one for each substance, which function as units for measuring quantities of substances as they are involved in chemical reactions.* Examples of these weights are recorded in the accompanying table.

Aluminum	26.98	Mercury	200.61
Aluminum oxide	101 96	Mercuric oxide	216.61
Ammonia	17 032	Nitrogen	28.016
Carbon dioxide	44 011	Oxygen	32.000
Chlorine	70.914	Potassium chlorate	122.557
Hydrogen	2.016	Potassium chloride	74 557
Hydrogen chloride	36.465	Water	18 016
Methane	16.043	Wood alcohol	32.043

These relative weights, which are based on a unit of 32 for the substance oxygen, are known as the *molecular weights* of the substances.

Molecular weights and their functioning. From the functional standpoint, the term unit-reacting weight is a significant designation for the molecular weight of a substance because it is a fact that *substances enter into and are made from chemical reactions in whole-number ratios of their respective molecular weights.* Thus:

$$\underset{2 \times 122.557}{\text{Potassium chlorate}} \longrightarrow \underset{3 \times 32}{\text{Oxygen}} + \underset{2 \times 74.557}{\text{Potassium chloride}}$$

Interpreted. *In general terms,* 2 × 122.557 parts by weight of potassium chlorate decompose to make 3 × 32 parts by weight of oxygen and 2 × 74.557 parts by weight of potassium chloride.

More specifically, if measured in grams, 2 × 122.557 gm of potassium chlorate decompose to make 3 × 32 gm of oxygen and 2 × 74.557 gm of potassium chloride.

Moreover, using molecular weights as the units for measuring, any given substance becomes involved in all reactions to which it is a party in whole-number multiples of its specific molecular weight. Quantitative information relating to specific reactions, as recorded below, illustrates the functioning of molecular weights for the substances concerned.

$$\underset{2 \times 216.61}{\text{Mercuric oxide}} \longrightarrow \underset{1 \times 32}{\text{Oxygen}} + \underset{2 \times 200.61}{\text{Mercury}}$$

$$\underset{1 \times 16.043}{\text{Methane}} + \underset{2 \times 32}{\text{Oxygen}} \longrightarrow \underset{2 \times 18.016}{\text{Water}} + \underset{1 \times 44.011}{\text{Carbon dioxide}}$$

$$\underset{2 \times 2.016}{\text{Hydrogen}} + \underset{1 \times 32}{\text{Oxygen}} \longrightarrow \underset{2 \times 18.016}{\text{Water}}$$

$$\underset{2 \times 26.98}{\text{Aluminum}} + \underset{3 \times 18.016}{\text{Water}} \longrightarrow \underset{3 \times 2.016}{\text{Hydrogen}} + \underset{1 \times 101.96}{\text{Aluminum oxide}}$$

When the molecular weights of the substances involved are known, and the whole-number molecular weight ratio for the reaction is also known, the quantitative story of the reaction becomes apparent.

Because molecular weights are relative values, they can be used (1) in general terms, to indicate simply the weight proportions in which the various substances are involved or, (2) by introducing a specific weighing unit to express concrete quantities of the substances, such as gram-molecular weights, ounce-molecular weights, or, indeed, any appropriate weighing unit.[1] *The molecular weight of a substance is a very real, experimentally determined, value that serves as a measuring unit for the substance in chemical reactions.*

The source of molecular weights. Molecular weights of many substances are the actual or calculated weights in grams of 22.4 liters of the substances in the gaseous state at 0° C and under a pressure equal to that exerted by a column of mercury 760 mm high. For example, the weight of 22.4 liters of oxygen under these conditions is 32 gm, which makes 32 the molecular weight of this substance. Molecular weights of substances which are not gaseous under these conditions are determined by other means but always in direct reference to the molecular weight of oxygen with a value of 32.

The mole as a unit. The weighing unit most frequently used by the chemist is the gram-molecular weight of the substance, and a special term has come into use to designate this unit, namely, *mole.* Thus, a mole of oxygen implies 32 gm of oxygen substance. A mole of carbon dioxide weighs 44.011 gm.

The millimole. For some uses the mole is too large a unit for appropriate use, for example, in some of the measurings used by the physiological chemist. Consequently, the millimole has come into use, and it has the usual significance of one-thousandth part of a mole. Thus, a millimole of carbon dioxide weighs 0.044011 gm or 44.011 mg.

Molecules, the ultimate particles of substances. Thoughtful study of these unit-reacting weight relations naturally raises questions in the mind of the student. Why does each substance have its own particular weight unit when it enters into chemical reactions? Why is the weight relation between substances involved in chemical reactions always a whole-number ratio of these specific molecular

[1] Metric units are preferred, and generally used, in scientific work. They are much simpler to use than the English units in common use. Also, they have international acceptance among scientists.

weight values? The real answer to these questions must be that no man knows. However, a significant theory has been developed and tested experimentally until chemists feel quite certain that the assumptions of this theory lie close to reality.

First assumption. *Substances are made up of discrete, ultraminute particles known as molecules.* These particles are too minute to be visible to the naked eye or even through the highest powered microscope.

Second assumption. Molecules of the same substance are alike as to composition, structure, and chemical behavior, but molecules of different substances differ significantly from one another. Moreover, molecules of the same substance, as found in nature, *show the same average weight regardless of source.*[2]

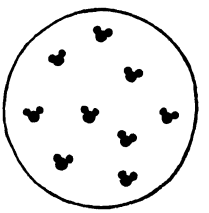


Fig. 27. A drop of *water* made up of myriads of *molecules of water.*

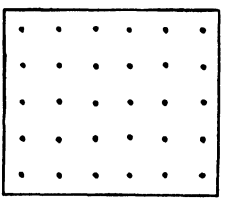


Fig. 28. A speck of *carbon* composed of millions of *molecules of carbon.*

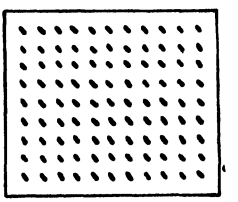


Fig. 29. A small portion of *hydrogen* composed of millions of *molecules of hydrogen.*

According to these assumptions, the smallest drop of water is an aggregate of millions of water molecules all alike in composition, structure, and chemical behavior (Fig. 27). The least visible speck of carbon is made up of identical, ultraminute molecules of carbon (Fig. 28). Any appreciable portion of hydrogen gas is composed of millions of hydrogen molecules (Fig. 29).

The molecular weight ratio. With these assumptions in mind, we are now in a position to formulate *an explanation for the observed fact that substances enter into and emerge from chemical reactions in some whole-number ratio of their respective molecular weights.* First, the ultimate units of the substances that engage in chemical reac-

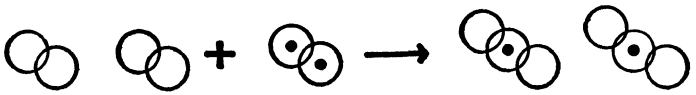
[2] It was originally assumed that all of the molecules of a given substance have exactly the same weight. This was before the existence of isotopic elements was recognized (p. 120). However, in natural materials the proportions in which lighter and heavier particles are distributed is such as to make the term "average weight" applicable.

tions are the molecules. *Secondly*, in the least possible reaction, definite and specific numbers of molecules of the substances involved enter into the reaction and definite numbers of molecules of the new substances emerge from the reaction. *The large-quantity reaction*, which can be seen by the eye or measured on a balance, *is but the many-times multiple of these ultimate unit engagements between the molecules.*

Thus, in the reaction of hydrogen with oxygen to make water:

	Hydrogen	+	Oxygen ⟶		Water
In large quantities	2 molecular weights of hydrogen	react with	1 molecular weight of oxygen	to make	2 molecular weights of water
because this is the inclusive result, millions of times repeated, of the ultimate unit reaction in which	2 molecules of hydrogen	react with	1 molecule of oxygen	to make	2 molecules of water

Diagrammatic representation



A third assumption. It is believed that the molecular weight of a substance, on any given weighing basis (grams, milligrams, ounces, etc.), includes a definite number of molecules, the same number for all substances. Calculations have been made by a variety of methods to determine the validity of this assumption. The findings are remarkably consistent and the figure which is currently accepted is that *the gram-molecular weight, or mole, of any substance comprises* 6.02×10^{23} *molecules.*[3]

Why does each substance have a specific molecular weight? If the average weight of the molecules of any naturally occurring sample of the substance is always the same, and if the number of molecules within the molecular weight quantities of substances in any specified weight unit are the same, it follows that the *aggregate weight of the molecules contained within the molecular weight quantity of the substance must be a fixed value for that substance.*

32 is this fixed weight for oxygen..... because on any given weighing basis, such as grams, this weight includes a definite number of constant-weight molecules of oxygen.

[3] 6.02×10^{23} = 602,000,000,000,000,000,000,000 (Avagadro's number).

18.016 is this fixed weight for water..... because on any given weighing basis it includes a definite number of constant-weight molecules of water.

Relative weights of molecules. Since actual weights of molecules must be infinitely small, too small to be considered on a practical weighing basis, it is usual to consider relative weights of molecules rather than actual weights. With the foregoing assumptions in mind, it is reasonable to conclude that *weights of single molecules of various substances are to each other as are the weights of equal numbers of molecules of these substances, hence, as their respective molecular weights.* For example:

the weight of 1 molecule of hydrogen	is to	the weight of 1 molecule of oxygen	is to	the weight of 1 molecule of water	as	2.016:32:18.016

since 2.016 gm of hydrogen, 32 gm of oxygen, and 18.016 gm of water contain the same numbers of molecules.

Another definition for molecular weight. It follows from this relationship that another definition for molecular weight is possible. Molecular weight may be defined as the weight of a molecule of a substance by comparison with the weight of a molecule of oxygen with an accepted value of 32 (p. 88).

ELEMENTS WITHIN SUBSTANCES

That elements occur within compounds in definite proportions by weight has already been called to attention in the Law of Definite Weight Proportions (p. 88). Let us pursue this relationship further using the molecular weight as the natural unit of the substance.

Atomic weights of elements. In building elements into substances nature seems to follow a very definite pattern. *For every element there is a specific weight known as its atomic weight.* This is *the least weight of the element that is to be found within the molecular weight of any substances containing this element.*

Moreover, *the atomic weight is a unit-combining weight for the element because each element is contained within molecular weights of all substances containing it in whole-number multiples of this weight.*

Atomic weights of elements

Aluminum	26 98	Magnesium	24 32
Barium	137 36	Nitrogen	14.008
Calcium	40.08	Oxygen	16.000
Carbon	12.011	Phosphorus	30.975
Chlorine	35.457	Potassium	39 100
Copper	63.54	Sodium	22.991
Hydrogen	1.0080	Sulfur	32.066
Iron	55.85	Zinc	65.38

Atomic weights for some of the elements are listed in the accompanying table; for a more complete list see the back cover of this text. The composition of a few substances, as given below, illustrate how atomic weights function.

Hydrogen oxide
$2 \times 1.008 \quad 1 \times 16$
Molecular weight

Potassium chlor ate
$1 \times 39.100 \quad 1 \times 35.457 \quad 3 \times 16$
Molecular weight

Carbon dioxide
$1 \times 12.011 \quad 2 \times 16$
Molecular weight

Hydrogen chloride
$1 \times 1.008 \quad 1 \times 35.457$
Molecular weight

Hydrogen sulf ate
$2 \times 1.008 \quad 1 \times 32.066 \quad 4 \times 16$
Molecular weight

Magnesium chloride
$1 \times 24.32 \quad 2 \times 35.457$
Molecular weight

If the number of atomic weights of the elements in the molecular weight of a compound is known, it is possible to anticipate the quantitative composition of the compound. For example:

Sodium	phosph	ate
3	1	4
atomic weights	atomic weight	atomic weights

Sodium phosph ate
$3 \times 22.991 \quad 1 \times 30.975 \quad 4 \times 16$
163.948 (molecular weight)

The composition of this compound is as follows:

In general terms: 163.948 parts by weight of sodium phosphate is composed of 3×22.991 parts by weight of sodium, 1×30.975 parts by weight of phosphorus, and 4×16 parts by weight of oxygen.

Or in specific quantities, in grams: 163.948 gm of sodium phosphate is composed of 3 × 22.991 gm of sodium, 1 × 30.975 gm of phosphorus, and 4 × 16 gm of oxygen.

Atoms, the ultimate units of the elements. This evidence of a systematic organization of the elements within molecular weights of compounds intrigued the early chemists. It continues to interest the chemist of today. (1) Why does each element have a specific atomic weight? (2) Why are elements combined within molecular weights of substances in whole-number multiples of these atomic weights? Again, it is necessary to turn to theory for a reasonable explanation. We have encountered the belief that the ultimate unit of the substance is the molecule. Further reasonings take us within molecules to discover how the elements are combined therein.

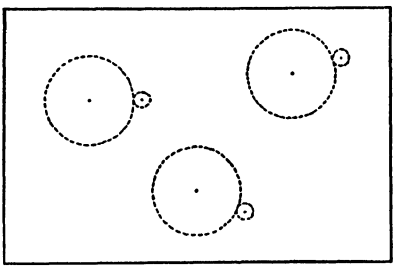


Fig. 30. Each molecule of hydrogen chloride is composed of 1 atom of hydrogen and 1 atom of chlorine.

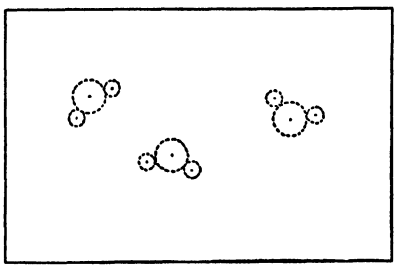


Fig. 31. Each molecule of water is composed of 2 atoms of hydrogen and 1 atom of oxygen.

First assumption. Elements are present within molecules in ultimate units called atoms (Figs. 30 and 31).

Second assumption. Atoms of the same element, from whatever natural source, have their own specific and constant average weights.[4] Thus, within molecules of hydrogen gas or within molecules of water, atoms of hydrogen always show the same average weight. And, oxygen atoms always exhibit their own specific atomic weight whether contributing to molecules of carbon dioxide or to molecules of water.

[4] The discovery of isotopic forms of elements (p. 120) meant that the older assumption that all of the atoms of a given element have exactly the same weight had to be abandoned. However, the constancy of the atomic weight, with the myriads of molecules involved, makes the concept of a constant average value appropriate.

Third assumption. Atoms of elements have definite combining capacities for atoms of other elements under the same conditions of combination. Thus:

Under conditions in which molecules of water are made, 2 atoms of hydrogen are always combined with 1 atom of oxygen (Fig. 31); hence, molecules of water are all alike. Again, under conditions in which molecules of sulfur dioxide are made, within each molecule 1 atom of sulfur is combined with 2 atoms of oxygen (Fig. 32); hence, molecules of sulfur dioxide are all alike. But, under other conditions, those in which molecules of sulfur trioxide are made, 1 atom of sulfur is found combined with 3 atoms of oxygen within each molecule (Fig. 33).

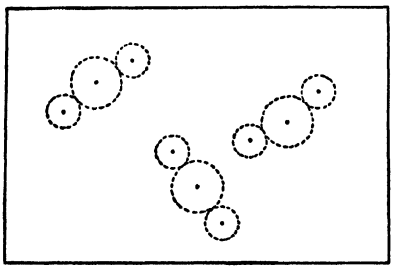


Fig. 32. Each molecule of sulfur dioxide is composed of 1 atom of sulfur and 2 atoms of oxygen.

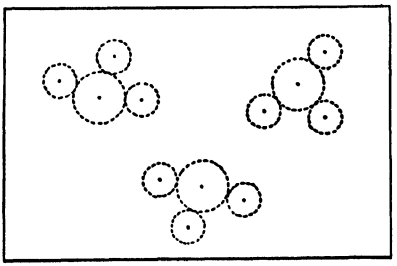


Fig. 33. Each molecule of sulfur trioxide is composed of 1 atom of sulfur and 3 atoms of oxygen.

Why are elements combined within molecular weights of substances in whole-number multiples of their atomic weights? The known composition of the molecular weight of the substance is believed to be determined by the composition of the individual molecules which make up this mass. Each molecule of a given substance is made up of atoms of the constituent elements, always the same number and ratio for each identical molecule. Therefore, *the number of atomic weights of the elements within the molecular weight of the substance corresponds to, and is determined by, the number of atoms of each of the elements within the molecule of the substance.* For example:

1. The molecular weight of water is composed of 2 atomic weights of hydrogen and 1 atomic weight of oxygen because, presumably, each of the millions of molecules of water that make up this weight is composed of 2 atoms of hydrogen and 1 atom of oxygen.

2. The molecular weight of hydrogen sulfate (p. 94) is composed of 2 atomic weights of hydrogen, 1 atomic weight of sulfur, and 4 atomic weights

of oxygen because, presumably, each molecule of hydrogen sulfate is composed of 2 atoms of hydrogen, 1 atom of sulfur, and 4 atoms of oxygen.

Another assumption of the atomic theory. It is believed that atomic weights of the various elements include the same number of atoms, distributed, of course, within molecules of substances. For example:

The 16 gm of oxygen element found within a gram-molecular weight of water is believed to represent the aggregate weight of 6.02×10^{23} atoms of oxygen element, one atom within each of the 6.02×10^{23} water molecules. And, 16 gm of oxygen within a mole of any other substance would likewise be the weight of 6.02×10^{23} atoms of oxygen. Also, a gram-atomic weight of hydrogen element (1.008 grams) is the aggregate weight of 6.02×10^{23} atoms of hydrogen, whether this quantity of hydrogen is within a mole of hydrogen chloride, of water, or of some other hydrogen-containing substance. Similarly, a gram-atomic weight of chlorine, carbon, or any other element, contains the same number of atoms.

Relative weights of atoms. It follows, then, that because all atoms of the same element have the same weight while atoms of different elements have different weights and because atomic weights of elements include equal numbers of atoms, the relative weights of single atoms of the various elements must be to each other as are the atomic weights of the elements. Thus:

the weight of 1 atom of hydrogen	is to	the weight of 1 atom of chlorine	is to	the weight of 1 atom of oxygen	as 1.008:35.457:16

Another definition for atomic weight. Atomic weight is the relative weight of an atom of an element in reference to the oxygen atom which has a relative weight of 16. This definition is in reference to the *theoretical* unit. The previously stated definition (p. 93) refers to a mass unit and is *experimentally determined.*

SUMMARY

Elements within substances. *The atomic weight of an element* is a fixed weight that is peculiar to each element. It is the least weight of the element found combined within molecular weights of substances containing it. It is a unit-combining weight because the element is combined within molecular weights of substances in whole-number multiples of its atomic weight.

The atom is the infinitesimal, ultimate unit of an element. Atoms

of elements are always combined with each other within molecules of substances. Atoms of each element have their own peculiar and constant weight.

Weights of single atoms of the various elements are to each other, relatively, as are the atomic weights of the elements.

As to substances. *The molecular weight of a substance* is a fixed weight, experimentally determined, that is peculiar to the substance. It is a unit-reacting weight, since a substance participates in chemical reactions in whole-number multiples of its molecular weight.

The molecule is the infinitesimal and ultimate unit of a substance. Molecules of each substance have their own fixed weights.

The *gram-molecular weight* of every substance includes 6.02×10^{23} molecules of the substance.

Weights of single molecules of various substances are to each other, relatively, as are the molecular weights of the substances.

The purpose of theory. A scientific theory includes reasoned guesses for the purpose of explaining some known behavior of nature for which no factual explanation has been discovered. They are "reasoned" guesses because they are subjected to tests in respect to the factual phenomenon involved and found to be consistent therewith. Any "guesses" pertaining to the theory in question that are not consistent with the facts at issue are discarded. A developing theory, therefore, is in a continual state of change—contributing ideas being retained, discarded, or replaced, but the natural phenomenon itself, that is, the fact, continues to stand.

Thus, the discovery of usable, tangible weight units (molecular weights) for measuring substances, as they are involved in reactions, and the weight units for measuring elements (atomic weights), as they are combined within substances, are factual findings and are not subject to change as far as nature is concerned. But the concepts of the molecule as a means for explaining the behavior of substances and of the atom as a means for explaining the behavior of elements are theoretical and continually subject to alterations.

A caution: One of the unfortunate stumbling blocks for beginning students of chemistry is that they are too prone to confuse that which is known (fact) with that which is firmly believed in but not known (theory) which serves to explain the fact. Obviously, they are related; both are of equal importance to the scientist. They should come to be of equal importance to the student of science.

QUESTIONS

1. What is the function of molecular weights? Of atomic weights?
2. Why does 2.016 constitute the molecular weight of hydrogen, while 44.011 is the molecular weight of carbon dioxide?

3. a. What are the basic assumptions relating to molecules?
   b. How many molecules are believed to be contained within 44.011 gm of carbon dioxide? 18.016 gm of water? 2.016 gm of hydrogen?
   c. What are the relative weights of single molecules of carbon dioxide, water, and hydrogen? Give reasons.

4. The following are whole-number reacting multiples for the substances concerned in the reactions specified:
   a. Supply molecular weights (table, p. 89) and interpret (1) in grams, (2) in general terms.
   b. Interpret in molecule terms.

$$\underset{3}{\text{Hydrogen}} + \underset{1}{\text{Nitrogen}} \longrightarrow \underset{2}{\text{Ammonia}}$$

$$\underset{2}{\text{Wood alcohol}} + \underset{3}{\text{Oxygen}} \longrightarrow \underset{4}{\text{Water}} + \underset{2}{\text{Carbon dioxide}}$$

5. What is the weight of a mole of water? Approximately how many moles are there in a liter of water? What is the weight of a millimole of water? How many molecules, supposedly, are contained in 1 millimole?

6. Why is 16 the atomic weight of oxygen? 14.008 the atomic weight of nitrogen? 40.08 the atomic weight of calcium?

7. What are the basic assumptions of the atomic theory?

8. What are the comparative weights of atoms of the following elements: carbon, hydrogen, oxygen, and iron? (See table, p. 94.) What is the basis for this comparison?

9. The following are whole-number atomic-weight multiples for the elements within molecular weights of the following substances:
   a. Compute the molecular weights of the substances.
   b. Tell what quantitative information is thereby provided concerning the composition of the substance (1) in grams, (2) in general terms:

$$\underset{1\quad 1\quad 3}{\text{Calcium carbonate}}$$

$$\underset{1\qquad 2}{\text{Mercuric chloride}}$$

$$\underset{2}{\text{Nitrogen (substance)}}$$

   c. What is the presumed composition of the molecule of each of these substances?

CHAPTER 10

SHORTHAND FOR CHEMICAL MEASURINGS

SHORTHAND IN RELATION TO ELEMENTS

Symbols for atomic weights of elements. The first discoverers in the early 1800's of *atomic weights* for such elements as were then known were John Dalton, an Englishman, and Jöns Berzelius of Sweden. Along with their findings came the desire to represent these experimentally determined, but awkward, values in some significant shorthand manner. Berzelius decided that these devices should suggest the names of the elements; Dalton thought that distinctive characters should be used for this purpose. Their two different ideas were as indicated below.

THE ELEMENT	ATOMIC WEIGHT	BERZELIUS' SUGGESTIONS	DALTON'S SUGGESTIONS
Carbon	12.011	C	●
Chlorine	35.457	Cl	
Hydrogen	1.0080	H	○
Nitrogen	14.008	N	⊕
Oxygen	16.000	O	⊙
Sulfur	32.066	S	⊕

Berzelius claimed that such characters as Dalton was suggesting and using "disfigured the page." Dalton, on the other hand, called Berzelius' characters "horrifying," claiming that they would be confused with abbreviations, merely, for the names of elements without regard to their quantitative significance. It was the idea of Berzelius

that continued to be used by scientists as more and more elements and their atomic weights were discovered.

So, today, the adopted shorthand character, or *symbol* as it is called, for the atomic weight of an element is the first letter (capitalized), or the first letter (capitalized) and some other significant letter (not capitalized), of the common or Latin name for the element. A partial list of elements and their atomic weights together with the symbols that represent them are given in the following table. A more extensive list is to be found on the back cover of this text.

THE ELEMENT	ITS ATOMIC WEIGHT	SYMBOL FOR ATOMIC WEIGHT	SYMBOL FOR THE ATOM
Barium	137.36	Ba	Ba
Carbon	12.011	C	C
Calcium	40.08	Ca	Ca
Chlorine	35.457	Cl	Cl
Copper (Cuprum)	63.54	Cu	Cu
Hydrogen	1.0080	H	H
Iron (Ferrum)	55.85	Fe	Fe
Lead (Plumbum)	207.21	Pb	Pb
Magnesium	24.32	Mg	Mg
Mercury (Hydrargyrum)	200 61	Hg	Hg
Nitrogen	14.008	N	N
Oxygen	16.000	O	O
Phosphorus	30 975	P	P
Potassium (Kalium)	39 100	K	K
Silver (Argentium)	107.880	Ag	Ag
Sodium (Natrium)	22.991	Na	Na
Sulfur	32.066	S	S
Tin (Stannum)	118.70	Sn	Sn
Zinc	65.38	Zn	Zn

Symbols for atoms of elements. Another use that is made of symbols is for representing *atoms* of elements. This use is also exemplified in the above table.

The two uses for symbols. The two functions of symbols, then, are as follows: (1) A symbol can be set down instead of the *atomic weight* to be translated into the actual atomic-weight value of the element when one so desires; (2) or, if one is dealing with atoms, the symbol can be set down to represent an atom of the element. Accordingly:

In relation to the atomic weight, the symbol C can be set down to represent

12.011 parts by weight of the element carbon,
or 12.011 gm of carbon,
or the atomic weight of carbon on any other weighing basis.

Or, the symbol C can be set down to represent 1 atom of the element carbon

SHORTHAND IN RELATION TO SUBSTANCES

Formulas for molecular weights of substances. Because elements are present within molecular weights of substances in whole-number multiples of their atomic weights, it is possible to represent the composition of the molecular weight of a substance by assembling the symbols for the atomic weights of the elements in the proportions in which they are known to occur in the substance. The expression thus assembled is known as the formula for the substance. Thus:

1. The substance	Hydrogen sulfate		
Atomic weights of elements and multiples	2×1.008	1×32.066	4×16
Atomic weights represented by symbols	2 H	1 S	4 O
Formula for molecular weight as it usually appears	H_2SO_4		
2. The substance	Oxygen		
Atomic weight of oxygen element and multiple	2×16		
Atomic weight of oxygen represented by its symbol	2 O		
Formula for molecular weight of oxygen substance	O_2		

The small subscript numbers associated with the symbols for elements indicate the whole-number multiples of the atomic weights of the elements to which they are directly attached. If no subscript appears with a symbol, the multiple for that atomic weight is 1.

The *formula*, therefore, is a shorthand device for representing the composition of the molecular weight of a substance.

Formulas for molecules of substances. The formula is also used to represent the composition of the molecule of the substance. This is in accord with the use of the symbol to represent the atom of the element.

These two uses for formulas are illustrated in the following example.

1. H_2O is the *formula for the molecular weight* of water	1. H_2O is the *formula for the molecule* of water
with	with
H and O as symbols for the atomic weights of the elements hydrogen and oxygen.	H as the symbol for the atom of hydrogen and O as the symbol for the atom of oxygen.

Empirical formulas. For some substances the molecular weight has not been determined, and there are others—notably among the bases and salts—which appear not to form true molecules (p. 126). For such substances *empirical formulas* are used; that is, the formula which expresses the ratio of the atomic weights of the constituent elements in the simplest possible terms. The formula for sodium chloride, NaCl, is an empirical formula. It indicates that this compound is composed of sodium and chlorine elements in the proportion of 1 atomic weight of sodium to 1 atomic weight of chlorine.

Formulas for more complex compounds. The formulas for certain compounds are complicated by the presence of one or more radical groups, such as the hydroxyl radical, the sulfate radical, or the nitrate radical, contributing to the molecular weight of the substance. These radicals are believed to indicate corresponding atom groups within the molecules of the substance. This condition must be represented in the formula.

Formulas for compounds containing complex radicals

Aluminum hydroxide	$Al(OH)_3$
Calcium nitrate	$Ca(NO_3)_2$
Ferric sulfate	$Fe_2(SO_4)_3$

When a multiple of the radical is required, the shorthand expression for the radical is enclosed in parentheses, and the number of radical weights within the molecular weight of the compound is indicated as represented in the formulas above.

Correct use of formulas. The formula for a substance is then a quantitative expression; it is not simply an abbreviation for the name. As such it is used correctly when it expresses this quantitative significance, that is, (1) to represent the *molecular weight* of the substance in the abstract, (2) to represent the *gram-molecular weight* or the molecular weight in specific weight units other than grams, and (3) to represent the *theoretical unit*, the *molecule* of the substance.

The formula used in computing the molecular weight of a substance. With the formula for a substance given, the atomic

weights of elements (see table) can be introduced, and the molecular weight for the substance can be computed. Thus:

Formula for potassium phosphate	K_3	P	O_4
Introducing atomic weights	3×39.100	1×30.975	4×16
Total elements within molecular weight..	117.300	30.975	64

Molecular weight for potassium phosphate..... 212.275

Interpretation of the formula. The interpretation of a formula will depend upon whether it is to be used in reference to the composition of a measurable quantity of the substance, that is, its molecular weight, or in reference to the composition of the molecule.

Example one. Given the formula H_2O_2 for *hydrogen peroxide:*

As the formula stands in relation to the molecular weight, it tells that 1 molecular weight of hydrogen peroxide is composed of 2 atomic weights of hydrogen and 2 atomic weights of oxygen.

With quantitative data supplied but still with reference to the molecular weight, this formula tells that 34.016 parts by weight of hydrogen peroxide are composed of 2×1.008 parts by weight of hydrogen and 2×16 parts by weight of oxygen.

Computed data

$$\underbrace{\underset{H_2}{2 \times 1.008}\quad \underset{O_2}{2 \times 16}}_{34.016}$$

Molecular weight

Or, *in terms of a specific weighing unit,* the formula H_2O_2 tells that 34.016 gm of hydrogen peroxide is composed of 2×1.008 gm of hydrogen and 2×16 gm of oxygen.

In relation to the molecule, the formula H_2O_2 tells that 1 molecule of hydrogen peroxide is made up of 2 atoms of hydrogen and 2 atoms of oxygen.

Example two. Given the more complex formula $Al_2(CO_3)_3$:

As the formula stands in reference to the molecular weight, it tells that 1 molecular weight of aluminum carbonate is composed of 2 atomic weights of aluminum and 3 carbonate radical weights. Each radical weight is composed of 1 atomic weight of carbon and 3 atomic weights of oxygen.

With quantitative data obtained but still with reference to the molecular weight, this formula tells that 233.993 parts by weight of aluminum carbonate are composed of 2×26.98 parts by weight of aluminum and 3×60.011 parts by weight of carbonate, each carbonate being composed of 1×12.011 parts by weight of carbon and 3×16 parts by weight of oxygen.

Computed data

$$\underbrace{\underset{Al_2}{2 \times 26.98}\quad \underbrace{\left(\underset{C}{12.011}\quad \underbrace{\underset{O_3}{3 \times 16}}_{48}\right)_3}_{3 \times 60.011}}_{233.993}$$

Molecular weight

In regard to its molecule, this formula, $Al_2(CO_3)_3$, tells that 1 molecule of aluminum carbonate is composed of 2 atoms of aluminum and 3 carbonate *atom groups*, each being composed of 1 atom of carbon and 3 atoms of oxygen.

Formulas for simple substances. It is reasonable to expect that formulas for simple substances will also represent the number of atomic weights of the element within the molecular weight of the substance. In some instances this is the case, and for such substances the *molecular formula* is the one customarily used. (See table, below.)

SUBSTANCE	MOLECULAR WEIGHT OF SUBSTANCE	ATOMIC WEIGHT OF ELEMENT	FORMULA FOR MOLECULAR WEIGHT	FORMULA FOR MOLECULE
Hydrogen	2.016	1.008	H_2	H_2
Nitrogen	28.016	14.008	N_2	N_2
Oxygen	32.000	16.000	O_2	O_2
Ozone	48.000	16.000	O_3	O_3
Phosphorus	123.900	30 975	P_4	P_4
Bromine	159.832	79.916	Br_2	Br_2
Chlorine	70.914	35.457	Cl_2	Cl_2
Fluorine	38.00	19.00	F_2	F_2
Iodine	253 82	126.91	I_2	I_2

However, various complications have been encountered in obtaining accurate molecular weights for simple substances. Consequently, it has become *an accepted convention to use the symbol for the element as the formula for the simple substance, except for the small group of simple substances*, cited in the table, *for which the molecular formulas are used.*

It will greatly facilitate the use of chemical shorthand if the student will commit to memory *this small group of molecular formulas.* Then, for all other simple substances, the symbol for the element can be set down to function as the formula for the substance.

EQUATIONS TO RECORD CHEMICAL REACTIONS

The formula equation. Once formulas for molecular weights of substances are obtained, it becomes possible to express in shorthand the quantitative story of the chemical reaction. The expression used for this purpose is known as the *chemical equation* or the *equation for*

the reaction. The following example illustrates the reasoning which underlies this chemical shorthand.

Example. When water decomposes to make the substances hydrogen and oxygen, the ratio of the molecular weights of the substances involved is 2:2:1.

Water	⟶	Hydrogen	+	Oxygen
2		2		1
Molecular weights		Molecular weights		Molecular weight

Therefore, by supplying the *formulas for the molecular weights* of these substances, the expression becomes:

$$2\ H_2O \longrightarrow 2\ H_2 + O_2$$

And, because the numbers of molecules of the substances involved in the ultimate unit reaction is believed to be consistent with the molecular weight involvement of the substances in the mass reaction, a similar expression can be used to express the molecule line-up.

Thus: $$2\ H_2O \longrightarrow 2\ H_2 + O_2$$

The equation interpreted. Now that the formula equation has been presented, let us take another example and put into words the various related meanings hidden in such a shorthand expression.

Methyl alcohol + Oxygen ⟶ Water + Carbon dioxide

$$2\ CH_3OH + 3\ O_2 \longrightarrow 4\ H_2O + 2\ CO_2$$

1. *As the equation stands*, with molecular weights as units for substances, this equation tells that 2 molecular weights of methyl alcohol react with 3 molecular weights of oxygen to make 4 molecular weights of water and 2 molecular weights of carbon dioxide.
2. But *with numerical values for* molecular weights of substances computed:

$$\underbrace{2\ CH_3OH}_{\text{M.W. } 32.043} + \underbrace{3\ O_2}_{\text{M.W. } 32} \longrightarrow \underbrace{4\ H_2O}_{\text{M.W. } 18.016} + \underbrace{2\ CO_2}_{\text{M.W. } 44.011}$$

$2\ CH_3OH$: 1×12.011, 3×1.008, 1×16, 1×1.008

$3\ O_2$: 2×16

$4\ H_2O$: 2×1.008, 1×16

$2\ CO_2$: 1×12.011, 2×16

In general, this equation tells that 2×32.043 parts by weight of methyl alcohol react with 3×32 parts by weight of oxygen to make 4×18.016 parts by weight of water and 2×44.011 parts by weight of carbon dioxide.

Or, *in actual quantities, in grams*, this equation tells that 2×32.043 gm of methyl alcohol react with 3×32 gm of oxygen to make 4×18.016 gm of water and 2×44.011 gm of carbon dioxide.

3. *In terms of* molecules, this equation as it stands without computations tells that, presumably, 2 molecules of methyl alcohol react with 3 molecules of oxygen to make 4 molecules of water and 2 molecules of carbon dioxide.

Chemical equalities expressed by the equation. Any equation, correctly assembled, illustrates the *Law of Chemical Change* (p. 16); namely, the quantities of the various *elements* that are present within the substances entering into the reaction are equal to the quantities of the *elements* to be found within the products of the reaction. For example:

Glucose + Oxygen ⟶ Water + Carbon dioxide
$C_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ H_2O + 6\ CO_2$

Quantities of elements within substances before the reaction:	=	*Quantities of elements within substances after the reaction:*
6 atomic weights of carbon in glucose		6 atomic weights of carbon in carbon dioxide
12 atomic weights of hydrogen in glucose		12 atomic weights of hydrogen in water
18 atomic weights of oxygen distributed in glucose and oxygen		18 atomic weights of oxygen distributed in water and carbon dioxide

It follows from the foregoing factual findings that the formula equation also expresses the *Law of Conservation of Mass;* namely, that the inclusive weight of the substances entering into the reaction is equal to the inclusive weight of the resulting substances (p. 16). This is illustrated in the following equation *using molecular weights for the substances, computed from their formulas, as the natural unit-reacting weights for the substances.*

Glucose	+	Oxygen	⟶	Water	+	Carbon dioxide
$C_6H_{12}O_6$	+	$6\ O_2$	⟶	$6\ H_2O$	+	$6\ CO_2$
6×12.011 12×1.008 6×16		2×16 M.W. 32		2×1.008 1×16 M.W. 18.016		1×12.011 2×16 M.W. 44.011
M.W. 180.162						

Substances before the reaction:		*Substances after the reaction:*	
Glucose 1×180.162	180.162	Water 6×18.016	108.096
Oxygen 6×32	192	Carbon dioxide 6×44.011	264.066
Inclusive weight of these substances	372.162	Inclusive weight of these substances	372.162

Assembling equations. Since the equation is a fundamentally important tool for recording measurements of substances that engage in a chemical reaction, it follows that knowing what equations represent, how to interpret them, and how to assemble them should

become part of the equipment of every serious student of chemistry. The interpretation of an equation has been presented, but the manner of obtaining an equation has not. Therefore, let us now assemble the equation for the reaction between iron and oxygen as an introduction to the method involved.

1. Know what substances participate in the reaction. The word equation serves as such a record.

2. Set down the *correct* formulas for these substances. Moreover, because the formula represents the composition of the substance, correct formulas should never be altered. These two steps are as follows:

$$\text{Iron} + \text{Oxygen} \longrightarrow \text{Ferric oxide (Iron rust)}$$
$$\text{Fe} + \text{O}_2 \longrightarrow \text{Fe}_2\text{O}_3$$

3. To arrive at the formula multiples, bear in mind that the number of atomic weights of iron and oxygen elements within the iron and oxygen substances before the reaction will all be found present within the ferric oxide made.

So, as to oxygen element, inspection of the above formulas shows that it is combined 2 atomic weights at a time in 1 molecular weight of oxygen substance whereas in ferric oxide it is combined in 3 atomic weights at a time. Hence, 6 atomic weights of oxygen must be provided. This calls for 3 molecular weights of oxygen substance before the reaction and 2 molecular weights of ferric oxide made:

$$\text{Fe} + 3\ \text{O}_2 \longrightarrow 2\ \text{Fe}_2\text{O}_3$$

But, these two molecular weights of ferric oxide product contain a total of 4 atomic weights of iron element which must be provided in 4 molecular weights of the original iron substance. Thus, the complete equation for this reaction is as follows:

$$4\ \text{Fe} + 3\ \text{O}_2 \longrightarrow 2\ \text{Fe}_2\text{O}_3$$

In general, then, the steps in assembling a chemical equation are:

1. Know *what substances are involved before and after the reaction.* For the beginning student it is helpful to assemble this information through the medium of the *word equation.*

2. Set down the *correct formula* for the molecular weight of each substance.

3. Keeping in mind the Law of Chemical Change (p. 107), by inspection of formula composition, arrive at such *whole-number*

formula multiples as will provide for equal numbers of symbol weights of elements within the formulas before and after the reaction thus represented.

VALENCE

A guide to assembling formulas. Up to this point our study of formulas has related to their quantitative significance. Perhaps the student now recognizes that the determination of the exact formula for any substance rests on laboratory findings. Does this mean, then, that formulas—once determined—must be memorized if they are to be used? Fortunately, for many substances this is not the case. A knowledge of the *valences* of the elements makes it possible to predict the probable combinations that will be made and to record the composition of the predicted compound by formula.

What is valence? The term *valence has reference to the specific combining capacities of the atomic weights of elements by comparison with the combining capacity of 1 atomic weight of hydrogen (1.008 parts by weight) with an accepted valence of 1.*

The accompanying table of formulas for molecular weights of substances illustrates valence relations within these representative compounds. The number of prime marks placed over the symbols for atomic weights of the constituent elements designates the combining capacity, or valence, of the element represented.

The combining capacities of various elements illustrated in formulas

GROUP I	GROUP II	GROUP III	GROUP IV
$H'\ Cl'$	$Na'\ Cl'$	$Na_2'\ O''$	$Na_2'\ S''$
$H_2'\ O''$	$K'\ Cl'$	$K_2'\ O''$	$K_2'\ S''$
$H_2'\ S''$	$Ca''Cl_2'$	$Ca''\ O''$	$Ca''\ S''$
$N'''H_3'$	$Al'''Cl_3'$	$Al_2'''O_3''$	$Al_2'''S_3''$
$C''''H_4'$	$C''''Cl_4'$	$C''''\ O_2''$	$C''''\ S_2''$

In forming compounds, the combining capacities of the contributing elements must be mutually satisfied. This is illustrated in the above formulas. Thus:

1 atomic weight of hydrogen with a valence of 1 exactly satisfies 1 atomic weight of chlorine which also has a valence of 1. But, 1 atomic weight of calcium with a valence of 2 requires 2 atomic weights of chlorine with a valence of 1 to form a compound.

Always, *atomic weights of elements, under the same conditions of combination, exhibit the same valences.* It follows, therefore, that when the valences exhibited by the given elements are known, their combining proportions and, hence, their formulas can be foretold.

Elements with variable valences. Many of the elements show only one valence throughout all of their combinations. Examples of such elements are: hydrogen (H′) and calcium (Ca″). But, there are other elements that show different valences depending on their partners and the conditions of the reaction. Thus, for example:

Sulfur, when in combination with hydrogen.....	$H_2'S''$
when in combination with metal elements	$Ag_2'S''$
Sulfur, when in combination with oxygen, usually	$S''''O_2''$
but under certain conditions (p. 48).....	$S''''''O_3''$

Certain of the metal elements exhibit differences in their combining capacities depending on conditions for combination. For example:

Copper, in cupric compounds, exhibits a valence of 2..	$Cu''Cl_2'$
Copper, in cuprous compounds, exhibits a valence of 1.....	$Cu'Cl'$

Other examples of elements showing variable valence will be discovered in the valence table at the back of this text.

The valences of complex radicals. The term "valence" applies also to the combining capacities of radical weights that are composed of two or more elements, such as the nitrate and sulfate radicals. Radicals of this order always have fixed, never variable, valences in reference to the adopted measuring standard, namely, the combining capacity or valence of the atomic weight (1.008) of hydrogen. Thus:

	Represented thus
Nitrate radical weight has a valence of 1.....	NO_3'
Sulfate radical weight has a valence of 2	SO_4''
Phosphate radical weight has a valence of 3.....	PO_4'''

With a knowledge of valences of such radicals, one is in a position to anticipate the composition of molecular weights of compounds that contain them. For example:

As to the composition of hydrogen sulfate:

		Represented thus
Since hydrogen has a valence of 1 and sulfate a valence of 2	the molecular weight of hydrogen sulfate must be composed of 2 atomic weights of hydrogen to 1 sulfate radical weight.	$H_2'SO_4''$

As to the composition of calcium phosphate:

Since calcium has a valence of 2 and phosphate a valence of 3	the molecular weight of calcium phosphate must be composed of 3 atomic weights of calcium to 2 phosphate radical weights.	*Represented thus* $Ca_3''(PO_4)_2'''$

Valence of some such radicals accounted for. The inclusive valence of a radical that is composed of two or more elements is really a measure of the valence that is not satisfied between the elements within the same. With some radicals this valence is easily accounted for, not so with others. Thus:

The valance of the sulfate radical is 2..... $(SO_4)''$

But within this radical the valence of each oxygen is 2 and of sulfur is 6 ..... $(S''''''O_4'')''$

Accordingly, the total valence carried by the oxygen inclusively is 8, against the valence of 6 carried by the sulfur. Hence, the left-over valence of 2 is the valence of the sulfate radical to be satisfied by combination with some other element.

But, the valence of some radicals is not thus easily accounted for. Among these are acid radicals of organic acids, such as acetate and tartrate (p. 147), and the student is advised just to accept the valences of these radicals as they stand without, at present, attempting to account for them.

Definition of valence. *Valence is the combining capacity of the atomic weight of an element, or of the radical weight of two or more combined elements, measured in reference to the combining capacity of the atomic weight of hydrogen (1.008) with an accepted valence of 1.*

Positive and negative valence. It is customary to speak of positive and negative valence because, in forming certain classes of compounds, elements and radical groups either become positively or negatively charged or show a tendency to do so. This tendency is a determining factor in the selectivity of elements as to partner elements for building compounds. In general, hydrogen, the metal elements, and the ammonium radical exhibit positive valence whereas the nonmetal elements, the acid radicals,[1] and the hydroxyl radical show a negative valence. The extent of charge, whether positive or negative, is consistent with the valence of the element or radical. Within compounds, the positive valence must equal the

[1] The term *acid radical* is applied to radicals which contribute to the formation of acids—the sulfate, nitrate, and phosphate radicals for instance. For further explanation see Chapter 13, p. 147.

negative valence because *the compound as a whole is neutral.* For example:

	Represented thus
The composition of potassium carbonate. Since the atomic weight of potassium carries 1 unit of positive electricity, or has a valence of 1-*positive*, and carbonate radical weight carries 2 units of negative electricity, or has a valence of 2-*negative*, a molecular weight of potassium carbonate is composed of 2 atomic weights of potassium and 1 carbonate radical weight.	$K_2^+CO_3^{--}$

The valences of atoms and atom groups. Valences of atomic weights of elements and of radical weights are factual findings. They have been discovered as the result of painstaking and thoughtful laboratory investigation. But, as always, the inquiring mind wants a *why* for this phenomenon of valence. And, again, this explanation is to be found in the combining capacities of the atoms of the elements. It is believed that the measurable combining capacities, both as to kind and extent—exhibited by atomic weights of elements and by complex radicals—are determined by the valences of the atoms as they build themselves into atom groups and into molecules of compounds. (Further explanation of valences of atoms will be found in Chapter 11.)

Another definition for valence. *In relation to atoms, valence is the combining capacity of the atom of an element, or of an atom group inclusively, measured in reference to the combining capacity of the atom of hydrogen with a valence of 1.*

How to assemble a formula. With a valence table at hand or with this information memorized *correctly*, it is possible to reason one's way to the assembly of formulas and to anticipate the composition of molecules.

Method. *First*, for the elements or radicals involved in the given compound, set down the correct symbols and represent the correct valence for the element or radical.

Second, determine, by inspection, the multiples in which these particular elements must combine in order exactly to balance the valences. Indicate these multiples by the use of subscript numbers attached to the symbol for the element. If a radical group requires a multiple, enclose the group in brackets and place the subscript outside of the bracket. These steps are illustrated in the following table.

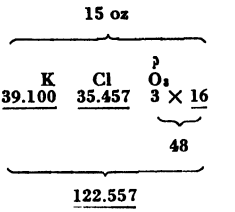
NAME OF COMPOUND	RADICALS WITH VALENCES	COMPLETED FORMULAS
Silver sulfide	$Ag^{+}S^{--}$	Ag_2S
Calcium carbonate	$Ca^{++}CO_3^{--}$	$CaCO_3$
Magnesium hydroxide	$Mg^{++}OH^{-}$	$Mg(OH)_2$
Calcium phosphate	$Ca^{++}PO_4^{---}$	$Ca_3(PO_4)_2$

FORMULAS AND EQUATIONS USED TO SOLVE PROBLEMS

The formula put to work. The formula for any compound is of practical value because it tells of the weight relationship that always exists: (1) between the constituent elements and (2) between the constituent elements and the compound as a whole. For example:

1. Suppose the problem is that of ascertaining the quantity of oxygen element that must be present in 15 oz of potassium chlorate, then:

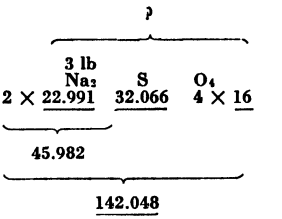
$$\underset{\text{oz of oxygen}}{x} : \underset{\text{oz of potassium chlorate}}{15} = 48:122.557$$



$$x = \frac{15 \times 48}{122.557} = 5.9 \text{ oz of oxygen combined in 15 oz of potassium chlorate}$$

2. Or the problem might be as to what quantity of sodium sulfate must be weighed out to contain 3 lb of the element sodium, in which case:

$$\underset{\text{lb of sodium}}{3} : \underset{\text{lb of sodium sulfate}}{x} = 45.982:142.048$$



$$x = \frac{3 \times 142.048}{45.982} = 9.3 \text{ lb of sodium sulfate necessary to contain 3 lb of sodium}$$

The equation put to work. The equation for any specific reaction makes it possible to obtain information concerning the weight relationship that must always exist between participating substances. For example:

Suppose the problem is: How much oxygen is necessary to react with 10 oz of methane?

The first step must be to obtain the *correct* equation for the reaction, then the molecular weights of these two substances through their formulas. Thus:

$$\underset{\text{Methane}}{\overset{10\text{ oz}}{CH_4}} + \underset{\text{Oxygen}}{\overset{?}{2\,O_2}} \longrightarrow \underset{\text{Water}}{2\,H_2O} + \underset{\text{Carbon dioxide}}{CO_2}$$

1×12.011, 4×1.008 → 16.043

2×16 → 32

Therefore $\underset{\text{oz of methane}}{10} : \underset{\text{oz of oxygen}}{x} = 16.043 : 64$

$$x = \frac{10 \times 64}{16.043} = 39.8 \text{ oz of oxygen necessary to react with 10 oz of methane}$$

The possibility of putting formulas and equations to work in such practical ways has almost inconceivable significance. Not only chemists but also manufacturers are interested in making use of these handy quantitative tools, since:

Through the aid of the *formula* the chemist or the manufacturer is able to compute:

1. The *quantity of any element* of his need which must be present in a given quantity of a compound containing it

2. The *quantities of the elements* concerned which must be obtained for making a given weight of a desired compound.

Through the aid of the *equation* the chemist or the manufacturer is able to compute:

1. The *quantity of any substance* which must be obtained before the reaction in order to make a desired quantity of a desired substance as product

2. The *quantities of substances* that will be made from given quantities of substances entering into the reactions concerned.

QUESTIONS

Note: In connection with this study refer to the table of atomic weights on the back cover of this text whenever necessary.

1. What does a chemical symbol represent? Illustrate with reference to N for nitrogen.

2. What does a chemical formula represent? Illustrate by reference to the formula CO_2 for carbon dioxide.

3. Assemble in good form the quantitative data provided by each of the following formulas and compute the molecular weight for each substance:

$$AgNO_3, \quad Ca(OH)_2, \quad H_3PO_4, \quad Fe_2(CO_3)_3$$

4. Making use of the quantitative data obtained in question 3, interpret each of the above formulas (a) in general terms; (b) in gram terms. Also interpret each of these formulas in terms of the molecule.

5. What quantitative information concerning the substance is provided by each of the following formulas?

$$O_2, \quad Br_2, \quad P_4$$

6. What information concerning a newly discovered substance must be known before it can be assigned a formula?

7. Interpret each of the following equations (a) with formulas representing molecular weights of substances; (b) with formulas representing molecules of said substances:

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$$
$$P_4 + 5\ O_2 \longrightarrow 2\ P_2O_5$$
$$2\ NaCl + H_2SO_4 \longrightarrow 2\ HCl + Na_2SO_4$$

8. In respect to each equation in question 6, compute the molecular weights of the substances involved and interpret the equation: (a) in gram terms; (b) in general terms.

9. Assemble word and formula equations for the reaction that results from each of the following contacts (select the necessary formulas from the accompanying list):

a. The decomposition of water
b. Reaction of copper and silver nitrate
c. Reaction of potassium iodide and lead nitrate
d. Rusting of iron

Formula list	
Ag	$AgNO_3$
Cu	$Cu(NO_3)_2$
Fe	Fe_2O_3
H_2	H_2O
O_2	KI
PbI_2	KNO_3
	$Pb(NO_3)_2$

10. In respect to the reaction between methane and oxygen (p. 114), how does the equation provide evidence as to:

a. The Law of Chemical Change
b. The Law of Conservation of Mass

11. In all sulfides the element sulfur exhibits a valence of 2. Explain the meaning of the term *valence*, and illustrate in reference to at least 3 sulfides.

12. Assemble formulas for the following compounds: potassium bromide, aluminum sulfide, calcium hydroxide, ammonium sulfate, and calcium phosphate. How can you tell that a given formula is assembled correctly?

13. What weight of sodium element is contained in 1 gm of sodium bicarbonate (formula $NaHCO_3$)?

14. Ferrous sulfate (formula $FeSO_4$) and ferrous carbonate (formula $FeCO_3$) both come in tablets of 0.3 gm. Compute the weight of iron in each tablet.

15. How much oxygen must be brought to the cells to react with 1 gm of glucose? How much carbon dioxide is made from the reaction? How much water? Formula equation for this reaction is as follows.

$$C_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O$$

16. a. In the making of cakes and biscuits what *relative* weights of sodium bicarbonate and cream of tartar must be mixed for exact reaction with no excess of either remaining?
    b. What *relative* weight of Rochelle salt will be left in the cake?
    c. If 2 *gm* of sodium bicarbonate are measured out, how much cream of tartar must be used and how much Rochelle salt will be left in the cake?

$$\underset{\text{Sodium bicarbonate}}{NaHCO_3} + \underset{\text{Cream of tartar}}{KHC_4H_4O_6} \longrightarrow H_2O + CO_2 + \underset{\text{Rochelle salt}}{KNaC_4H_4O_6}$$

CHAPTER 11

WITHIN ATOMS OF THE VARIOUS ELEMENTS. VALENCE

In our study thus far *atoms* have been considered as the ultimate combining units of the elements used by nature for building substances. Atoms have been considered in their quantitative relations, as particles with specific weights and definite combining capacities, as they are built into molecules of substances. But the interest of the scientist does not end at this point. His quest for greater insight into the nature of matter has led to experimental studies which have yielded a great body of evidence as to the nature of elements. Out of these discoveries have come the present-day theories as to the structure and behavior of atoms.

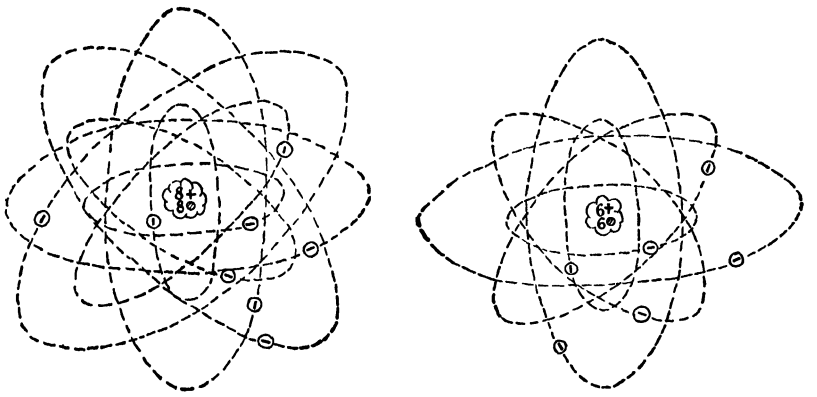
The modern concept of atomic structure has grown out of discoveries from researches that have been, and continue to be, among the most brilliant of all time. These include experimental investigations of radioactive elements begun about 1896 by the French scientist Henri Becquerel and carried forward by Marie and Pierre Curie, the British scientist Lord Rutherford, and other great scientists—even to the present day. We shall not attempt to enter into the complexities of these researches nor, by any means, into all of the details of inner-atom theory.

General structural features of atoms. Up to about 1900, the generally accepted idea of the atom was that of John Dalton and his contemporaries; namely, that atoms were hard, impenetrable, indestructible units of matter—a very different picture from the modern concept of atom structure.

It is now believed that within the atom of every element there is a nuclear mass which occupies an infinitesimal portion of the space

occupied by the atom as a whole. Outside of this nucleus, at relatively vast distances from it—that is, in terms of measurements on an atomic scale—there are moving particles distributed around the nucleus, at various energy levels, in concentric shells or layers. These ultraminute particles are believed to revolve continuously around the nucleus with a speed of approximately 150,000 miles per second or very nearly the speed at which light travels.

Particles within atoms. There are now 102 known elements; hence, there must be at least 102 different atoms. For building these various atoms, nature appears to make use of three kinds of particles.



Oxygen atom *Carbon atom*

Fig. 34. An atom is composed of a nucleus surrounded by moving electrons—diagrammatic representations of atoms of oxygen and carbon.

First, there are the ***protons***, which are relatively heavy and carry 1 ultimate unit of positive electricity. Secondly, there are the ***neutrons***, which have about the same weight as the protons but are neutral as to charge. These particles are found in the nucleus. Thirdly, there are negative ***electrons***, which are relatively weightless[1] but carry 1 unit of negative electricity commensurate with the positive charge carried by the proton. The electrons are not found in the nucleus; they are the moving particles located in the field external to the nucleus.

All atoms of the same element have the same number of protons in their nuclei and an equal number of electrons in their external fields.

[1] Using the weight of the oxygen atom, with a value of 16, as the basis for comparison, a *proton* has a weight of 1.00758, a *neutron* a weight of 1.0087, and an electron weighs 0.000548.

This number is specific and different for each of the 102 known elements. For example, all carbon atoms have 6 nuclear protons and 6 electrons in the external field; all oxygen atoms have 8 nuclear protons and 8 electrons. The number of neutrons in atoms of the same element can vary slightly although, in general, they are either equal to or in excess of the number of protons. For example:

Carbon atom	*Oxygen atom*	*Chlorine atom*
6 protons, 6 neutrons in nucleus	8 protons, 8 neutrons in nucleus	17 protons, 18 neutrons in nucleus
6 electrons in external field	8 electrons in external field	17 electrons in external field

Because the number of protons equals the number of electrons, *the atom as a whole is neutral* when it is in possession of only its own family of particles.

WITHIN THE NUCLEI OF ATOMS

Composition, weight, and charge. The particles within the nucleus, the protons and neutrons, each carry one unit of weight; therefore, the weight of the nucleus corresponds to the number of particles composing the nucleus. And, because the electrons surrounding the nucleus are negligible as to weight, it follows that practically the entire weight of the atom is located in the nucleus.

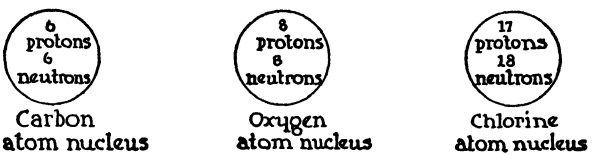


Fig. 35. Atom nuclei contain protons and neutrons.

The nuclei of all atoms are positively charged owing to the presence of protons; the extent of the charge is determined by the number of protons. Thus, the carbon atom with its 6 protons and 6 neutrons has a weight of 12 and carries a charge of 6 positive; the chlorine atom with 17 protons and 18 neutrons has a weight of 35 and a nuclear charge of 17 positive.

The atomic number. *The extent of positive charge carried by the nucleus of an atom determines its atomic number.* It corresponds to the number of protons in the nucleus, and, consequently, also indicates the number of electrons in the surrounding field. The atomic

number is significant because it *identifies the element*, also, because all elements with the same atomic number are *chemically identical.* (See atomic numbers listed in table of atomic weights.)

Isotopic elements. It has been discovered that there are three different forms of hydrogen element. These are identical as to chemical behavior but different in their atomic weights. For example, any specimen of water taken from a natural source is composed 99.98 per cent of hydrogen with a weight of 1; 0.2 per cent of hydrogen with a weight of 2; and about one part in a billion is hydrogen with a weight of 3. The same is true for other compounds of hydrogen. These three forms of the same element are known as *isotopes* of hydrogen. The light variety is simply called *hydrogen;* the element with a weight of 2 is known as *deuterium* or heavy hydrogen; and the rare

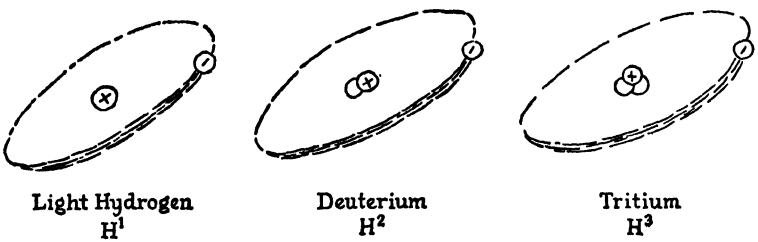


Fig. 36. Isotopes of hydrogen element.

isotope with a weight of 3 is called *tritium.* Elements other than hydrogen also form isotopes. Carbon, for example, occurs predominantly (98.9 per cent) as carbon with atomic weight 12, but a small fraction (1.1 per cent) is found to have a weight of 13. In fact, most of the elements appear to have two or more isotopes, that is, *chemically identical elements with different atomic weights.*

To explain the existence of isotopes, it is necessary to turn to the structure of the isotopic atoms. It is believed that nuclei of all isotopes of a given element contain the same number of protons, as indicated by the atomic number, but can contain different numbers of neutrons. Neutrons contribute to the weight of the atom but do not affect its chemical behavior. Thus, atoms of hydrogen isotopes all contain 1 proton, but hydrogen, deuterium, and tritium respectively contain no neutron, 1 neutron, and 2 neutrons (Fig. 36). Likewise, carbon atoms of atomic weight 12 contain 6 protons and 6 neutrons, whereas carbon atoms with a weight of 13 contain 6 protons and 7 neutrons. Theoretically defined, *isotopic atoms are atoms*

of the same element whose nuclei have the same atomic number since they contain the same number of protons, but different numbers of neutrons hence have different atomic weights.

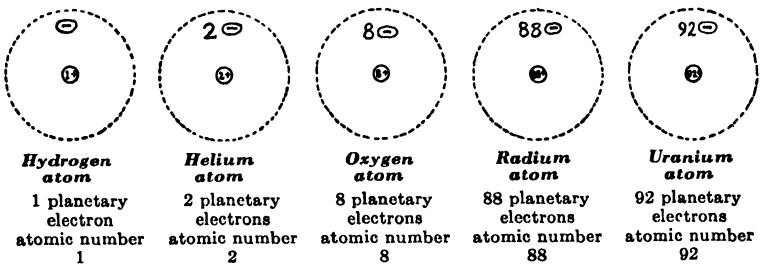
Because practically all, perhaps all, elements exist in one or more isotopic forms, the constant atomic weight of the element referred to in the table of atomic weights must represent the average atomic weights of the isotopic forms.

Shorthand representation of isotopes. The adopted practice for representing isotopes of elements is that of making use of the symbol for the atom with exponents expressive of its mass, that is, the inclusive number of protons and neutrons. For example, for isotopes of:

Hydrogen..... H^1 and H^2
Carbon..... C^{12} and C^{13}

IN THE FIELD SURROUNDING THE NUCLEUS

The moving bodies which surround the nuclei of the various atoms are negatively charged electrons held in the field by the attraction of the positively charged nucleus. There are as many electrons in the atom's external field as there are protons in its nucleus (Fig. 37).



Hydrogen atom	*Helium atom*	*Oxygen atom*	*Radium atom*	*Uranium atom*
1 planetary electron	2 planetary electrons	8 planetary electrons	88 planetary electrons	92 planetary electrons
atomic number 1	atomic number 2	atomic number 8	atomic number 88	atomic number 92

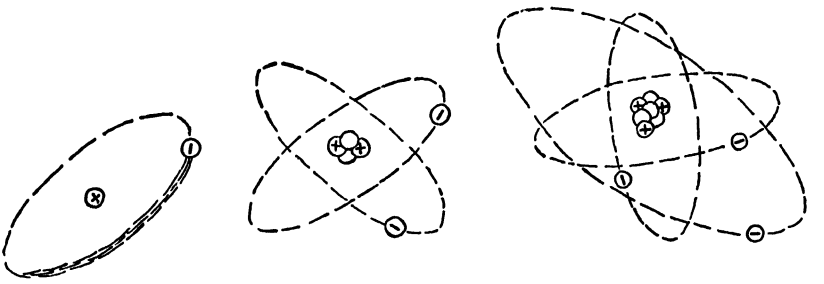
Fig. 37. The number of planetary electrons is the same as the number of protons in the atom's nucleus.

Thus, the *atomic number* acquires another significance (p. 119) in that it *tells how many electrons a neutral atom has in its external field.*

Distribution of electrons. The electrons are distributed around the nucleus in one or more concentric *shells* or energy levels. For each shell there appears to be a maximum electron capacity, and, when a shell becomes filled and sometimes before this, electrons must

SHELLS	MAXIMUM ELECTRON CAPACITY
1st	2
2nd	8
3rd	18
4th	32

find places in a shell farther out from the nucleus. In general, atoms appear to follow a definite system of electron distribution from hydrogen, with its one electron, to the newly reported element with atomic number 101.



Hydrogen *Helium* *Lithium*

Fig. 38. Diagrammatic representation of atoms of hydrogen, helium, and lithium—illustrating electron distribution.

The "just right" electron placements. There are certain electron distributions that appear to give stability within the external field of the atom. All atoms show a tendency to achieve these "just right" configurations. They are as follows:

The *first* distribution scheme provides for 2 electrons; both are in the shell closest to the nucleus.

The *second* distribution scheme provides for 10 electrons:

2 in the inner shell
8 in the second and outer shell

The *third* distribution scheme provides for 18 electrons:

2 in the inner shell
8 in the second shell
8 in the third and outer shell

The *fourth* distribution scheme provides for 36 electrons:

2 in the inner shell
8 in the second shell
18 in the third shell
8 in the fourth or outer shell

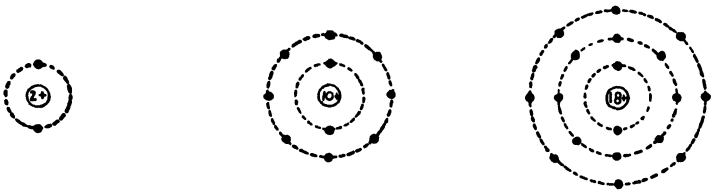
The *fifth* and *sixth* distribution schemes provide for 54 and 86 electrons, respectively, distributed in concentric shells as follows:

54 positions in five shells thus: 2, 8, 18, 18, 8
86 positions in six shells thus: 2, 8, 18, 32, 18, 8

Six "satisfied" elements. The elements whose atoms can just fill these stable electron configurations are:

atoms of helium with 2 planetary electrons
atoms of neon with 10 planetary electrons } (Fig. 39)
atoms of argon with 18 planetary electrons
atoms of krypton with 36 planetary electrons
atoms of xenon with 54 planetary electrons
atoms of radon with 86 planetary electrons

Atoms of these six elements appear to be "self-satisfied." They are neutral and have no combining capacities for atoms of other elements. This is consistent with the factual findings that the six elements—helium, neon, argon, krypton, xenon, and radon—are chemically inert and show no tendency to enter into chemical combination



Helium atom atomic number 2 ***Neon atom*** atomic number 10 ***Argon atom*** atomic number 18

Fig. 39. Diagrams indicating the number of electrons in each shell of the atoms of three of the six "self-satisfied" elements.

with other elements. The simple substances formed by these elements are known as the *inert gases.*

The valence shell of an atom. Each of the atoms of these "self-satisfied" elements, which compose the inert gases, have 8 electrons in their outer shells (with the exception of helium with its complete shell of 2). It is reasoned from this that a group of 8 electrons in the outer shell constitutes a balanced electron pattern which all atoms attempt to achieve, either in their own right or by combinations. *The outermost shell is known as the* ***valence shell*** *because it appears to determine the combining capacities of the atom.*

Atoms of other elements. But, what about atoms of those elements that cannot reach one of the "just right" electron configurations? They are believed to distribute their electrons as nearly as possible according to the preferred configuration, beginning with the 2 positions in the inner shell and proceeding progressively to other shells. Any electron-vacant positions occur in the outer shell (or in

the two outer shells in the case of atoms with large numbers of electrons). The atoms with atomic numbers 1 to 18, inclusively, distribute their planetary electrons as indicated in the following table.

Distribution of electrons in shells of atoms of elements—numbers 1–18

ATOMIC NUMBER	ELEMENT	SYMBOL	1ST SHELL	2ND SHELL	3RD SHELL
1	Hydrogen	H	1		
2	Helium	He	2		
3	Lithium	Li	2	1	
4	Beryllium	Be	2	2	
5	Boron	B	2	3	
6	Carbon	C	2	4	
7	Nitrogen	N	2	5	
8	Oxygen	O	2	6	
9	Fluorine	F	2	7	
10	Neon	Ne	2	8	
11	Sodium	Na	2	8	1
12	Magnesium	Mg	2	8	2
13	Aluminum	Al	2	8	3
14	Silicon	Si	2	8	4
15	Phosphorus	P	2	8	5
16	Sulfur	S	2	8	6
17	Chlorine	Cl	2	8	7
18	Argon	A	2	8	8

(For electron configurations of other elements, consult periodic table on front cover of this text.)

Two varieties of compensating adjustment. All of these atoms are neutral as to charge, and they are stable in respect to such shells as have their full quotas of electrons. But, when the valence shell is incomplete, there appears to be a condition of "strain." To relieve this condition, two types of compensating adjustment are believed to be possible: (1) a mutual lending and borrowing of electrons between atoms; and (2) a sharing of electrons between atoms (p. 127).

Lending and borrowing of electrons. Atoms of certain elements, notably those which most nearly approach one of the inert gas electron configurations, appear to *acquire stable electron patterns by lending or borrowing electrons.* For this type of adjustment the

atom must either completely empty or completely fill its valence shell. The lending of electrons appears to be limited to atoms that can achieve a stable configuration by lending 1, 2, or perhaps 3 electrons; borrowing seems to be limited to 1 or 2 electrons for each atom. When greater adjustment is required, the atom appears to share electrons rather than to either lend or borrow.

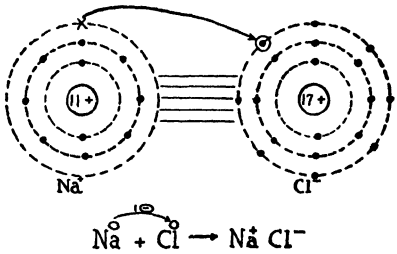


Fig. 40. The sodium atom lends the 1 electron from its outer shell, and the chlorine atom, with only 1 place to fill, borrows 1 electron. The sodium atom thus acquires a charge of 1 positive, thereby becoming a sodium ion. The chlorine atom, with one extra electron, forms a chloride ion with a charge of 1 negative. These 2 ions are attracted to each other, thus forming the compound sodium chloride.

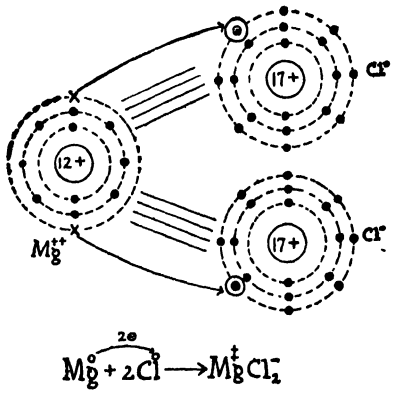


Fig. 41. When the atoms mutually concerned are magnesium and chlorine atoms, each magnesium atom upon lending the 2 electrons from its outer shell engages 2 chlorine atoms, each of which claims 1 of these electrons to fit into 1 otherwise vacant position. The magnesium atom becomes a magnesium ion with a positive charge of 2. Each chlorine atom becomes a chloride ion with a negative charge of 1. The oppositely charged ions are attracted to each other, thus making magnesium chloride.

The accompanying diagrams (Figs. 40 and 41) illustrate this type of adjustment, showing the number of electrons in each shell and the transfer of electrons from the valence shell of atoms of one element to atoms of another element.

An atom which has thus discharged one or more electrons from its outer shell will have an excess of protons in its nucleus over the number of electrons in the external field. The atom has, therefore, acquired a positive charge, the extent of which is determined by the number of electrons loaned. Likewise, the atom which thus borrows electrons acquires a negative charge commensurate with the number

of electrons borrowed. *Atoms which have become thus positively or negatively charged are known as ions.* Thus:

$$\underset{\text{Sodium atom}}{Na^0} - 1\ominus \longrightarrow \underset{\text{Sodium ion}}{Na^+} \qquad \underset{\text{Chlorine atom}}{Cl^0} + 1\ominus \longrightarrow \underset{\text{Chloride ion}}{Cl^-}$$

Ionic compounds. The oppositely charged ions formed when atoms lose or gain electrons have a mutual attraction and move up near to each other to form a neutral group. This results in what is known as an *ionic compound.* These ionic compounds, in the solid state, form crystals which appear to be composed of alternate positively and negatively charged *ions* (Fig. 42) rather than of discrete molecules.

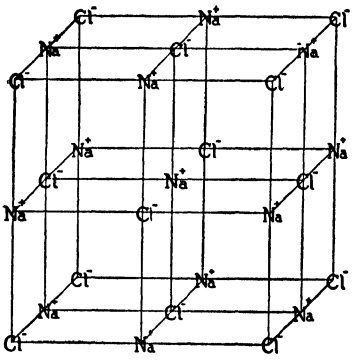


Fig. 42. Diagram showing structure of sodium chloride crystal with sodium ions and chloride ions alternating in cubical formation.

Valence in ionic compounds. *The valence of the element which thus enters into ionic combinations is believed to be determined by the number of electrons which the atom either lends or borrows.*

Accounting for known facts. The assumptions relating to lending and borrowing on the part of atoms help to account for known facts concerning elements. These assumptions explain the selectivity exhibited by certain elements in entering combinations. Thus, sodium and potassium, which become positively charged, readily form combinations with such elements as chlorine, bromine, oxygen, and sulfur, which become negatively charged. However, sodium and potassium do not combine with each other.

Ionic compounds, when dissolved in water, give evidence of the presence of charged particles because these solutions conduct an electric current (p. 220).

Elements whose atoms show similar electron configurations show similar chemical behavior. For instance, sodium and potassium compounds are very much alike; likewise magnesium, calcium, and barium compounds. Chlorides, bromides, and iodides have many similarities.

Metal and nonmetal elements. The elements whose atoms lend electrons are found to be the metal elements. The movement of the electrons from atom to atom helps to explain why metal substances conduct an electric current. On the other hand, the elements whose atoms function as electron receivers are nonmetal elements.

Compensation by sharing electrons between atoms. There are many substances that cannot be regarded as composed of oppositely charged particles. To account for their composition, another

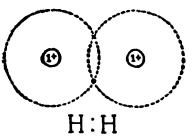


Fig. 43. Each of 2 hydrogen atoms is sharing its 1 electron with the other atom, thus providing 2 *electrons* for the valence shell of each atom. This is the simplest of the 6 "just right" electron configurations.

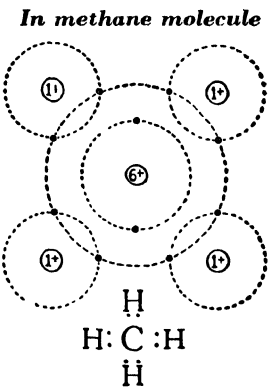


Fig. 44. The carbon atom has 4 valence electrons; a complete valence shell requires 8 electrons. Each of 4 hydrogen atoms moves up to the carbon atom and shares the electrons in such a way that the carbon atom has *8 electrons* in its valence shell and each hydrogen atom has *2 electrons* in its valence shell.

theory as to atom combination must be considered. In such substances, it is believed that atoms have combined to form stable electron configurations by *sharing electrons.* In such adjustments, two or more atoms move up to each other so that, through an overlapping of orbits, the full complement of 8 electrons (for hydrogen atoms 2 electrons) is obtained in the outer shell of each atom. In this way ***covalent molecules are formed.***

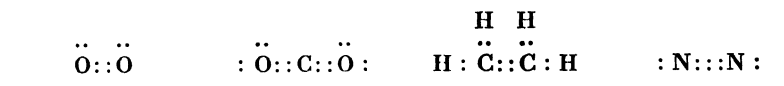
Molecules of simple substances, of many compounds (notably the carbon compounds), and also of radical groups are presumed to be formed in this way. The accompanying diagrams (Figs. 43 and 44) illustrate this type of combination.

Only the electrons in the outermost shells of the atoms are involved in the electron sharing which results in forming covalent molecules. Accordingly, it is the custom when building structural formulas for such molecules to represent only the electrons in the valence shells of the contributing atoms. A pair of valence electrons shared by two atoms constitutes a mutual bond which holds the atoms together in the molecule. The following are typical structural formulas for covalent molecules.



Representing a molecule of *water* | Representing a molecule of *ammonia* | Representing a molecule of *hydrogen chloride* | Representing a molecule of *chlorine*

In some combinations two, or even three, pairs of electrons are believed to be shared in forming a molecule, thus giving rise to *double* and *triple* bonds between atoms, as suggested by the following:



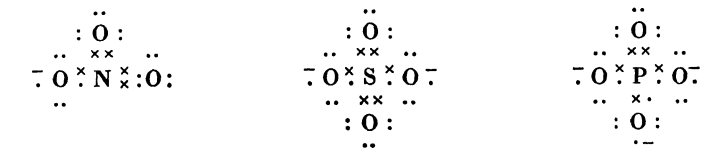
Representing a molecule of *oxygen* | Representing a molecule of *carbon dioxide* | Representing a molecule of *ethylene* | Representing a molecule of *nitrogen*

The covalent molecule. The compensation made between atoms through the mutual sharing of electrons is known as *covalence.* Since the atoms have neither loaned nor borrowed electrons, they maintain their neutral condition within the molecules which are established in this manner. Thus, the fact is explained that, within simple substances as well as within many compounds, although each contributing element exhibits a definite valence it remains neutral as to charge.

In general, the molecules established through covalent combinations are closely bound units and less active chemically than those in which the atoms are associated through the electrovalent combination in ionic compounds.

Covalence among atoms in radicals. Covalent groupings are also encountered among the complex radicals, such as the nitrate, sulfate, phosphate, and hydroxyl. Within such compounds the radi-

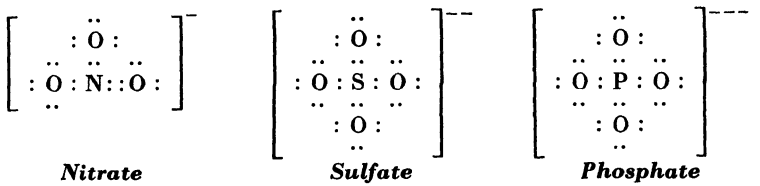
cals are negatively charged, indicating that in making up the atom group one or more electrons were acquired from some outside atom. Atom groups thus charged are known as *ions* and contribute to the formation of ionic compounds. The following formula representations for typical radicals suggest the valence compensations among the various atoms as well as the charge carried by the atom group as a whole.



Nitrate atom group ***Sulfate atom group*** ***Phosphate atom group***

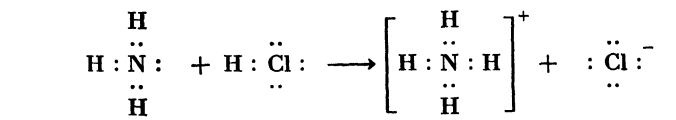
Electrons provided by the central nonmetal atom are represented by (x); electrons of oxygen atoms by dots (·); and the symbol (−) indicates electrons borrowed from or shared with atoms outside of the group itself.

The following are the more conventional representations for these radicals:



Nitrate ***Sulfate*** ***Phosphate***

The positively charged ammonium ion (NH_4^+) is another example of a covalent atom group. This ion appears when ammonia reacts with either water or acids. The molecule reaction is illustrated below:



Ammonia molecule ***Hydrogen chloride molecule*** ***Ammonium ion*** ***Chloride ion***

Formation of the ammonium ion illustrates the theory that a pair of unused electrons in the valence shell may attract another atom. The fourth hydrogen atom in the ammonium ion is held by an elec-

tron pair which is provided by nitrogen only, the hydrogen atom having left its valence electron with the chloride ion. Such a bond, when both electrons have been provided by one of the atoms, is known as a *coordinate bond.* This type of bond is presumed to account for the formation of ion complexes—for example, hydrates, which will be encountered later.

In thinking of these covalent molecules it should be kept in mind that electrons are in continuous motion, revolving around the nuclei of atoms. This motion persists within the molecule, and the shared electrons are thought of as being located sometimes in the external field of one of the combined atoms and sometimes in the field of the other atom. It is also to be kept in mind that atoms and molecules are three dimensional—in spite of diagrams with their obvious two-dimensional limitations. Thinking in three dimensions is particularly helpful when trying to get a picture of the double and triple bond combinations.

Valences exhibited by atoms of elements. *The valence of an element is believed to be determined by the number of electrons which its atom lends, borrows, or shares in forming combinations with atoms of other elements.* Lending and borrowing of electrons results in electrovalent or ionic compounds. Sharing of electrons results in forming covalent molecules or in forming atom groups known as radicals.

QUESTIONS

1. Describe, in general, the conditions believed to exist within (a) the nucleus of an atom; (b) the external field of an atom.
2. There are three isotopes of oxygen, represented as follows: O^{16}, O^{17}, O^{18}. What is meant by the term "isotope"? Illustrate by reference to the presumed composition of the atoms suggested above.
3. What is the atomic number of an element and what is its significance?
4. On the basis of their atomic numbers, account for the negative valence of 2 of sulfur, for the positive valence of 1 of potassium. What type of compound would result from reaction of potassium with sulfur? Represent by formula.
5. Why, theoretically, are there no compounds of helium?
6. What, in general, determines the valences exhibited by ions within ionic compounds?
7. What is meant by the expression "a covalent molecule"? Explain why such molecules are neutral. Illustrate by reference to the compound hydrogen sulfide; the compound carbon tetrachloride.
8. Define valence from the standpoint of atom behavior.

CHAPTER 12

RADIOACTIVE ELEMENTS

As has already been mentioned, the discovery of radioactive elements and the scientist's subsequent experimental quest for greater understanding of this natural phenomenon were instrumental in bringing about the modern understanding of matter and new concepts of atom structure. But radioactive elements are also of interest in their own right because of their uses both actual and potential.

Historical. Prior to about 1900 it was supposed that all elements were completely stable, meaning that they never underwent destruction. Earth was believed to possess just so much of each of these elementary building materials and, aside from an occasional meteor bringing element material from the outside universe or loss of small quantities of gases at the outer boundaries of earth's atmosphere, the quantities of none of the elements underwent change. Then came the discovery that certain of the elements were undergoing a process of natural, spontaneous disintegration accompanied by the discharge of radiations around the material. These became known as radioactive elements.

The first inkling of this situation came in 1896 when Henri Becquerel, a French scientist, was engaged in a study of material containing the element uranium. In his laboratory, some of this material came in contact with a photographic plate which was well protected from light. To the amazement of the experimenter this plate became "light struck" and Becquerel postulated that this effect must come from some form of radiation emanating from the mass of material, seemingly rays not unlike the x-rays which had been discovered only a year previously by Wilhelm Roentgen.

Madame Marie Curie undertook the problem of discovering the source of the radiations, and, when the uranium compounds had

been separated from the mass, she discovered that the residue contained an even more active substance. In 1898, after the laborious task of separating the substance containing the radioactive element from a ton of uranium ore, Marie and Pierre Curie reported the discovery of a new element which they named *radium*. Since then other naturally occurring radioactive elements have been discovered. They are, for the most part, elements of high atomic number and high atomic weight. In fact, all elements after lead, atomic number 82, have radioactive isotopes. Among the lighter-weight elements exhibiting natural radioactivity are potassium (K^{40}) and carbon (C^{14}); however, these isotopes occur in relatively small proportions in relation to the element as a whole.

The radiations. The naturally occurring, heavy elements give out three varieties of radiations known, respectively, as alpha, beta, and gamma radiations.

Alpha (α) *radiations* are particles, each of which carries 2 units of positive electricity and has a mass of 4. Hence, these particles have been identified as nuclei of helium atoms. They travel with a speed approximately one tenth the speed of light. They are not penetrating since they can be stopped within a few inches from their source by impact against air or by such obstructions as a sheet of paper or very thin metal. On contact with the body they do not penetrate beyond the surface layer of skin.

Beta (β) *radiations* are negatively charged, relatively weightless particles, which travel with speeds approximating the speed of light (186,000 miles per second). As a result they are more penetrating than the alpha radiations, but they can be stopped by thin sheets of metal—1 mm of silver or lead. They penetrate tissue to about the depth of 1 cm. The beta particles have been identified as swiftly moving *electrons*.

Gamma (γ) *radiations* appear as energy manifestations rather than as particles. They are electromagnetic radiations similar to x-rays (Fig. 45), but, in general, of shorter wave length and, consequently, more penetrating. This accounts for the fact that, therapeutically, gamma rays and x-rays have similar uses.[1] These radiations penetrate tissue but are stopped by heavy metals, notably lead. A shield

[1] Actually, it is not possible to distinguish between x-ray and gamma ray, but when the radiation originates in a radioactive element it is referred to as gamma radiation whereas radiations coming from the cathode tube are known as x-rays.

of lead 1.3 cm (½ in.) thick will absorb about 50 per cent of this energy, but even a thickness of 15 cm (6 in.) permits the passage of some radiation.

Source of radiations. Both alpha and beta radiations are believed to originate within the nuclei of radioactive elements. Their ejection means the loss of some of the nuclear contents. Hence, this leaves a nucleus of different composition and, consequently, a different element.

It will be recalled that the nucleus of each atom is believed to be composed of a definite number of positively charged protons, a different number for each element, together with a somewhat variable

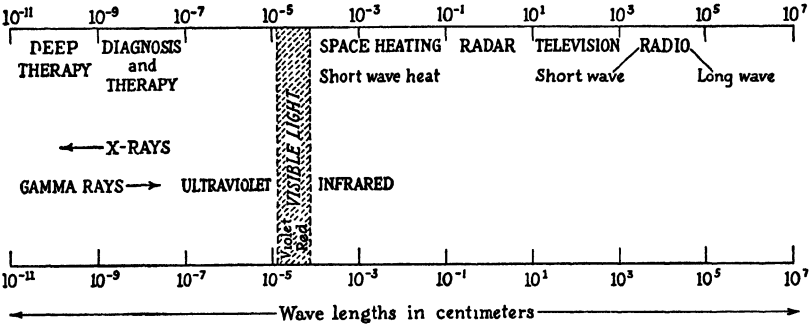


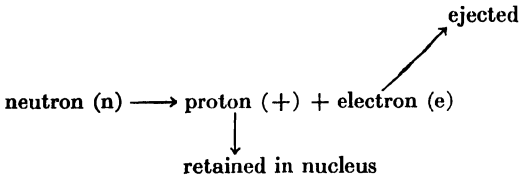
Fig. 45. Diagrammatic representation of range of electromagnetic radiations, with wave lengths indicated in centimeters. The *gamma radiations* and *x-rays* have short wave lengths and consequently great penetration.

number of neutrons (p. 120). Since neutrons are neutral in charge, they can be packed close together. But protons, with their positive charges, although distributed among neutrons, tend to repel each other. In the heavy elements with high atomic numbers, the nucleus is crowded with particles, many of them positively charged, and a condition of strain develops within the nucleus. Under these conditions, some of the atoms begin to eject particles from their nuclei and are said to be *radioactive.*

The disintegration of uranium. The diagram on page 135 (Fig. 46) illustrates the disintegration of the element uranium (U^{238})— terminating in a stable isotope of lead (Pb^{206}).

The ejection of an *alpha particle* means the loss from the nucleus of 2 protons and 2 neutrons, thus reducing the atomic number by 2 units and the atomic weight by 4 units.

The alpha particles are not difficult to explain, but how are beta particles accounted for since there are no electrons in the nucleus? The ejection of a ***beta particle*** increases the atomic number by one unit but does not change the atomic weight. One commonly accepted theory is that a beta particle results from the explosion of a neutron to make a proton and an electron. *The electron is ejected from the nucleus*[2] while the *proton remains behind.*



Gamma radiations frequently accompany these nuclear disturbances and are believed to be the result of energy adjustments within the atom accompanying the loss of nuclear material.

A series of new nuclei, hence different elements. When an atom becomes thus activated, a series of new nuclei appear. The ejection of particles is believed to continue, step by step, until a stable nucleus is attained. In the disintegration of uranium isotopes, a number of elements appear, including the well-known element *radium* and its daughter element *radon*, but the series does not end until a stable isotope of *lead* is reached. Actually, scientists find that in uranium ores, such as pitchblend, these intermediate elements all occur in varying proportions. The proportion of uranium element to lead element affords a clue as to how long this disintegration has been going on, hence to the age of the ore.

Fate of the ejections. Alpha, beta, and gamma radiations, as they escape into the surrounding air, leave a train of charged particles, or ions, in their wake. The charged *alpha* and *beta particles* set up disturbances among the orbital electrons of other atoms along their path. *Gamma rays* are claimed to produce ions, by virtue of their energy, through activating electrons in the external fields of atoms, thereby causing electrons to escape from their orbits.

[2] Electrons are obtained from sources other than radioactive elements. A current of electricity is believed to be a flow of electrons directed through a conducting medium. Any electric spark, from small sparks to immense ones like a flash of lightning, marks the passage of small or enormous showers of electrons from one location to another. But, while electrons are electrons—all alike—only those of radioactive element origin are referred to as beta particles.

Thus, all three give rise to *ions*, some positively charged, some negatively charged, and, therefore, are known as *ionizing radiations*. Sooner or later, the *alpha particle* attracts to itself a pair of electrons, thus forming an atom of helium.[3] The *beta particles*, or electrons, gradually lose energy from impacts with various atoms and, at length, come to rest in the external field of some atom or group of atoms.

Half-life periods of radioactive elements. The rate of disintegration of radioactive elements is calculated in half-life periods. Each element, indeed, each isotope, has its own specific half-life period, hence its own rate of disintegration.

The term *half-life* may be defined as the period of time required for a given weight of the specific radioactive element to decrease to half of its original value. Thus, at the end of 2 half-life periods only ¼ of the original element remains; at the end of 3 half-life periods only ⅛ of the element remains. From this point of view, a radioactive element never becomes completely inactive. However, for an element with a short half-life period, the activity will presently be negligible in degree.

Radium has a half-life period of 1620 years; consequently, it exhibits a relatively steady radiation. The parent element uranium has

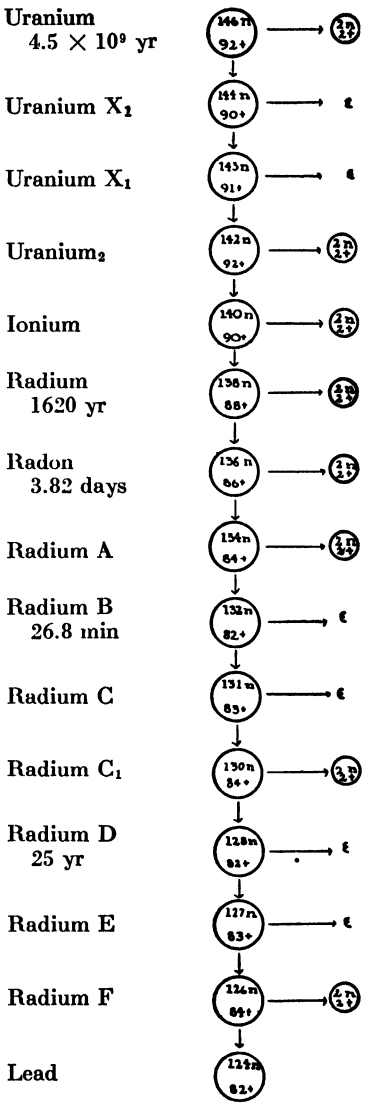


Fig. 46. Disintegration of atom nuclei, beginning with that of uranium, and the series of elements involved.

[3] The inert gas helium is found where deposits of naturally occurring radioactive elements occur.

a half-life of 4,500,000,000 (4.5×10^9) years. Other elements have briefer half-life periods; that of radon is 3.82 days, that of radium B is 26.8 minutes, and that of radium D is 25 years (Fig. 46).

Radium and radon. Of the naturally occurring radioactive elements, both *radium* and its daughter *radon* have special interest because of their therapeutic use, notably in treatment of cancer. For

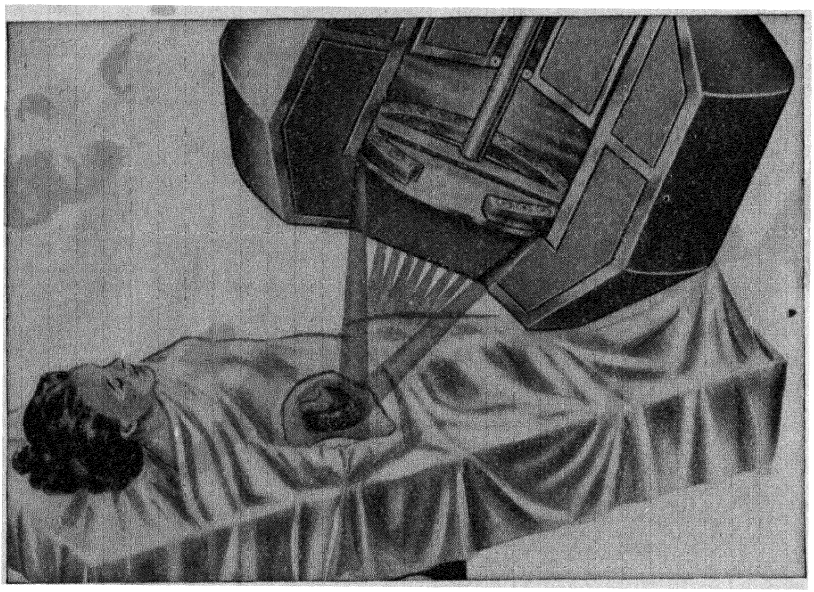


Fig. 47. The radium beam used in therapy—an artist's concept. Radiations from 25 capsules of radium are focused on a tumor. Note the spreading of the radiations from each capsule of radium; also observe the shielding, by thick walls of metal, that is provided by the instrument. (From *Science News Letter*, 61:215, 1952. Courtesy of Science Service, Washington, D.C., and The Roosevelt Hospital, New York City.)

this use *radium* compounds, usually radium sulfate, are sealed in capsules of platinum or some other heavy metal. These radium-carrying capsules are then implanted directly into the tissues to be irradiated. Other methods for bringing the radiations in contact with diseased tissues include a "beam" of radiation which may be focused on the tumor from radium which is carefully shielded in a specially devised machine as suggested in Figure 47.

The element *radon*, following radium in the radioactive series, is one of the inert gases. For therapeutic use it is collected from radium chloride held in solution in water. The radon is pumped off from the solution and collected in

fine tubing of glass or metal which, subsequently, is passed along to a machine that automatically cuts it into short lengths and at the same time seals in the gas. Radon, thus enclosed in platinum capsules or in tiny gold-walled "radon seeds," can be implanted directly into the diseased tissue. A wall of 0.5 mm of either of these metals will retain effectively both alpha and beta radiations but will allow the escape of gamma radiations. Radon reaches its maximum activity about 4 hours after it is collected. With a half-life period of 3.82 days, its therapeutic life is brief; at the end of 30 days 99.5 per cent of its radiation has been expended.

The therapeutic value of these radioactive elements lies in the fact that gamma radiation is destructive to tissue cells (see p. 140). It is sometimes possible to place the radon or radium in the tissue in such a way that malignant cells will receive sufficient damage to destroy them without damaging normal, healthy tissue to a degree beyond which nature cannot restore the cells. This is the principle on which both gamma radiation and the related x-rays are used therapeutically.

Artificially made radioactive elements. The radioactive disintegrations discussed thus far are naturally occurring phenomena associated, for the most part, with elements of high atomic number and high atomic weight. In 1934 the Joliot-Curie team announced the production of laboratory-induced radioactivity as the result of bombarding the lightweight metal aluminum with alpha particles.

$$Al^{27} + He^{4} \longrightarrow P^{30} + n^{1}$$

Subsequently, other "lightweight," stable elements have been activitated by bombardment with alpha particles, deuterons, neutrons, or protons obtained from radioactive sources, and a variety of radioactive isotopes of common elements have been artificially produced.

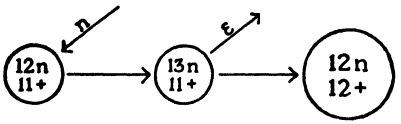
The theory, in part, which explains these nuclear reactions is that when the nucleus of any "lightweight" atom is made heavier by the capture of a neutron or when it acquires too heavy a charge by the capture of a proton, a disturbed, hence, a radioactive, nucleus is made. Consequently, such readjustments set in, including the ejection of particles or release of energy or both, as will stabilize its content. The making, by artificial means, of radioactive sodium is an example, as follows.

It is known that when a sodium compound is bombarded with neutrons, the very small portion of the

stable sodium element attacked	becomes ⟶	a "heavy" radioactive sodium isotope which ejects electrons	leaving ⟶	stable magnesium which takes the place of the sodium

Explanation. Within the atoms affected

the stable nucleus of the ordinary sodium atom captures a neutron **becomes** a "heavy" radioactive sodium atom nucleus; a neutron changes to a proton and electron; the proton is retained, the electron is ejected **leaving** a stable nucleus of a magnesium atom



$Na^{23} + n \longrightarrow Na^{24} \longrightarrow Mg^{24} + e$

Another source of radioactive elements has been the atomic pile; many and varied isotopes have been recovered as the result of nuclear fission. Among the radioactive elements that have come to have considerable importance in various types of research are: hydrogen (H^3), carbon (C^{14}), phosphorus (P^{32}), and iodine (I^{131}). Radioisotopes of cobalt (Co^{60}) and of gold (Au^{198}) have come into use in the treatment of cancer. Further information concerning radioactive elements here mentioned is given in the table below.

ELEMENT	ISOTOPE	HALF-LIFE PERIOD	RADIATIONS	REMARKS
Hydrogen	H^3	12.5 yr	Beta	Known as tritium
Carbon	C^{14}	6360 yr	Beta	
Phosphorus	P^{32}	14.30 days	Beta	
Potassium	K^{40}	15×10^8 yr	Beta, Gamma	Of natural occurrence
Calcium	Ca^{45}	152 days	Beta	
Cobalt	Co^{60}	5.26 yr	Beta, Gamma	
Iron	Fe^{59}	46 days	Beta, Gamma	
Iodine	I^{131}	8 days	Beta, Gamma	
Gold	Au^{198}	2.7 days	Beta, Gamma	

Information from Behrens, Charles F. (ed.): *Atomic Medicine*, 2nd ed. Williams and Wilkins Company, Baltimore, 1953.

Unusual isotopes used as tracers. Following the discovery of isotopes and the production of artificially induced radioactivity in various elements, scientists recognized that the more unusual forms of some of the commonly encountered elements might provide effective means for studying reactions within living cells. Deuterium (H^2), the heavy, stable isotope of hydrogen in "heavy water," was discovered by Urey in 1932, and shortly thereafter substances containing the less abundant isotopes of carbon, oxygen, nitrogen, and sulfur were separated

in small but useful concentrations from natural materials. By 1937, important findings had already begun to appear as a result of incorporation of the unusual isotopes of hydrogen (H^2) and nitrogen (N^{15}) in fatty acids and amino acids to be used as foods for animals. These first tracer elements were not radioactive but, because of their significant difference in mass, could be identified in material under study.[4]

In 1934, radioactive phosphorus was produced in the cyclotron of the University of California, and this became the first of the radioactive isotopes to be introduced into a compound for use in biological research. A radioactive compound of phosphorus (P^{32}) has been used in a variety of studies, notably in the study and therapeutic treatment of leukemia and polycythemia, disorders affecting the blood-forming cells. Other artificially produced radioactive elements which are used as biological tracers include the following: radioactive iron (Fe^{59}) in iron salts for the study of anemia and the building of hemoglobin; radioiodine (I^{131}) in iodides for the study of thyroid tissue and the therapeutic effect of the radiation on thyroid tissue; radioactive calcium (Ca^{45}) in calcium compounds to learn more of the metabolism in bones and teeth.[5] One of the most important of the newly produced isotopes is radioactive carbon (C^{14}), which, because of its long half-life period, lends itself to study of organic reactions of biological importance; this isotope of carbon is also of use in industrial processes. Researches with tracer isotopes have been extended to a limited extent to the study of microorganisms. Tubercle bacilli have been rendered radioactive, and a radioactive virus has been reported. Agriculturalists are also using tracer elements to obtain greater knowledge of factors contributing to plant growth.[6]

The principle underlying the use of radioactive tracers is that all isotopes of any given element exhibit the same chemical behavior. The living animal does not discriminate in the use of isotopes; consequently the compounds, marked because of the presence of these unusual elements, follow the same fate as the element occurring naturally in the same substances. The unusual, *stable* isotopes can be detected by differences in mass; the *radioactive* isotopes record their presence, even in the tissues of the living animal, by radiations which can be recorded on a Geiger-Müller counter. The radiations include neutrons, electrons, and gamma radiation; hence, protection of individuals coming in contact with this material must be considered.

The early methods for separation of substances containing stable isotopes, also production of radioactive elements in the cyclotron, yielded quantities too small to be measurable by weighing. One of the outcomes of the development

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[4] Schoenheimer, Rudolf: *The Dynamic State of Body Constituents.* Harvard University Press, Cambridge, Mass., 1946.

[5] Behrens, Charles F. (ed.): *Atomic Medicine*, 2nd ed. Williams and Wilkins Company, Baltimore, 1953, Chaps. 17 and 18.

The Contributions of Atomic Energy to Medicine: Hearings before the Subcommittee on Research and Development of the Joint Committee on Atomic Energy, Congress of the United States, June 2, 3, and 4, 1954. U.S. Govt. Printing Office, Washington, D.C., 1954.

[6] *The Contributions of Atomic Energy to Agriculture:* Hearings before the Joint Committee on Atomic Energy, Congress of the United States, March 31 and April 1, 1954. U.S. Govt. Printing Office, Washington, D.C., 1954.

of the uranium pile for production of atomic bombs has been to provide a source from which many of these radioactive elements can be obtained in weighable quantities—milligrams, grams, and in some instances even kilograms. Moreover, these are available to institutions equipped for such research at a cost which makes their use a practical possibility. One of the foremost scientists engaged in atomic research makes the following statement concerning the importance of this development. "It is not out of the question that the greatest gains to humanity from atomic-energy development will result from the widespread use of tracers to solve a multitude of problems rather than from the harnessing of the power itself."[7]

Effects of radiations on tissue. Early in the study of radioactive elements, the pioneer laboratory workers became aware of potential damage to tissues. Becquerel, the Curies, and others reported tissue injury which was slow to heal following accidental or deliberate exposure.[8] But, in spite of this early recognition of damage to tissues many of the pioneer workers suffered, some even died, as the result of lack of protective measures.

All of the radiations emanating from radioactive elements are destructive to living cells. These radiations produce changes in substances within the cells, the exact nature of which is, as yet, uncertain, although a number of interesting theories have been advanced.[9] Not all cells are equally sensitive to radiation. In general, the most sensitive tissues are those whose cells are in the process of active multiplication; these include blood-forming cells, epithelial cells, and reproductive tissues; cancer cells also come under this category. Bone cells, muscle cells, and nerve cells are less sensitive to radiation. Be-

[7] Seaborg, Glenn T.: "Artificial Radioactive Tracers: Applications to Chemistry and Medicine," *Science*, 105:349–52, 1947.

[8] The following item is reprinted with permission of *Scientific American*, August 1901: "All the leading workers on the subject of radium rays have in turn subjected their own persons to some painful experiments for the advancement of their fascinating branch of science. Giesel placed a radium preparation in a celluloid case on his arm for two hours. The skin showed only a slight reddening at first, but two or three weeks afterward inflammation set in and the skin came off. Becquerel placed a very active radium preparation in his waistcoat pocket for six hours. The resulting sore—which took 10 days to develop—required 39 days to heal. Another sore took 34 days to develop. No action was produced when the tube was encased in lead. Madame Curie underwent experiments of similar nature. The preparation was in her case enclosed in a thin metallic box, and applied for only half an hour; but the resulting burn took a fortnight to heal."

[9] Glasstone, Samuel: *Sourcebook on Atomic Energy*, D. Van Nostrand Company, Inc., New York, 1950, p. 502.

Spoerl, Edward: "The Lethal Effects of Radiation," *Scientific American*, 185:22–25, 1951.

cause the rays are intangible, the results of damage do not become apparent immediately. Consequently, the uninformed worker is likely to discount the risks involved. It becomes important that workers who may be exposed to radiation should understand the necessary protective measures.

Principles underlying protection. The principles for protection against excessive exposure to radiation are known, and, when intelligently applied in practice, the worker is afforded a high degree of safety.[10]

1. ***Minimize exposure to radiations.*** This implies avoiding unnecessary exposure and, when exposure is necessary, streamlining

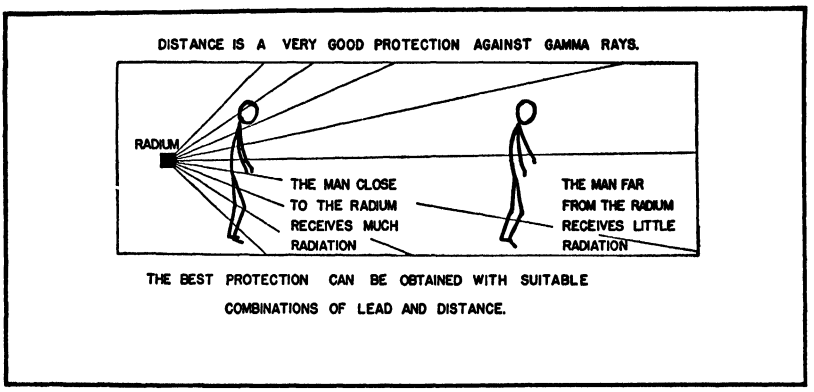


Fig. 48. Protection in radiology. (Reproduced from an exhibit prepared by Edith H. Quimby and John Pool. Courtesy of the Radiological Society of North America, Inc.)

procedures to *reduce time of exposure.* Radiation laboratories are equipped with various types of monitoring devices by which the degree of radiation in an area can be measured. Workers often wear film badges, essentially photographic films, devised to measure the radiation to which the film, and its wearer, have been exposed. These instruments, of course, give no protection; however, they do give information as to the extent of radiation in the area.

2. ***Maintain an appropriate distance from source of radiation.*** The farther the worker is from the source of the radiation, the greater his safety. This is illustrated in Figure 48. Because radiations disperse in all directions, the *intensity of the radiation received*

[10] Frazier, P. M.; Buchanan, C. R.; and Morgan, G. W.: "Radiation Safety in Industrial Radiography with Radioisotopes," *Isotopics*, 5:9–29, 1955.

decreases in proportion to the square of the distance from the source of radiation. Thus, if we ignore the absorption of radiation by air particles and the rebound of some of the radiation from nearby obstructions, a person receiving a given amount of radiation at 1 ft from a source may reduce the quantity of radiation received to $\frac{1}{4}$ by moving to 2 ft from source. If he moves to a distance of 3 ft from source he then receives only $\frac{1}{9}$ the radiation he received in the first position. The use of long-handled instruments when working with radioactive material is another application of this principle.

3. ***Use of effective shields.*** Radiations tend to be absorbed on contact with material. In general, the denser the material the more effective it is in shielding. As we have learned (p. 132) alpha particles present no serious problem except through immediate contact. The thin platinum and gold capsules used to enclose radium and radon cut off beta radiations (p. 132). But, for protection against gamma radiations, heavy lead-walled containers and lead shields are used. In buildings, thick walls of cement, or cement reinforced with metal, are employed to afford suitable protection.

Because conditions for use of radioactive materials vary in different situations according to the element, the quantity of material, whether encountered as a gas, a solid, or in solution, the methods used vary in different situations. But, in all instances these *three principles* must be taken into consideration. In general, intelligent application of these principles will enable personnel who have adequate knowledge of the situation to set up practices which reduce the danger to the workers to levels that compare favorably with those encountered in other professional or industrial hazards.[11]

Nuclear Fission and Atomic Energy. What is perhaps the most momentous development in nuclear reactions came in 1939 when the fission of uranium element was recognized. When uranium-containing material was bombarded with neutrons, it was discovered that various other elements with approximately half of the atomic weight and atomic number of uranium element appeared. It proved to be the uranium isotope U^{235} that was fissioned; that is, the nuclei of atoms of this element split on impact with neutrons giving rise to

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[11] Quimby, Edith: "Safety in the Use of Radioactive Isotopes," *Am. J. Nursing*, 51:240–43, 1951.

Brucer, Marshal: "Radioisotope Hazards and Protection in a Hospital," *J.A.M.A.*, 147:1745–50, 1951.

Glasstone, Samuel: *Sourcebook on Atomic Energy*, Chap. 18, "Radiation Protection and Health Physics."

two smaller nuclei and the escape of from 2 to 3 neutrons for each atom thus broken up. This in itself was a significant discovery, but of even greater importance was the sudden release of a tremendous energy product. Energy production on such a scale is unknown so far as ordinary chemical reactions are concerned, or even the release of energy in the course of radioactive disintegration. Moreover, the ejection of neutrons opened up the possibility of a self-perpetuating or chain reaction.

$$U^{235} + n^1 \longrightarrow \text{2 nuclear fragments} + \text{Neutrons} + \text{Energy product}$$

The atomic bomb with its terrible threat of destruction is one outcome of this discovery. But also, as by-products of this reaction have come many of the radioactive isotopes which have been made available for research. A great and as yet undeveloped potentiality arising from this epoch-making discovery is a new source of energy which may be harnessed for peaceful use in performing much of the needful work of the world.

QUESTIONS

1. What, factually, is a radioactive element? Name three. How is the radioactivity of elements explained?
2. Describe each of the three radiations given off by the heavy, naturally occurring radioactive elements.
3. Radium has a half-life of 1620 years; radon has a half-life of 3.82 days. What does this mean?
4. Look up information as to current research being carried on with the use of radioactive isotopes of common elements. List the isotopes so used and the types of problems under study.
5. What are possible sources of isotopic forms of such elements as carbon, phosphorus, potassium, and iodine?
6. Why is it important that workers be protected from undue exposure to radioactive elements?
7. How can such elements as radium and radioactive iodine be used therapeutically when radiation is injurious to all living cells?
8. State three principles involved in minimizing exposure to workers where radioactive elements are in use. Illustrate by at least one example how each of the principles is carried out in practice.
9. The directions in hospital *X* regarding the temporary storage of radium or radon on the ward call for their being stored in a heavy lead container and located at least 6 ft away from any patient or worker on the unit. Explain the necessity for these precautions.
10. A worker handling a known quantity of radium with forceps receives x millicuries of radiation per second when his fingers are 3 in. from the radioactive source. How much radiation, comparatively, would he receive with his fingers at a distance of 12 in. on the long-handled forceps?

CHAPTER 13

INTRODUCTION TO ACIDS, BASES, AND SALTS

Among the inorganic compounds acids, bases, and salts are of outstanding importance not only because of the frequency with which they are encountered but also because of their chemical activity. Acids and salts also occur among the organic compounds. We are about to enter upon a series of studies in which these compounds will be encountered, sometimes as reacting substances, sometimes as products. Our first step will be to become acquainted with the composition of acids, bases, and salts as a means of recognizing substances which come under these classifications.

Composed of radical parts. Every acid, base, and salt is composed of two more or less loosely combined parts called radicals. Some radicals, such as chloride, are composed of but one element; others, such as nitrate, are composed of two (or more) closely combined elements.

When a pair of these compounds, such as an acid and a base, an acid and a salt, or a base and a salt are in contact *in water solution*, an interchange of their partner radicals in a double decomposition reaction may occur. For example:

When hydrochloric acid and silver nitrate are the compounds in contact with each other in water solution, an interchange of partner radicals begins at once to take place to make nitric acid and silver chloride; the latter compound, being insoluble, precipitates:

$$\text{Hydrogen chloride} + \text{Silver nitrate} \longrightarrow \text{Hydrogen nitrate} + \text{Silver chloride} \downarrow$$

$$HCl + AgNO_3 \longrightarrow HNO_3 + AgCl \downarrow$$

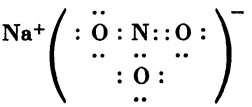
The following formulas represent typical compounds. The dot, which is not customarily used in the formula, is introduced to set

off the radical parts of each compound and to indicate the point of loose combination.

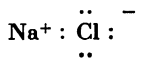
Hydrogen chloride		*Sodium nitrate*	
$H \cdot Cl$		$Na \cdot NO_3$	
hydrogen radical	chloride radical	sodium radical	nitrate radical
Hydrogen nitrate		*Sodium chloride*	
$H \cdot NO_3$		$Na \cdot Cl$	
hydrogen radical	nitrate radical	sodium radical	chloride radical
Hydrogen sulfate		*Potassium hydroxide*	
$H_2 \cdot SO_4$		$K \cdot OH$	
hydrogen radical	sulfate radical	potassium radical	hydroxide radical
Hydrogen acetate		*Ammonium hydroxide*	
$H \cdot C_2H_3O_2$		$NH_4 \cdot OH$	
hydrogen radical	acetate radical	ammonium radical	hydroxide radical

Theoretical explanation. The explanation for the easily displaced radicals in these compounds is believed to relate to the molecular structure. Many bases and most salts are *ionic compounds* (p. 126); as such they do not form discrete molecules but build crystalline structures in which oppositely charged ions are held together by the attraction of the opposite charges. In water the ions are set free in solution. The following are examples.

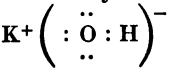
Sodium nitrate



Sodium chloride

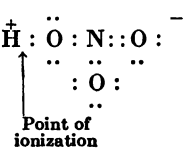


Potassium hydroxide



Acids are believed to form covalent molecules (p. 128) as do also some bases and some salts, but these molecules have a more or less marked tendency to separate into ions when such compounds enter water solution. The point of ionization in the molecule of a typical acid is illustrated in the following diagram.

Positive pole of molecule, consisting of an ionizable hydrogen atom.



Negative pole of molecule, composed of the nitrate atom group, a close combination

BASES

Constituent radicals. The radicals which enter into the composition of every base are as follows.

A metal radical which is composed of a displaceable metal element or the ammonium radical (NH_4)	and	*The hydroxyl or hydroxide radical* which is composed of hydrogen and oxygen in close combination

Outstanding bases. Some bases of more or less frequent occurrence are listed in the accompanying table.

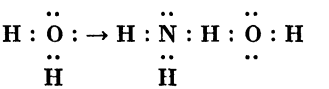
CHEMIST'S NAME	COMMON NAME	COMPONENT OF	FORMULA FOR MOLECULAR WEIGHT AND MOLECULE
Sodium hydroxide	Caustic soda		NaOH
Potassium hydroxide	Caustic potash		KOH
Calcium hydroxide	Slaked lime	Limewater Milk of lime	$Ca(OH)_2$
Magnesium hydroxide		Milk of magnesia	$Mg(OH)_2$
Ammonium hydroxide*	Aqua ammonia	Household ammonia	NH_4OH

* ***Note:*** Although it is customary, and often convenient, to refer to ammonium hydroxide as a compound, no such substance has ever been separated from solution. Solutions to which this name is applied exhibit behavior characteristics of ammonium compounds and also of bases. Ammonium hydroxide is made when ammonia gas dissolves in water. Thus:

Ammonia + Water → Ammonium hydroxide

$NH_3 + H_2O \rightarrow NH_4OH$

The molecule involvement



The radical common to bases. All such bases contain the *hydroxyl* radical; this accounts for the properties common to bases. The variable, and that which determines the specific base, is the *metal* or *ammonium radical.*

In reaction with red litmus. When bases are in water solution, they react with selected colored substances in a characteristic manner. One such colored compound is *red litmus*, and the product made from its reaction with bases is *blue litmus*.

In water solution

Sodium hydroxide + Red litmus ⟶ Blue litmus
Ammonium hydroxide + Red litmus ⟶ Blue litmus
} in conspicuous quantities

Some bases, copper hydroxide for instance, are so slightly soluble that they do not give appreciable reaction with red litmus.

Strong and weak bases. *A strong base is very active chemically.* Sodium and potassium hydroxides are very strong bases; calcium and magnesium hydroxides are strong, but they are not very soluble, and bases must be in water solution to participate in reactions peculiar to them. *A weak base is much less active chemically* than a strong base. Ammonium hydroxide is a weak base. The theoretical explanation for these differences will be considered later (Chap. 17).

ACIDS

Constituent radicals. The radical parts which enter into the composition of every acid are as follows:

A hydrogen radical which is composed of easily displaced hydrogen element

and

A radical, called ***an acid radical,*** which is composed of:

1. A *nonmetal element*, such as chlorine, bromine, iodine, or sulfur. These radicals are called:
   chlor*ide* radical..... Cl
   brom*ide* radical..... Br
   iod*ide* radical..... I
   sulf*ide* radical..... S

2. A *nonmetal element and oxygen*, such as,
   nitr*ate*.... (NO_3) nitr*ite*..... (NO_2)
   chlor*ate*... (ClO_3) chlor*ite*.... (ClO_2)
   sulf*ate*.... (SO_4) sulf*ite*..... (SO_3)
   phosph*ate*. (PO_4) phosph*ite*.. (PO_3)

3. *Carbon, hydrogen, and oxygen*, as in the
   acet*ate* radical..... ($C_2H_3O_2$)
   tartr*ate* radical..... ($C_4H_4O_6$)
   ole*ate* radical..... ($C_{17}H_{33}CO_2$)

Any compound which is composed of a hydrogen radical and any one of the many so-called acid radicals is an acid.

The radical common to acids. The radical that is common to all acids is the *hydrogen radical*, while the variable, consequently that which determines the specific acid, is the acid radical.

Representative acids and naming scheme. Representative acids are listed in the accompanying table together with the *two names* which are applied to them: *one name* mentions both the hydrogen radical and the acid radical but does not specify that the compound is an acid; the *second name* does not mention the radicals present but tells that the compound is an acid.

It should be noted that there is a definite system for naming acids. This is illustrated in the table on page 149.

In general, the naming system for acids is as follows; the dash indicates the position for naming the particular nonmetal element involved.

	One name	The other name
If an acid does not contain oxygen	Hydrogen—ide	Hydro—ic acid
If the acid does contain oxygen	Hydrogen—ate	———ic acid
	Hydrogen—ite	———ous acid
	Hydrogen hypo—ite	Hypo—ous acid
	Hydrogen per—ate	Per———ic acid

Organic acids. The organic acids listed in the accompanying table are representative of many such acids. As with all acids, they contain the replaceable hydrogen radical. Their acid radicals contain *carbon*, *oxygen*, and *usually hydrogen*, which, in contrast to the hydrogen element comprising the hydrogen radical, is not easily displaced by other elements.

In reaction with blue litmus. When in water solution, acids exhibit a marked tendency, as do bases, to react with selected colored substances to make substances of a different color. One such substance is *blue litmus*, with which many acids react to make *red litmus*. This, it will be noted, is the reverse of the effect produced by bases (p. 147).

In water solution

Hydrochloric acid + Blue litmus ⟶ Red litmus
Sulfuric acid + Blue litmus ⟶ Red litmus } in conspicuous quantities
Acetic acid + Blue litmus ⟶ Red litmus

NAMES FOR ACIDS WHICH SPECIFY BY NAME THE *two radicals* PRESENT	NAMES WHICH DO *not* NAME THE RADICALS BUT TELL THAT COMPOUNDS ARE ACIDS	FORMULA FOR MOLECULAR WEIGHT AND MOLECULE

1. Acids that do not contain oxygen

Hydrogen chlor*ide*.....	*Hydro* chlor*ic acid*	H Cl
Hydrogen iod*ide*.....	*Hydro* iod*ic acid*	H I
Hydrogen sulf*ide*.....	*Hydro* sulfur*ic acid*. ...	H_2S

2. Commonly occurring acids that do contain oxygen

Hydrogen nitr*ate*.....	Nitr*ic acid*	H NO_3
Hydrogen sulf*ate*..... .	Sulfur*ic acid*.	H_2 SO_4
Hydrogen carbon*ate*.	Carbon*ic acid*	H_2 CO_3
Hydrogen phosph*ate*. . .	Phosphor*ic acid*	H_3 PO_4

3. Acids that contain a smaller proportion of oxygen

Hydrogen nitr*ite*.....	Nitr*ous acid*.....	H NO_2
Hydrogen sulf*ite*..... ..	Sulfur*ous acid*.....	H_2 SO_3
Hydrogen phosph*ite*.....	Phosphor*ous acid*.....	H_3 PO_3

4. Acids that contain a still smaller proportion of oxygen

Hydrogen *hypo* chlor*ite*.....	*Hypo* chlor*ous acid*..	H ClO
Hydrogen *hypo* phosph*ite*...	*Hypo* phosphor*ous acid* ..	H_3 PO_2

5. Acids that contain a higher proportion of oxygen than in corresponding *ate* or *ic* acid

Hydrogen *per* chlor*ate*.....	*Per* chlor*ic acid*.....	H ClO_4
Hydrogen *per* iod*ate*.....	*Per* iod*ic acid*.....	H IO_4

6. Organic acids

Hydrogen acet*ate*.....	Acet*ic acid*.....	H $C_2H_3O_2$
Hydrogen tartr*ate*.....	Tartar*ic acid*.....	H_2 $C_4H_4O_6$
Hydrogen ole*ate*.....	Ole*ic acid*.....	H $C_{17}H_{33}CO_2$

Strong and weak acids. *Strong acids* are *very active chemically.* Hydrochloric, nitric, and sulfuric acids are strong acids. *Weak acids* are much less active chemically. Acetic, tartaric, and most organic acids are weak; boric acid is a very weak acid.

SALTS

Constituent radicals. Radicals that contribute to every salt are as follows.

A metal radical or *Ammonium radical*	and	*An acid radical*

Representative salts. There are a great many more salts than there are acids and bases inclusively. A few representative salts are listed below.

NAME OF SALT	FORMULA	COMMON NAME, WITH SUGGESTIONS AS TO USE AND OCCURRENCE
Sodium chloride	$NaCl$	The major and desired component of table salt
Calcium chloride	$CaCl_2$	Also in table salt as an impurity
Mercuric chloride	$HgCl_2$	Bichloride of mercury, Corrosive sublimate } a disinfectant
Sodium bromide	$NaBr$	Used as sedatives
Potassium bromide	KBr	
Ammonium chloride	NH_4Cl	Used as a diuretic
Sodium carbonate	Na_2CO_3	Washing soda
Sodium bicarbonate	$NaHCO_3$	Baking soda
Calcium carbonate	$CaCO_3$	In limestone, marble, and chalk cliffs
Ferrous carbonate	$FeCO_3$	In Blaud's pills, a hematinic
Silver nitrate	$AgNO_3$	Lunar caustic
Sodium nitrite	$NaNO_2$	Used to decrease blood pressure
Calcium phosphate	$Ca_3(PO_4)_2$	The major salt component of bones and teeth
Calcium sulfate	$CaSO_4$	One of the salts causing "hard water"
Magnesium sulfate	$MgSO_4$	Epsom salt
Sodium stearate	$NaC_{17}H_{35}CO_2$	Component of soap
Zinc stearate	$Zn(C_{17}H_{35}CO_2)_2$	A dusting powder

Nomenclature. The chemist's method for naming salts is very simple. It consists of specifying the two radicals that are present. The acid radicals carry the same names as when they contribute to acids. Consequently, from a naming standpoint, salts are:

	EXAMPLES	FORMULAS
Metal (or ammonium).....*ides*	Sodium chloride.....	Na Cl
	Ammonium chloride.....	NH_4Cl
Metal (or ammonium).....*ates*	Sodium chlorate.....	$NaClO_3$
	Ammonium chlorate.....	NH_4ClO_3
Metal (or ammonium).....*ites*	Sodium chlorite.....	$NaClO_2$
	Ammonium chlorite.....	NH_4ClO_2
Metal (or ammonium) *hypo*...*ites*	Sodium hypochlorite.....	NaClO
	Ammonium hypochlorite....	NH_4ClO
Metal (or ammonium) *per*....*ates*	Potassium permanganate...	$KMnO_4$
	Potassium perchlorate.....	$KClO_4$

REACTIONS BETWEEN ACIDS, BASES, AND SALTS

When acids, bases, and salts react with one another, it is usually through an exchange of radicals. Thus, the double decomposition reaction is typical of such contacts. For the present we shall limit our study to the observable mass reaction, but later we shall expand this study to include consideration of the ion involvements.

Acid and base. When an acid and a base are brought in contact in water solution, the hydrogen radical of the acid and hydroxyl radical from the base combine to produce water. The other two radicals—metal (or ammonium) and acid radicals—are those of a salt.

Acid + **Base** ⟶ **Water** + **Salt**

Hydrogen radical + Acid radical — Metal radical + Hydroxyl radical — Metal radical + Acid radical

If the salt product is soluble, it remains in solution unless the water is evaporated. If the salt is insoluble, it begins to precipitate almost at once. Thus:

With hydrochloric acid and sodium hydroxide, the products are water and sodium chloride.

Hydrochloric acid + Sodium hydroxide ⟶ Water + Sodium chloride

$$HCl + NaOH \longrightarrow HOH + NaCl$$

Sodium chloride is quite soluble, but if the water is evaporated (indicated thus ↑) crystals of this salt presently begin to gather and their precipitation follows.

$$HCl + NaOH \longrightarrow \underset{\text{separates as gas}}{H_2O\uparrow} + \underset{\text{crystals}}{NaCl\downarrow}$$

With sulfuric acid and barium hydroxide as the initial acid and base, the salt product is barium sulfate, which is so slightly soluble that its precipitation (represented thus ↓) begins to take place at once (Fig. 49); hence, there is no need to evaporate the water for separation of this salt product.

$$\underset{H_2SO_4}{\text{Sulfuric acid}} + \underset{Ba(OH)_2}{\text{Barium hydroxide}} \longrightarrow \underset{2\ HOH}{\text{Water}} + \underset{BaSO_4\downarrow}{\text{Barium sulfate}\downarrow}$$

Of practical importance. Reactions between acids and bases are of interest to the chemist. They are also frequently encountered outside of the laboratory when it is desired to neutralize a solution of either acid or base. The following are only a few of numerous possible instances.

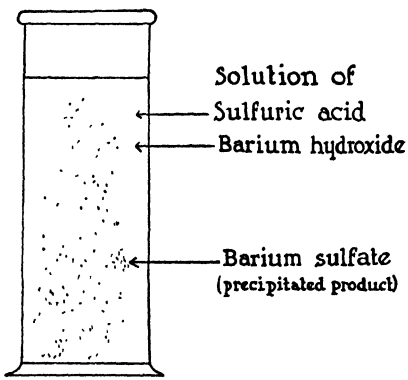


Fig. 49. An acid with a base, an insoluble salt as a product.

In manufacture of salts. There are hundreds of salts, all with their various uses, and one method for making them is from reactions between appropriate acids and bases. It is an excellent method because, the only other product being water, the salt can be separated easily. If the salt is insoluble it separates automatically by precipitation; if soluble, as water is evaporated, the salt crystallizes out of the solution.

A base as antidote for acid poisoning. A base, administered as quickly as possible, is commonly prescribed as an antidote for acid poisoning. For this purpose calcium hydroxide, the base component of lime water, or magnesium hydroxide, base component of milk of magnesia, is frequently advised because, in order to make sure that all of the acid is completely counteracted, a solution of either of these bases can be taken in considerable excess of the need without its having a harmful effect.

And, vice versa, the weak acids of fruit juices, or dilute acetic acid in vinegar, are usual antidotes for injury by bases.

A base used to reduce gastric acidity. Aluminum hydroxide is an example of a base that is used to decrease the concentration of hydrochloric acid in the stomach in the treatment of gastric ulcer. This base is so slightly soluble that

the reaction takes place slowly; thus, a moderate but prolonged medicinal effect is obtained.

Acid and salt; base and salt; salt and salt. There are such similarities among reactions that follow from these three varieties of contacts that they are discussed here in relation to each other.

Reactions dependent on removal of product. As a preliminary to the discussion of reactions of acids with salts, bases with salts, and salts with salts, it should be stated that, whereas the possibility of a reaction from every such contact is always present, for reasons that will be considered later, certain conditions must be met if the reaction is actually to take place. Outstanding among these conditions is the need for the continual removal of one of the products from the solution. If this happens, the reaction will move forward. Such a removal is accomplished under conditions as follows.

1. When a product is an insoluble, or slightly soluble, gaseous substance
2. When a product is an insoluble, or slightly soluble, solid substance
3. When a product is unstable and decomposes as rapidly, or almost as rapidly, as it is made

Acid and salt. When an acid and a salt are brought in contact in water solution (if they do not both provide the same acid radical), a double decomposition reaction can take place to make another acid and another salt. Thus, when sulfuric acid and sodium nitrate are together in water solution, the potential products are nitric acid and sodium sulfate.

$$\text{Acid} + \text{Salt} \longrightarrow \text{Acid} + \text{Salt}$$

$$H_2SO_4 + 2\ NaNO_3 \longrightarrow 2\ HNO_3\uparrow + Na_2SO_4$$

Actually, however, *for the reaction to be carried forward, one of these products must be continuously removed from the solution.* This is easily accomplished by raising the temperature of the solution somewhat above 86° C (Fig. 50). At this temperature nitric acid, which is liquid at ordinary temperatures, becomes an insoluble gas which bubbles up out of the solution (represented by an upward-pointing arrow ↑) as rapidly as it is made. But, when the initial acid and salt are sulfuric acid and barium chloride, the reaction is carried forward to completion because of the insolubility of the salt product, barium

sulfate, which is automatically removed from the solution (represented by a downward-pointing arrow ↓).

$$H_2SO_4 + BaCl_2 \longrightarrow 2\ HCl + BaSO_4\downarrow$$

Acid and carbonate. This is a special case of an acid and salt contact, and one of considerable importance. The acid product is always carbonic acid, which promptly decomposes to make carbon dioxide and water. When carbon dioxide is made in excess of the amount that can be held in solution (p. 202), bubbles of the gas escape from the solution. The decomposition of carbonic acid with the

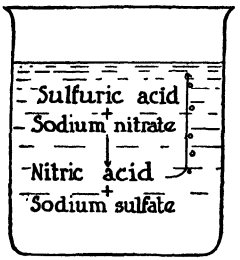


Fig. 50. Reaction carried to completion by removal of one of the products.

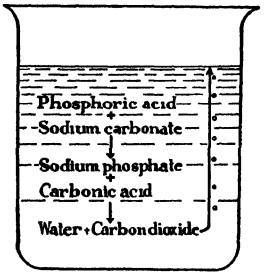


Fig. 51. An acid with a carbonate.

escape of carbon dioxide gas results in carrying this reaction toward completion. The reaction of phosphoric acid with sodium carbonate (Fig. 51) is an example.

Acid + Carbonate (salt) ⟶ Carbonic acid + Salt

↳ Water + Carbon dioxide

$$2\ H_3PO_4 + 3\ Na_2CO_3 \longrightarrow 3\ H_2CO_3 + 2\ Na_3PO_4$$

$$\hookrightarrow 3\ H_2O + 3\ CO_2\uparrow$$

Base and salt. When a base and a salt, which contain different metal radicals, are introduced into the same solution, a reaction takes place to make another base and another salt, provided conditions are such that one of the products is removed from the solution about as rapidly as it is made. Thus, with calcium hydroxide and potassium oxalate as the initial base and salt, the reaction goes forward because most of the calcium oxalate is removed from the solution, owing to its very slight solubility.

$$\underset{\text{Base}}{Ca(OH)_2} + \underset{\text{Salt}}{K_2C_2O_4} \longrightarrow \underset{\text{Base}}{2\,KOH} + \underset{\text{Salt}}{CaC_2O_4\downarrow}$$

(oxalate)

Salt and salt. If two salts which contain different radicals—as in the instance of calcium chloride and silver nitrate—are in contact with each other in water solution, a double decomposition reaction is possible. However, the reaction moves forward only if one of the products is continuously removed from the solution. In the reaction of silver nitrate with calcium chloride, this is accomplished because of the negligible solubility of silver chloride (p. 202).

$$\underset{\text{Salt}}{CaCl_2} + \underset{\text{Salt}}{2\,AgNO_3} \longrightarrow \underset{\text{Salt}}{Ca(NO_3)_2} + \underset{\text{Salt}}{2\,AgCl\downarrow}$$

Some uses for reactions of:

Acid + Salt → Acid + Salt
Acid + Carbonate → Carbonic acid (unstable) + Salt
Base + Salt → Base + Salt
Salt + Salt → Salt + Salt

For making acids, bases, and salts. Both commercially and in the laboratory, selected contacts of the type under consideration provide a means for making desired acids, bases, or salts. The selection of compounds to be used for this purpose will depend on various considerations, such as the availability and cost of the initial compounds and whether the properties of the products are such as to make it possible to separate the desired substance.

The problem of hard water. The difficulties encountered in using hard water are due to the presence of soluble calcium and magnesium salts picked up by the water as it courses through the soil. Soap is a mixture of salts, such as sodium stearate, sodium palmitate, and sodium oleate.

Salts of hard water		**Salts of hard soaps**	
Calcium chloride.....	$CaCl_2$	Sodium stearate.....	$NaC_{17}H_{35}CO_2$
Calcium sulfate.....	$CaSO_4$	Sodium palmitate.....	$NaC_{15}H_{31}CO_2$
Calcium hydrogen carbonate.....	$Ca(HCO_3)_2$	Sodium oleate.....	$NaC_{17}H_{33}CO_2$
Corresponding magnesium salts			

When soaps are put into hard water, their salts react with the salts of hard water and are destroyed, thus preventing the soaps from performing their cleansing service. The calcium (or magnesium) stearate, palmitate, and oleate, as salt products, are insoluble—they form the familiar flaky precipitate which collects on the sides of the bowl or pan when one uses soaps with hard water. Therefore, reactions in the forward direction are continuously favored, and the soap is continuously destroyed until such time as no more of the salts of hard water remain.

Calcium chloride (of hard water) + Sodium stearate (of soap) → Calcium stearate↓ + Sodium chloride

$$CaCl_2 + 2\,NaC_{17}H_{35}CO_2 \rightarrow Ca(C_{17}H_{35}CO_2)_2\downarrow + 2\,NaCl$$

With some of the new detergents (p. 328) this problem is avoided because no insoluble product results from their encounter with calcium and magnesium salts.

Salts of hard water with salts of softening agents. Because of the nuisance that accompanies the use of soaps with hard water, a custom of long standing is that of introducing a "softening agent" before the water is used for cleansing. The softening agent, a salt—frequently sodium carbonate or sodium phosphate—reacts with the offending salts to make insoluble calcium (or magnesium) salt products, such as calcium carbonate or calcium phosphate, which precipitate out of solution. The soap can then be used with the water without its being used up in reaction.

Soluble salts of hard water; Salt as softening agent

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2\,NaCl$$

$$Ca(HCO_3)_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2\,NaHCO_3$$

Acid with carbonate for leavening. Sour milk and baking soda are used as ingredients for some dough mixtures for the purpose of obtaining carbon dioxide gas for their leavening. Sour milk contains lactic acid, baking soda is sodium bicarbonate; hence, the lactic acid and sodium bicarbonate, distributed throughout the flour mixture, react to make carbonic acid and sodium lactate. But the carbonic acid decomposes to water and carbon dioxide, and the myriads of

Lactic acid; Sodium bicarbonate; Sodium lactate

$$HC_3H_5O_3 + NaHCO_3 \longrightarrow H_2CO_3 + NaC_3H_5O_3$$

$$H_2CO_3 \rightarrow H_2O + CO_2\uparrow$$

bubbles of this gas, because of their expansion and attempt to escape into the air, "lift" the dough mass to produce the leavening effect. These reactions take place at ordinary temperatures, but they proceed more rapidly as the temperature of the biscuit dough or cake batter is increased in the heat of the oven. The sodium lactate left in the cake or biscuits is responsible, in part, for the characteristic flavor of baked foods made with sour milk.

Acid with carbonate for producing carbon dioxide in fire extinguishers. Inasmuch as carbon dioxide is a gas, nonburnable, harmless, and easily obtained, it is one of the gases used for extinguishing fires. In one type of apparatus (Fig. 52), it is made through the reaction of sulfuric acid with sodium bicarbonate. In the apparatus is a small bottle of the acid and a solution of sodium bicarbonate. When inverted, the acid flows gradually out of the bottle into contact with the carbonate, and the two reactions—making of carbonic acid followed by its decomposition to make carbon dioxide—begin to take place very speedily.

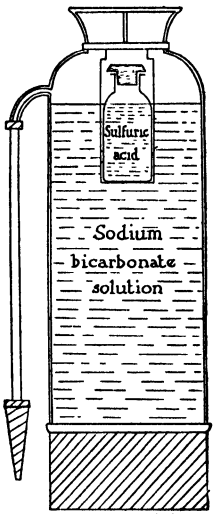


Fig. 52. One type of fire extinguisher.

$$H_2SO_4 + 2\ NaHCO_3 \longrightarrow 2\ H_2CO_3 + Na_2SO_4$$
$$\hookrightarrow 2\ CO_2\uparrow + 2\ H_2O$$

The stream of water and carbon dioxide, ejected forcefully and well directed, will both lower the temperature of the burning materials and spread a blanket of nonburnable gases between the substances participating in the burning.

Salts of the food. Absorption of salts from the digestive tract depends on their solubility in water. Because most chlorides are soluble in water, the presence of hydrochloric acid in the stomach results in the formation of chlorides from less soluble salts and thus favors absorption of salts. Nutritionists claim that foods which contain oxalic acid, and the associated oxalate salts, decrease the absorption of calcium salts. This is attributed to reactions which make calcium oxalate, a compound that is relatively insoluble in water (p. 202). For example:

$$\begin{array}{ccccccc} \text{Potassium oxalate} & + & \text{Calcium chloride} & \longrightarrow & \text{Calcium oxalate} & + & \text{Potassium chloride} \\ K_2C_2O_4 & + & CaCl_2 & \longrightarrow & \downarrow CaC_2O_4 & + & 2\ KCl \end{array}$$

Thus, insoluble calcium salts will be lost in the feces. Many fruits contain some oxalate and certain vegetables—notably spinach, beet greens, and chard—contain considerable quantities. This means that provision of calcium salts in the diet should be adequate to make allowance for such losses and still supply the calcium to meet physiological needs.

Salts with proteins, as acids, in disinfection. Silver nitrate and mercuric chloride are claimed to act as disinfectants by reacting with the proteins of bacterial cells. Since proteins are acids (hydrogen proteinates), these reactions are essentially that of a salt with an acid. Both silver proteinate and mercuric proteinate are insoluble in water; therefore, the reactions continue the destruction of protein as long as any disinfectant salt is present.

$$\begin{array}{ccccccc} \textbf{Salt} & + & \textbf{Acid} & \longrightarrow & \textbf{Salt} & + & \textbf{Acid} \\ \text{Silver nitrate} & + & \text{Hydrogen proteinate} & \longrightarrow & \text{Silver proteinate}\downarrow & + & \text{Hydrogen nitrate} \\ \text{Mercuric chloride} & + & \text{Hydrogen proteinate} & \longrightarrow & \text{Mercuric proteinate}\downarrow & + & \text{Hydrogen chloride} \end{array}$$

Poison-antidote reactions. The reaction of silver nitrate with protein can be destructive to human tissue cells as well as to bacteria. For this reason silver nitrate—or any other soluble silver salt—is a poison. Sodium chloride is prescribed as an antidote for silver nitrate poisoning. It must be applied in solution, freely and promptly, in order to destroy the silver nitrate before it enters the cells.

$$AgNO_3 + NaCl \longrightarrow \downarrow AgCl + NaNO_3$$

Silver chloride, being insoluble in water, cannot pass through the cell membrane and attack the cell proteins.

The use of silver nitrate (1 per cent) in the eyes of newborn infants is a prophylactic measure to protect against possible infection by gonococci. Frequently this is followed by irrigation with isotonic salt solution (sodium chloride 0.86 per cent solution) to destroy any remaining silver nitrate and prevent any serious attack on the tissue cells.

The principle of destroying a soluble, poisonous compound by a reaction to form an insoluble compound can be applied to other poison-antidote reactions as well.

More will be said concerning these important compounds as time goes on.

QUESTIONS

1. What radical is common to all acids? What is the name and composition (in general) of the associated radical? Illustrate by reference to a list of at least 10 acids.
2. What radical is common to bases? What is the composition of the associated radical? Illustrate by reference to a list of at least 10 bases.
3. What radicals contribute to salts? Illustrate by reference to at least 10 salts not mentioned in this chapter.
4. Why is red litmus called a base indicator and blue litmus an acid indicator?
5. How do the acids included within each of the following groups differ from one another in composition?
   a. Hydrosulfuric acid, sulfuric acid, and sulfurous acid
   b. Hydrochloric acid, hypochlorous acid, chloric acid, and perchloric acid
   c. Nitric acid and nitrous acid
6. Summarize the reactions to be expected from contacts of: acids with bases, acids with salts, salts with bases, and salts with salts. Mention one condition that favors the completion of these reactions.
7. Ferrous carbonate, used as a hematinic, is not very soluble in water. Explain how the absorption of the iron of the salt is favored by hydrochloric acid in the stomach.
8. What is the usual cause of the "hardness" of water? What reactions take place when a soap (such as sodium palmitate) is used in hard water? How does washing soda function in "softening" hard water?
9. Sodium chloride is suggested as an antidote for poisoning by silver nitrate. How does it function? Lime water is the usual antidote for poisoning by oxalic acid. How does it function?

CHAPTER 14

A STUDY OF METALS. REACTION EXPECTATIONS

Earlier in our study, reference was made to the physical bases on which substances known as metals were assembled as a special group (p. 24). The similarities of these substances do not end here; they also exhibit similarities in chemical behavior. We will now investigate the chemical behaviors characteristic of metals in general, focusing our attention on metals of common occurrence.

Some understanding of the reactions to be expected from contacts of metals with other substances is of practical interest to many people because of the frequent use of metals for instruments, utensils, and various kinds of equipment. Care of such equipment and the prevention of destructive corrosion involves protection of the metal from contacts known to result in chemical reaction as well as knowledge of contacts which can be brought about without injury to the metal.

REACTION EXPECTATIONS AS TO CONTACTS WITH METALS

Metals with oxygen. Metals, with the exception of gold, platinum, and—under ordinary atmospheric conditions—silver, react with oxygen to form oxides (p. 56).

In general, the speeds of such reactions are directly related to the established activity of the metal elements (p. 161). Sometimes environmental conditions operate either to facilitate or to inhibit the apparent speed of reactions. For example, some metal oxides, once reaction begins, adhere to the surface of the metal and in this way

reduce the surface exposed to oxygen. This effect is noteworthy in the cases of both chromium and aluminum oxide.

Theoretically, the tendency of metals to react with oxygen is related to the electron configuration of the oxygen atom and the *tendency of metal atoms to discharge electrons* from their valence shells (p. 127). Such an electron exchange is suggested below in relation to the reaction of magnesium with oxygen.

Magnesium + Oxygen ⟶ Magnesium oxide

$$2\,Mg^{0} + O_2^{0} \longrightarrow 2\,Mg^{++}O^{--}$$

(2 × 2e)

Metals in order of their chemical activities

Potassium
Sodium
Calcium
Magnesium
Aluminum
Zinc
Chromium
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Mercury
Silver
Platinum
Gold

Metals with water. We shall study first some reactions which *do* take place between *water and metals*, then sum up what to expect, in general, from such contacts.

1. When a small piece of *potassium* is placed on *water* reaction sets in at once as the potassium, being lighter than water, darts here and there on the surface. (For the sake of safety the water should be in a large, shallow plate.) *Hydrogen* is made, but enough heat is produced so that it (hydrogen) begins to burn as soon as it comes in contact with oxygen of the air. *Potassium hydroxide*, white and soluble, is also made as is indicated when a strip of red litmus paper is dipped into the solution (Fig. 53).

Potassium + Water ⟶ Hydrogen + Potassium hydroxide

$$2\,K + 2\,HOH \longrightarrow H_2 + 2\,KOH$$

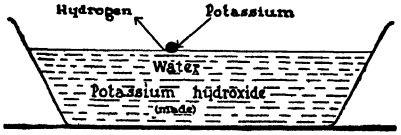


Fig. 53. Potassium in reaction with water.

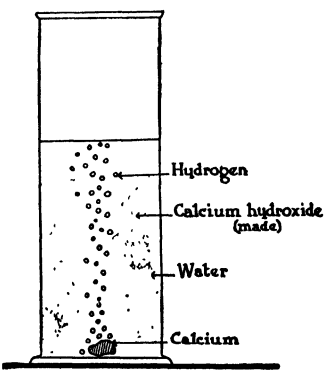


Fig. 54. Calcium reacts with water.

2. If exactly the same procedure is followed with a piece of *sodium* and water, a similar reaction takes place. But, since sodium is less active than potassium, the reaction is less speedy.

3. When *calcium* is the metal used and a small lump is dropped into *water*, a reaction similar to the two foregoing reactions sets in as soon as contact is made, although it is slower because of the lesser activity of the calcium (Fig. 54).

$$\text{Calcium} + \text{Water} \longrightarrow \text{Hydrogen} + \text{Calcium hydroxide}$$

4. With *magnesium*, reaction with *water* is very slow at ordinary temperatures but proceeds appreciably, although still slowly, at temperatures around 60° C. Similar substances are made.

$$\text{Magnesium} + \text{Water} \longrightarrow \text{Hydrogen} + \text{Magnesium hydroxide}$$

But, if magnesium and water are raised to still higher temperatures, *magnesium oxide*, not magnesium hydroxide, is made.

$$\text{Magnesium} + \text{Water} \longrightarrow \text{Hydrogen} + \text{Magnesium oxide}$$

By this time one would be justified in beginning to wonder whether water in contact with *all* metals will result in similar reactions. Thus far only contacts such as are encountered in the laboratory have been dealt with. But what about such contacts as water with aluminum, water with iron, and water with nickel? These are familiar contacts, and, at first thought, remembering that kettles and saucepans of aluminum, iron, and nickel seem to last indefinitely even with constant use, the student may be inclined to doubt the occurrence of reactions between any of these metals and water. But:

5. As to the *aluminum* dish and *water*, if the student thinks a bit further, the whitish layer which collects on the aluminum will be recalled. This is a layer of *aluminum oxide* which sticks so tightly to the remaining aluminum that the sharp edges of steel wool must be used to scrape it off. *Hydrogen* is also made, but so slowly that one is not ordinarily aware of it. However, if the aluminum is ground up to increase considerably the surface of contact with the water, and if the reaction is enclosed and the hydrogen collected, evidence can be obtained to show that this gaseous substance actually is made (Fig. 55). It follows that aluminum kettles do get thinner, although very slowly.

$$\text{Aluminum} + \text{Water} \longrightarrow \text{Hydrogen} + \text{Aluminum oxide}$$

6. As for *iron* and *water*, because iron is less active than aluminum, reaction with boiling water is inappreciable. Accordingly, the iron kettle handed down through generations of families does not seemingly get thinner. But, if *steam* is obtained and heated to 300° or 400° C (superheated steam) and if the *iron* is ground to a powder, thereby increasing greatly the surface of contact between the steam and iron, reaction does take place although slowly.

Iron + Water ⟶ Hydrogen + Magnetic iron oxide
$3\,Fe + 4\,H_2O \longrightarrow 4\,H_2 + Fe_3O_4$

Water in contact with iron at very high temperatures is not commonly encountered, but whenever such contacts are obtained, as would be the case if iron pipes were used to convey superheated steam, slow reaction most certainly occurs.

7. For even slight reactions between water and nickel or lead, increasingly high temperatures are required.

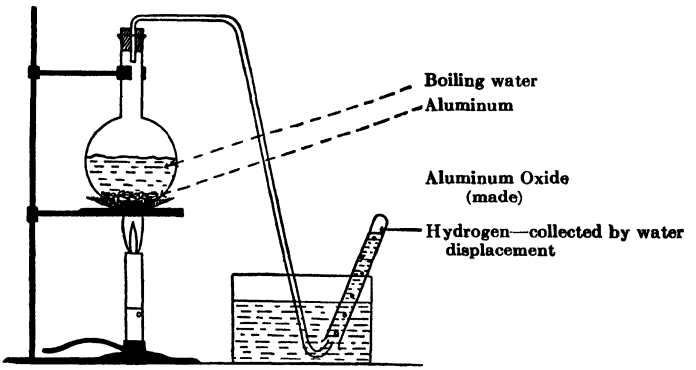


Fig. 55. Aluminum reacting with boiling water.

But when, in the order of activity of metals, copper is reached, there is a change. *None of the metals "below hydrogen" gives any evidence of reaction with water*, no matter how high the temperature obtained. Thus:

Copper (of sterilizers) + Water (superheated steam) ⟶ *No reaction*
Silver (of spoons, etc.) + Water (boiling) ⟶ *No reaction*
Platinum + Water (even at very high temperatures) ⟶ *No reaction*
Gold + Water (even at highest temperatures) ⟶ *No reaction*

This is one reason why, when metals are listed in the order of their chemical activities, hydrogen (which is not a metal) is placed in the position indicated since "*metals above hydrogen*" behave differently from "*metals below hydrogen.*" Thus:

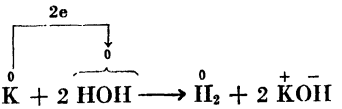
Metal (above hydrogen) + Water ⟶ Hydrogen + Base or Metal oxide (if at ordinary temperatures) (if at elevated temperatures)

Metal (below hydrogen) + Water ⟶ No reaction

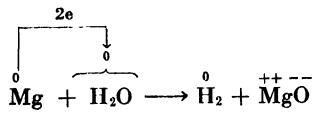
With these generalizations in mind and with the metals listed in order of their activity (p. 161), it is possible to judge—with a good chance of being right: (1) whether the given metal substance will react with water; (2) whether ordinary or higher temperatures are necessary for appreciable reaction; and (3) what products, if any, to expect.

Charge changes involved. Underlying the visible mass reaction is the ultimate unit reaction which involves an interchange of electrons. This electron interchange is suggested by the following equations.

At ordinary temperature, with active metals:



At elevated temperature, with less active metals:



Metals with acids. Observation of the behavior of metals in contact with acids affords further evidence as to the relative activity of metals. The "*metals above hydrogen*" will be observed to behave somewhat differently from the "*metals below hydrogen.*"

Metals above hydrogen with acids. The metals above hydrogen, as listed on page 161, range from potassium, which is a dangerously active metal, down to and including lead. All of these metals can be *expected* to react with acids to make hydrogen (the substance) and salts. If a series of tubes which contain zinc, a moderately active metal, is set up and water solutions of various acids are added, as specified in Figure 56, it will be found that in every instance the element hydrogen is displaced from the acid by zinc. The result is that gaseous hydrogen is made along with the respective zinc salts. The hydrogen, being insoluble, bubbles out as rapidly as it is made. The several salts, being more or less soluble and colorless, do not become evident unless one pours off the solution and evaporates the water.

Zinc + Hydrochloric acid ⟶ Hydrogen + Zinc chloride
Zn + 2 HCl ⟶ H_2 + $ZnCl_2$

Zinc + Phosphoric acid ⟶ Hydrogen + Zinc phosphate
3 Zn + 2 H_3PO_4 ⟶ 3 H_2 + $Zn_3(PO_4)_2$

If, instead of zinc, aluminum, chromium, or iron is in contact with the above acids, or with other acids, one can expect to obtain as products hydrogen and aluminum salts, chromium salts, or ferrous salts.

A general statement for reactions from such contacts[1] is as follows.

Metal (above hydrogen) + **Acid** → **Hydrogen** + **Salt**

Speed of reaction. 1. The speed with which hydrogen and the salt are made from the reaction of an acid with a metal depends, as with all reactions, upon the *area of contact* between the acid and metal (p. 18). This condition involves both the extent to which the metal is spread out in contact with the acid and the concentration of the acid in the solution.

2. But the *activity or "strength" of the acid* is another reaction-speed factor. For example, in the series of contacts of the same metal with different acids, as indicated in Figure 56, if approximately the same surface of contact is presented by the metal, in this case zinc, and if concentrations of the several acids are such that they present the same area of hydrogen radical to the metal, the comparative speeds of reactions will be:

Greatest between the zinc and hydrochloric acid, strongest acid
Somewhat less speedy between zinc and sulfuric acid, next strongest
Appreciably less speedy between the zinc and phosphoric acid
Considerably less so between the zinc and tartaric acid
Very slow, but still appreciable, between zinc and acetic acid

3. On the other hand, if *different metals*, presenting similar surface areas, are in contact with the *same acid*, of definite concentration,

---

[1] Although reaction "expectations" from such contacts are as stated, there are exceptions, notably with nitric acid because of its instability. It is true that from reaction of nitric acid with magnesium and metals above it in activity the products may be hydrogen and the salts:

Magnesium + Nitric acid → Hydrogen + Magnesium nitrate

But with less active metals the products are water (instead of hydrogen), a salt or an oxide of the metal, and frequently an oxide of nitrogen such as nitrogen peroxide, which is a dense, brown, poisonous gas.

Iron + Nitric acid → Water + Ferric nitrate + Nitrogen peroxide (NO_2)
Fe + 6 HNO_3 → 3 H_2O + $Fe(NO_3)_3$ + 3 NO_2

Tin + Nitric acid → Water + Stannic oxide + Nitrogen peroxide
Sn + 4 HNO_3 → 2 H_2O + SnO_2 + 4 NO_2

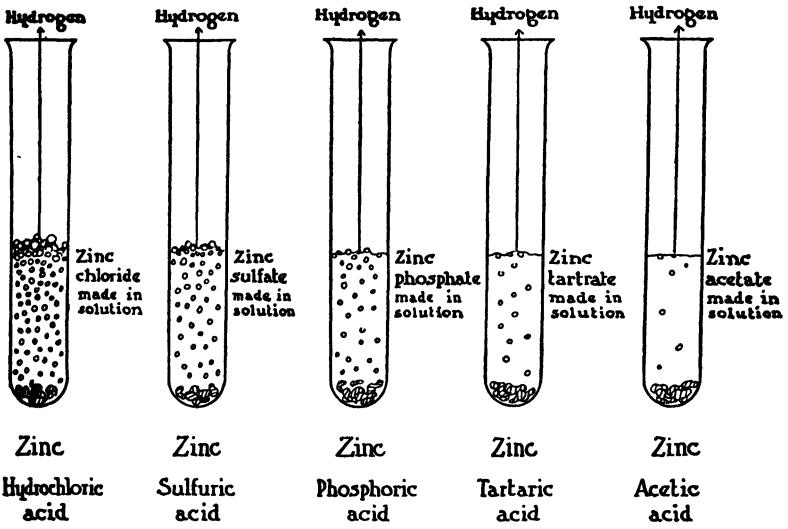


Fig. 56. The same metal with different acids.

the speed with which hydrogen and the salt are made will depend upon the *activity of the metal.* This is illustrated in Figure 57 in which hydrochloric acid is the representative acid.

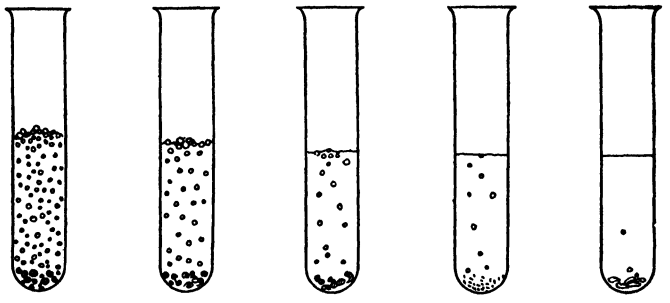
The electron exchange. These reactions, whether rapid or slow, are attributed to the *tendency of metal elements to lose electrons* when in the presence of acids. Positively charged hydrogen atoms (hydrogen ions) released by acids in water solution are believed to attract the electrons, thus forming molecules of hydrogen. The electron exchange is suggested in the following equation.

$$\overset{2e}{\overbrace{}}$$

$$\overset{0}{Mg} + 2\,H\overset{+}{Cl}^{-} \longrightarrow \overset{0}{H_2} + \overset{++}{Mg}\overset{-}{Cl_2}$$

Metals below hydrogen with acids. There is considerable variation in the chemical behavior of metals below hydrogen (p. 161) and acids; therefore, no one inclusive statement can be made. Even so, certain reactions, or lack of reactions, can be anticipated from such contacts.

Of all metals *platinum* and *gold* are the least active and, except for a few seldom-encountered contacts, *these metals do not react with acids.*



* Caution is necessary since this reaction is violent.
† Hydrogen is made so slowly as not to be evident to the eye.

Fig. 57. Different metals in reaction with the same acid.

As for *copper*, *mercury*, and *silver*, reactions or lack of reactions with acids that are commonly encountered in laboratories are summarized as follows:

Copper, Mercury, Silver

(1) + Hydrochloric acid ⟶ No reaction

(2) + Hydrosulfuric acid ⟶ Hydrogen + Sulfide salt

(3) + Sulfuric acid ⟶ Water + Sulfate + Sulfur dioxide

(4) + Nitric acid ⟶ Water + Nitrate + Nitric oxide or Nitrogen peroxide

1. It will be noted that *no* reaction results from contacts between hydrochloric acid and these metals.[2]

2. Reaction between silver and hydrosulfuric acid (hydrogen sulfide) is of everyday occurrence. It is when hydrogen sulfide gets into the air from various sources, such as from so-called sulfur springs and from the burning of soft coal, that exposed silverware becomes covered with a layer of black silver sulfide, commonly referred to as silver tarnish.

Silver + Hydrosulfuric acid ⟶ Silver sulfide + Hydrogen

[2] The reaction that frequently occurs when laboratory supplies of copper and hydrochloric acid are brought into contact is not between copper and this acid but with the surface layer of copper tarnish (p. 5) that has collected on the copper as it stands exposed to air.

3. Outstanding among the reactions that take place between copper, mercury, and silver with oxygen-containing acids are those between sulfuric and nitric acids with copper. Water and salts are always produced and other products—usually oxides of sulfur and nitrogen—depend upon the concentration and temperature of the acid.

In hot, concentrated acid

$$\text{Copper} + \text{Sulfuric acid} \xrightarrow{\text{heat}} \text{Water} + \text{Copper sulfate} + \text{Sulfur dioxide}$$
$$\text{Cu} + 2\,H_2SO_4 \longrightarrow 2\,H_2O + CuSO_4 + SO_2$$

In dilute nitric acid

$$\text{Copper} + \text{Nitric acid} \longrightarrow \text{Water} + \text{Copper nitrate} + \text{Nitric oxide}$$
$$3\,\text{Cu} + 8\,HNO_3 \longrightarrow 4\,H_2O + 3\,Cu(NO_3)_2 + 2\,NO$$

In concentrated nitric acid

$$\text{Copper} + \text{Nitric acid} \longrightarrow \text{Water} + \text{Copper nitrate} + \text{Nitrogen peroxide}$$
$$\text{Cu} + 4\,HNO_3 \longrightarrow 2\,H_2O + Cu(NO_3)_2 + 2\,NO_2$$

For further information concerning the behavior of metals below hydrogen with acids, the student is referred to more comprehensive tests on inorganic or general chemistry.

Reactions of acids with metals of practical concern. *In laboratories.* Because reactions between acids and metals do occur and because many acids are used in laboratories (outstandingly hydrochloric, sulfuric, and nitric acids which are exceedingly active), most pieces of apparatus (test tubes, beakers, flasks, evaporating dishes, etc.) are made not of metals but of glass, porcelain, or plastic.

In plumbing. Drainage pipes are usually of metal—iron, lead, or sometimes copper alloy.[3] Therefore, in chemical laboratories the disposal of acids, especially strong acids, must be accompanied by such a generous flush of water as to dilute the acids greatly and carry them away from contact with the metal of the plumbing. This applies, too, to laboratories in hospitals where nitric acid, used in making certain tests, frequently causes perforations in drainage pipes if it is not flushed away thoroughly.

In household concerns. Cooking utensils are made of selected metals, chiefly aluminum, iron, and nickel, and all three of these metals react with acids. To be sure, the acids of food mixtures—mainly acetic, citric, tartaric, and lactic acids—are weak and in very dilute

[3] A modern development in laboratory plumbing is the introduction of Pyrex glass as a substitute for metal pipes.

solution in foods, but appreciable reactions do take place with these metals, especially when foods are held in the cooking utensil at high temperatures and in long contact.

The products of these reactions, as should be anticipated (p. 165), are hydrogen and salts of the metals and acids involved—aluminum citrate, aluminum acetate, iron citrate, iron acetate, etc.

Aluminum + Acetic acid ⟶ Hydrogen + Aluminum acetate
Iron + Citric acid ⟶ Hydrogen + Ferrous citrate

Are the salts injurious? The hydrogen from the above reactions, being gaseous and insoluble, bubbles out as fast as it is made. The salts, however, remain mixed with the food mass and may be absorbed from the intestinal tract. Seemingly, these iron, aluminum, and nickel salts are not physiologically harmful; in fact, the iron salts may even help to supply iron needed by the body.

This is one of the important reasons for the selection of aluminum, iron, and nickel for making cooking utensils. Lead is never used for this purpose; the lead salts, which would result from contact of this metal with food acids, are poisonous.

Copper cooking utensils are used, but they are lined with tin, nickel, or a plastic material. Therefore, there is no direct contact between the copper and food acids.

Metal oxides with acids. In considering contacts of acids with metals, it is appropriate to consider, also, the effect of acids on metal oxides, inasmuch as most metals acquire coatings of oxides (p. 56). For instance, *aluminum oxide* occurs as a thin, white, impervious coating over aluminum metal; the *iron oxide* of iron rust is red and forms a loose, porous coating over the remaining iron; copper develops a coating of black *copper (cupric) oxide.*[4] Most metal oxides, including these three, react with acids to produce salts and water.

Metal oxide + Acid ⟶ Salt + Water

But since these oxides are only slightly soluble, the reactions are slow. For example, when a solution of hydrochloric acid is in contact with ferric oxide, or a solution of nitric acid with copper oxide

[4] It should not be assumed, however, that all metal tarnish is due to reactions of metals with oxygen. Some metals, including zinc, lead, and copper, although they do combine with oxygen, have a greater tendency to react with water and carbon dioxide from the air to form complex basic carbonates. Zinc basic carbonate [$ZnCO_3 \cdot 3\ Zn(OH)_2$] and lead basic carbonate [$2\ PbCO_3 \cdot Pb(OH)_2$] are both white; copper basic carbonate [$CuCO_3 \cdot Cu(OH)_2$] is the familiar green tarnish that appears on this metal.

(Fig. 58), reactions soon begin to be apparent, as is evidenced by the appearance of yellowish-brown ferric chloride from the first reaction and blue cupric nitrate from the second reaction. If the acids are weak, such as tartaric, lactic, and acetic acids, reactions with metal oxides are slow, but in time become appreciable.

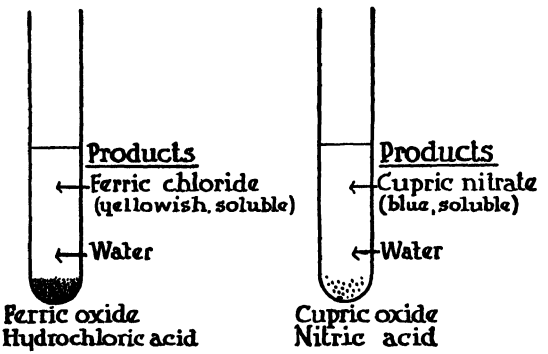


Fig. 58. Acids react with metal oxides.

Thus, when grapes with their tartaric acid, or tomatoes with their citric and other acid components, are heated in an aluminum kettle which has become covered on the inside with a dull coat of aluminum oxide, the dull coating disappears. The reason is that these weak acids react slowly with the aluminum oxide to make water and the salts aluminum tartrate and aluminum citrate.

Tartaric acid + Aluminum oxide → Water + Aluminum tartrate

$$3\ H_2C_4H_4O_6 + Al_2O_3 \longrightarrow 3\ H_2O + Al_2(C_4H_4O_6)_3$$

Citric acid + Aluminum oxide → Water + Aluminum citrate

$$2\ H_3C_6H_5O_7 + Al_2O_3 \longrightarrow 3\ H_2O + 2\ AlC_6H_5O_7$$

Similar reactions remove iron rust, or ferric oxide, from rusted iron utensils, with water and the ferric salts of the acids concerned appearing as products.

Some reactions of practical interest. Obviously, when acid-containing foods are cooked in dulled aluminum or rusted iron utensils, the aluminum or iron salts that are made become mixed with the food mass. The harmless nature of these salts was mentioned previously (p. 169).

Many of the pastes used in the home for removing metal tarnish contain acids. Much of the effectiveness of these preparations is due to the reaction of the acid with the metal oxide to make salts which are soluble in water and can therefore be washed away.

Magnesium oxide is one of the compounds that can be used *medicinally* to decrease the concentration of hydrochloric acid in the stomach. As the metal oxide comes in contact with the acid a reaction takes place to make magnesium chloride and water. Because magnesium oxide is relatively insoluble in water the reaction proceeds slowly; the undissolved portion of the oxide tends to

remain in the stomach, thus providing for a continuing reaction over a prolonged period.

Metals with bases. The reactions to be expected from contacts of bases with metals are limited. In general, such reactions occur chiefly from contacts of the two bases potassium and sodium hydroxide with the three metals aluminum, zinc, and tin. The products of these reactions are hydrogen and the aluminate, zincate, or stannite salts.

Aluminum + Sodium hydroxide ⟶ Hydrogen + Sodium or Potassium
Zinc Potassium hydroxide aluminate
Tin zincate
stannite

Aluminum + Sodium hydroxide ⟶ Hydrogen + Sodium aluminate

$$2\,Al + 6\,NaOH \longrightarrow 3\,H_2 + 2\,Na_3AlO_3$$

The reaction between aluminum and sodium hydroxide can be violent, even with the base in moderate concentrations. Relative speeds of reaction between this base and the three metals mentioned above are represented in Figure 59.

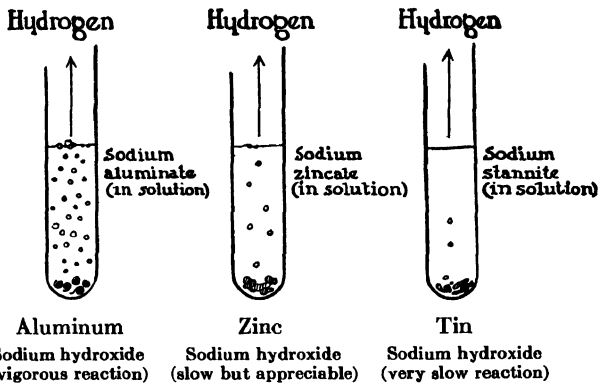


Fig. 59. Certain bases react with aluminum, zinc, and tin.

Solutions of potassium hydroxide with these metals give like results, save that the salts produced are potassium salts.

Practical applications. *In laboratories*, contacts between sodium and potassium hydroxides with aluminum, zinc, and tin are carefully avoided unless reaction is desired. *In housekeeping practices*, contacts between sodium hydroxide and these metals are of more or less frequent occurrence. The following are examples.

1. Any commercial lye is quite likely to be over 90 per cent sodium hydroxide. In the household, such reagents are advised for use in making soaps and for cleaning drains. For both of these purposes the lye must be in water solution. This solution should not be prepared in either an aluminum container or one of galvanized iron (iron covered with a layer of zinc) because of the inevitable reaction of aluminum and zinc with sodium hydroxide.

This solution may be used for cleaning out drains since drainage pipes are usually of lead or iron. Hence, although the lye will flush out the accumulation of fat, which is the usual cause of stoppage in kitchen plumbing, it does not react with the metal of the pipes.

2. Sodium carbonate is used quite generally in housekeeping, either under the label of washing soda, or as an unmentioned component of some cleaning agents which have commercial labels. Sodium carbonate is a salt, but when in water solution some of it reacts with water to make *sodium hydroxide*, not in high concentration to be sure (p. 249), but in sufficient concentration to react slowly with aluminum and zinc. Hence, whenever washing-soda solution is permitted to stand in aluminum utensils, or in galvanized iron pails and tubs, slow reaction does take place because of the dilute solution of sodium hydroxide that is made.

$$Na_2CO_3 + 2\ HOH \longrightarrow 2\ NaOH + H_2CO_3$$

Metals with salts. Whether or not a salt in solution will react with a metal substance with which it is in contact depends on whether the metal element in the metal substance is more active or less active than the metal element in the salt. (See table, p. 161.)

Thus:

Copper + Silver nitrate ⟶ Silver + Cupric nitrate
Iron + Cupric chloride ⟶ Copper + Ferrous chloride
Zinc + Lead nitrate ⟶ Lead + Zinc nitrate

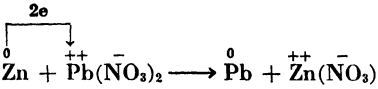
but

Copper + Magnesium sulfate ⟶ No reaction
Iron + Sodium chloride ⟶ No reaction
Zinc + Potassium carbonate ⟶ No reaction

In general, then, reaction can be expected to follow from contact of a salt with a metal when:

Metal (substance) which contains a more active metal element	+ **Salt** which contains a less active metal	⟶ **Metal** (substance) of a less active metal element	+ **Salt** of the more active metal

Electron interchange. In these reactions between metals and salts, it is believed to be *the power of the more active metal element to discharge its valence electrons into the shell of the less active metal element that brings about the reaction.* This also helps to explain why the reverse reaction does not occur. A typical reaction is represented thus:



Some practical consequences. *In the laboratory.* A good reason for having laboratory apparatus made of glass, porcelain, or polyethylene (p. 285) is that laboratory workers are continually using various salts, some of which would react with metals which might be used for utensils. Aluminum beakers, for example, could reasonably be used to hold solutions of magnesium, calcium, sodium, or potassium salts. But, if used to hold salts of zinc, chromium, or iron, reactions would take place—and all such salts are used in experimental work in laboratories.

In housekeeping activities. Salts and metal substances that are more or less commonly encountered in the household include:

The salts	***Metals***
Potassium chloride, Sodium chloride, Calcium chloride, Magnesium chloride (components of meats and vegetables)	Aluminum (various utensils)
Iron salts (components of such foods as beans, eggs, oatmeal, oysters, spinach)	Zinc (metal covering for the sheet-iron of pails and tubs)
	Iron (cooking utensils)
	Nickel (cooking utensils)
	Silver (cutlery)

When foods containing potassium, sodium, calcium, and magnesium salts are cooked in containers made of any of the above metal substances, likewise when silverware is used in handling these foods, no reaction occurs as far as the salts and metals are concerned. When foods that contain iron salts are cooked in aluminum utensils, some reaction can be expected between these salts and the aluminum, but not if the foods are cooked in containers of iron or nickel.

Sodium salt + Aluminum ⟶ No reaction
Magnesium salt + Aluminum ⟶ No reaction
Iron salt + Aluminum ⟶ Iron + Aluminum salt
Iron salt + Nickel ⟶ No reaction

In hospital practice. In hospitals, aside from salt and metal contacts which are encountered in food preparations, other such contacts are as follows.

Salts	***Metals***
Potassium permanganate (for irrigations)	Chromium (plated instruments, table tops, etc.)
Sodium chloride, Magnesium sulfate (for dressings and packs)	Nickel (plated instruments, etc.)
Mercuric chloride (as disinfectant)	
Silver nitrate	

Dressings and packs that carry sodium chloride and magnesium sulfate can be handled with chromium- or nickel-plated instruments without any reaction occurring between these salts and these metals. But, when solutions of mercuric chloride or silver nitrate are in use, care should be observed to prevent contact of these solutions with metal instruments and equipment because soluble mercuric and silver salts will react with chromium, iron, and nickel.

$$\text{Mercuric chloride} + \text{Nickel} \longrightarrow \text{Mercury} + \text{Nickel chloride}$$
$$\text{Silver nitrate} + \text{Chromium} \longrightarrow \text{Silver} + \text{Chromium nitrate}$$

The problem of metal corrosion. Year in and year out there is a tremendous economic loss through corrosion of metals. Corrosion, rusting, and the more limited surface attack known as tarnishing all result from chemical changes. *Underlying all of these destructive attacks is the loss of electrons by the metal elements* with the resulting formation of metal compounds, oxides, salts, and bases. Many of these reactions belong to the types we have just studied.

Protection of metals from corrosion implies protection from contact of metals with possible reactants—some of which are elusive gaseous substances in the air. Many types of protective surfaces have been applied to metals to cut off surface of contact; these include paints, lacquers, plastics, and sometimes the corrosion products themselves—as with oxides of aluminum and chromium. Sometimes protection is accomplished by plating, that is, covering an active metal with a thin surface of a less active metal by means of a displacement reaction. But these measures are really effective only so long as the protective surface remains intact. One of the most effective means yet discovered has come with the development of alloys, some of which are highly resistant to corrosive reaction.

Conditions in the environment frequently function either to hasten or check the speed of metal corrosion. Thus, dry metal is less subject to attack than metal exposed to moisture. Conditions of strain involving the metal structure predispose to attack—these include dents and bends, scratches, nicks, and cuts—whether produced accidentally or by design. Observation of corroded equipment often reveals strain at the point where corrosion began. Implications for care of equipment, also for preferred design, are obvious.

ALLOYS

Alloy is the term applied to a mixture of two or more metals that have been melted together, then cooled to the solid state. Some alloys, when cooled, are solid solutions, meaning that the metals are present as such and in even distribution. Copper with nickel, chromium with nickel, and chromium with nickel

and iron form such alloys. Other alloys are composed of the metals as such, but during cooling and solidifying they separate somewhat from each other so that the mass becomes more or less stratified. Copper and lead form alloys of this type.

Properties. The properties of alloys are frequently quite different from those that might be expected from the metals involved. Some alloys provide material of greater hardness, as with silver coins. Some alloys are highly resistant to conduction of an electric current, for example, nichrome which is used in electrical heating units. Some alloys are more easily corroded than is the metal alone; this is the case with brass and with aluminum alloys. But, some alloys are highly resistant to corrosion, as with Monel metal and the so-called "stainless steel." It should be emphasized, however, that the popular expressions of "rustless" and "stainless," as applied to utensils and equipment made of specific alloys, are generally misleading because there is no alloy that is not subject to staining, rusting, or corroding by the right reagents under the right conditions. The following is a limited selection of alloys and some of their properties and uses.

Steel, an alloy of iron[5]

with 1.5–4 nickel	strong, more resistant to corrosion than iron alone
with 7–10 nickel, 18 chromium	strong, relatively stainless; used for chemical and food-processing equipment
with 12–18 chromium	heat and, relatively, corrosion resistant; used for turbines, blades, pistons, cutlery
with 12–15 silicon	very hard and relatively corrosion resistant, also resistant to acids; called *Duriron*

Other alloys

Monel 67 nickel, 28 copper, 5 iron	relatively corrosion resistant; used in household for kitchen equipment—table tops, sinks, utensils, for door and window screens; in chemical industries for tanks, vats, boilers, etc.
Sterling silver 92.5 silver, 7.5 copper	
Brass 63–90 copper, 33–10 zinc	

QUESTIONS

1. What, in general, are the physical characteristics of metals?

2. Summarize typical reaction expectations for metal contacts with water, oxygen, acids, bases, and salts. Illustrate each generalization by an example—some metal contact not specifically cited in this chapter.

3. Represent by formula equations the charge changes involved in typical reactions with metals. What, in general, is the nature of the charge change undergone by the metal element in these reactions?

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[5] Figures are for per cent of other metals present.

4. From the standpoint of reaction with water, which should be more durable for pressure cookers, aluminum or steel? Explain.

5. What, if any, reactions would you expect from each of the following metal contacts? If reaction occurs, assemble the equation for the reaction. If no reaction is expected, tell why.

a. Sour milk in an aluminum dish
b. Iron rust in contact with vinegar
c. Silver knives, forks, or spoons in contact with sodium chloride
d. Ammonium hydroxide used to clean metal surfaces
e. Tarnished silver in contact with a metal polish containing oxalic acid

6. Why is it inadvisable to expose nickel-plated instruments to contact with bichloride of mercury? Does the same objection hold for chromium-plated instruments? If the solution is silver nitrate? If the solution is magnesium sulfate?

7. Many commonly used cleaning solutions contain sodium carbonate. What, if any, effect would you expect on contact of such a solution with aluminum? With iron utensils?

8. What is an alloy? What is the composition of "stainless steel"? Does this designation mean that the material is not subject to chemical attack? Explain. Are all alloys corrosion resistant? Illustrate.

9. Select a single specific piece of metal equipment for consideration and discuss everyday contacts which would favor corrosive reaction. State briefly what care this equipment should receive to keep it in good condition and prevent corrosion. Give reasoning.

CHAPTER 15

A STUDY OF WATER

Water is a substance which nature provides so generously that most people just take it for granted and use it without ever considering how little they really know about it.

PHYSICAL PROPERTIES AND APPLICATIONS

Color, odor, and taste. Water is colorless, odorless, and tasteless. These properties may have no great significance in human affairs, but, since water is so universally present, perhaps it is just as well that it is thus inconspicuous.

As a solvent. Water is the best of all liquid solvents, meaning that more substances dissolve in water to an appreciable extent than in any other liquid. It acts as a solvent in varying degrees: many substances, including sugars, are *very soluble* in water; many others, among them all gaseous substances of the atmosphere, are only *slightly soluble;* and numerous substances, including most components of earth's solid crust, are *negligibly soluble.*

Because of this solvent property, naturally occurring water is never pure. As it courses through the soil it dissolves some of the soluble substances with which it comes in contact and carries them along in solution. To this is due varying tastes (palatable and otherwise) of water solutions in different localities and also the so-called "hardness" of water which occurs when certain soluble calcium and magnesium salts are collected in solution in this manner (p. 155). When it is necessary to have water which is relatively free from dissolved salts and other substances, it is customary to separate it from these substances by the process of distillation.

The student should be able to cite, from his own observations,

still other instances in which the tendency of water to act as a solvent is of practical importance.

Maximum density of water at 4° C. Once water has reached a temperature of 4° C it behaves in a manner peculiar to itself in regard to the effect that further decrease in its temperature has on its volume, hence on its density.

Most substances contract continuously as their temperatures go down further and further; hence, these substances become increasingly denser as they get colder and colder. If, therefore, the substance is liquid and mobile, and if it is not at the same temperature throughout, stratification will set in, with the coldest portion of the

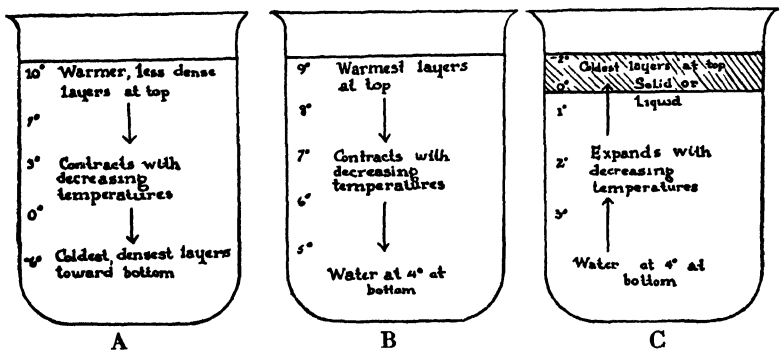


Fig. 60. A, Most liquids; *B*, water down to 4° C; *C*, water below 4° C.

liquid dropping down to the bottom and the warmest rising to the top (Fig. 60 A). Therefore, most liquids reach their freezing temperatures at the bottom of the mass and *freeze from the bottom up.*

Water behaves as do other liquids down to 4° C. As its temperature from any level above 4° is lowered the water contracts continuously and becomes continuously denser *until it attains this temperature* (Fig. 60 B). But, from 4° C on down, it behaves in a peculiar manner: instead of contracting as it gets colder, it expands, and hence rises so that coldest layers—either water or ice—are at the top (Fig. 60 C). Important phenomena result from this peculiar property of water; some are as follows.

1. *In summer*, as should be expected, the warmest layers of water in a pond or lake are at the top with colder and colder layers toward the bottom. This is a familiar fact to anyone who has dived into deep water in this season of the year.

2. But *in winter* the coldest water, or water at 0° C or below, is at the top of the pond with warmer layers underneath (Fig. 60 C). Thus it is that *water freezes first at the top, then from there on down.* Moreover, the floating layer of ice acts as an insulating cover above the warmer, liquid water underneath in which fish can live during the winter season. Only shallow bodies of water ever freeze solid throughout.

3. Most important, the maximum density of water at 4° C is a *climate-control factor.* If water did increase in density from 4° C down, all water at 0° C or below would be at the bottom of ponds and lakes where it would freeze. Under such conditions, during long cold winters, ponds and lakes might fill solid with ice from bottom to top, in which case the year's season of low temperatures would be prolonged, and the summer's heat might not be able to melt all of the ice back to liquid water.

Freezing and boiling temperatures.[1] Water, if pure, freezes at 0° C or somewhat below this temperature. Water, if pure, boils at 100° C or somewhat above or below this temperature, depending on the pressure upon its surface. Both of these temperatures are easily attained, and advantage is taken of this fact in many practical ways. Thus, (1) ice can be obtained easily for cooling purposes; (2) if water is boiling it can be depended on to be at a temperature of about 100° C when such a temperature is desired—as for cooking and sterilizing; (3) steam can be obtained easily and, in a closed container, raised to still higher temperatures—for cooking more speedily or for the greater penetration desired for effective sterilization.

High specific heat of water. Less than 200 years ago a Scotch chemist, Joseph Black, discovered that different materials have different heat capacities, meaning that the same weights of different materials collect different quantities of heat in effecting the same temperature change. These heat capacities of materials are called their specific heats. Defined from a quantitative angle: *specific heat or heat capacity of a material is the number of calories (small) of heat which 1 gm of the material must collect to raise its temperature through 1° C.* The following are some representative specific heats which have been determined as the result of much careful experimentation.

Specific heat		*Meaning that, for raising its temperature through 1° C*
Water	1.0	1 gm of water must collect 1 cal of heat.
Alcohol	0.5	1 gm of alcohol must collect 1/2 cal of heat.
Air	0.2	1 gm of air must collect 1/5 cal of heat.
Aluminum	0.2	1 gm of aluminum must collect 1/5 cal of heat.
Iron	0.1	1 gm of iron must collect 1/10 cal of heat.

[1] See pages 3 and 4 for comparison with the other meanings for freezing and boiling points that make them exact, unvariable values.

A more extensive table would only serve to emphasize still further the fact that water must collect more heat for bringing about the same temperature change than must equal weights of other materials.

Some important consequences are as follows:

1. The high heat capacity of water is of *vital* significance. Because of this property the water component of blood is able to collect the considerable quantity of heat made in the cells and carry it to the body surface, with less of a rise in its temperature than would be the case if any liquid other than water had been provided by nature as the heat-transportation medium.

2. The chief reason why it is cooler near bodies of water than a few miles inland, during the summer, is that the heat capacity of water (sp ht 1) is so much greater than that of air and land (sp ht about 0.2). For example: of the portion of the day's heat which goes to a lake region, the water claims most of it for a *slight rise in temperature.* The rest is collected by the surrounding air and land for attaining approximately the same temperature increase. Farther inland, for an equal portion of the day's heat, with air and land as the chief collecting materials, their *temperature must rise higher* since their specific heats are so much less than that of water. This is one reason for the later spring around lakes and at the seashore than farther inland.

3. The heat that is collected by water, or any other material, as its temperature rises, must be given up to the surroundings as its temperature goes down. Accordingly, it is the high specific heat of water that makes it so efficient for *heating buildings.* In the furnace the circulating water picks up an enormous quantity of heat—more than would any other liquid for the same temperature increase. Later, the hot water gives up this heat for warming rooms to which it is conveyed.

4. Through the medium of the hot-water bottle or hot flatiron, this rule of nature is used *for securing desired warmth,* and the difference in the efficiency of water and iron for this use lies in their differing specific heats. The hot-water bottle or hot flatiron, put into the bed, must throw off as much heat in lowering its temperature from, let us say, 50° C (122° F) to 22° C (72° F) as it collected in increasing its temperature to this extent. Therefore, given the same weight of water and of iron, and the same temperature decrease, the water, since it had previously collected more heat than the iron, must have more to surrender.

High latent heat of fusion of water. Another important discovery is the fact that as a substance changes from solid to liquid it must collect a certain amount of heat which becomes "stored" in the substance in liquid state *without producing an increase in temperature.* If just enough heat is provided for the melting, the beginning solid and the resulting liquid remain at the same temperature. This disappearing heat is called the *latent heat of melting or of fusion.* Moreover, in melting, each substance—gram for gram—absorbs, or

renders latent within the liquid, its own definite quantity of heat. Thus, from a quantitative angle, *the latent heat of fusion of a substance is the number of calories of heat which the substance must absorb in order to change 1 gm of the substance from the solid state to the liquid state without effecting any change in its temperature.*

The following are latent heats of fusion which have been experimentally obtained for the substances specified.

Latent heat of fusion	*Meaning that:*
Water..... 79 71	79.71 cal of heat must be absorbed to change 1 gm of water solid at 0° C to 1 gm of water liquid at 0° C.
Alcohol..... 24 9	24.9 cal of heat must be absorbed to change 1 gm of alcohol solid at −114.4° C to 1 gm of alcohol liquid at −114.4° C.
Copper..... 42.0	42.0 cal of heat must be absorbed to change 1 gm of copper solid at 1083° C to 1 gm of copper liquid at 1083° C.

This short list serves to stress the facts concerned as well as would a longer list. Each substance has its own latent heat of fusion. *Water has a relatively high latent heat of fusion.* Some of the consequences are as follows.

1. In late winter or early spring, in regions around frozen-over lakes, once the ice has collected enough heat provided by the sun during the lengthening days to raise its temperature up to 0° C, from then on every gram of ice must collect 79.71 calories of heat just for its melting to liquid water still at 0° C. At such times, the greater portion of the day's heat is requisitioned by the great expanse of ice upon the lake just to accomplish its melting, leaving a smaller quantity of heat to be collected by the surrounding air and land for raising their temperatures.

2. Farther inland, where there are but scattered and small quantities of ice to be melted, the major portion of the sun's heat during the day is collected by air and land whose temperatures, because of the low specific heats of these materials, rise considerably. This is another reason (p. 179) why the advance of spring is slower around lakes than it is farther inland.

But as water freezes in the late fall, what must happen to the latent heat of fusion which it collected in the spring? And how does this affect the advance of fall around the lake in comparison with regions farther inland?

3. Man has learned how to put the high latent heat of melting of water to various uses, among them preservation of foods, making rooms more comfortable in summer, and therapeutic purposes. Only in very small part is the *coldness* of ice responsible for the chilling of refrigerators and their contents, most of the cooling being accomplished *during the melting* of the ice, as each gram of ice takes the necessary 79.71 calories of heat from its environment to become *latent* heat of fusion in the liquid water.

4. Again, the desired cooling from the application of the ice bag or ice pack—for easing headache, checking muscular contractions and infections, and for other therapeutic uses—is obtained only in very small part from the low temperature of the ice but rather from the heat that is absorbed, and lost temporarily as heat, as the ice at 0° C changes to liquid water likewise at 0° C. Much of this heat for melting is taken from skin areas where the ice bag or ice pack is applied.

High latent heat of vaporization. Likewise, when a substance changes from liquid to gaseous state, it must absorb heat and, once again, this heat disappears as heat. The substance in the gaseous state is exactly the same temperature as it was in the liquid state. The heat thus absorbed, which remains hidden in the gaseous substance as long as the substance continues in this state, is called *latent heat of vaporization*, and it is definite in quantity for each substance at each temperature at which it vaporizes. Quantitatively defined, then, *latent heat of vaporization of a substance is the number of calories (small) of heat which 1 gm of the substance must absorb in order to change from liquid to gaseous state without undergoing any temperature change.* The heat of vaporization for some substances, including some values for water at temperatures specified, are as follows; and it should be noted that the latent heat of vaporization of water is very high.

Latent heat of vaporization	*Meaning that:*
Water at 0° C 596.0 cal	596.0 cal of heat must be absorbed to change 1 gm of water liquid at 0° C to 1 gm of water gas at 0° C.
at 20° C 584 9 cal	584.9 cal of heat must be absorbed to change 1 gm of water liquid at 20° C to 1 gm of water gas at 20° C.
at 40° C 574.1 cal	574.1 cal of heat must be absorbed to change 1 gm of water liquid at 40° C to 1 gm of water gas at 40° C.
at 100° C 539.5 cal	539.5 cal of heat must be absorbed to change 1 gm of water liquid at 100° C to 1 gm of water gas at 100° C.
Alcohol at 78° C 204.0 cal	204.0 cal of heat must be absorbed to change 1 gm of liquid alcohol at 78° C to 1 gm of alcohol gas at 78° C.
Ether at 35.6° C 83.9 cal	83.9 cal of heat must be absorbed to change 1 gm of liquid ether at 35.6° C to 1 gm of ether gas at 35.6° C.

1. The high latent heat of vaporization of water is of *vital* significance because it serves as one of the means whereby nature takes care of the considerable quantity of heat, from 2000 to 3500 Calories (large) per day, which is made in cells from kinetic or other energies required for living needs (p. 64). This heat is carried by the blood to lungs and skin where nature disposes of it in two ways. By far the larger portion is used for vaporizing the water which is excreted at these areas, approximately 574 calories of heat being necessary for the vaporization of every gram of water at normal body temperature; and, since it is latent, this heat causes no temperature increase whatsoever in these areas or the adjoining air. A smaller portion of the heat, brought to body surfaces, is radiated as appreciable heat which, of course, keeps the body warm and warms the surrounding air. Herein is provided the *major mechanism for body temperature control.*

2. Man has learned to put latent heat of vaporization to various uses, including its use for cooling purposes. Ever since prehistoric times natives of warm climates have known that water stored in a porous jar and kept in a shady, breezy place becomes cooler. Why? A dampened sheet hung in a breezy, shady doorway cools the adjacent air. A cold-water sponge cools the normal person, likewise the fever-stricken patient. And again, why?

These are but some of the important functionings of the *physical properties of water* in the concerns of earth and man. But even these limited considerations should serve to increase one's respect for water, for the ways in which nature has always used its properties, and for the ways in which man has learned to use them.

CHEMICAL PROPERTIES AND APPLICATIONS

Water plays an exceedingly important part in reactions of everyday concern, sometimes as a medium in which reacting substances are brought in contact with one another, sometimes by direct involvement in the reactions themselves. The participation of water in chemical reactions is sometimes a nuisance, but, because of the widespread occurrence of water, such contacts are unavoidable. However, there are many, many reactions in which water plays an exceedingly important part. These include cookery processes in which reactions with water are involved; all digestive reactions are between water and components of food; and, many of the vitally important reactions within the cells of plants and animals involve water. Reactions with water are also of consequence in many industrial processes. This study will now be directed to chemical reactions that can be expected to occur from contacts with water.

Water with metals. The reactions that can be expected to occur when metal substances come in contact with water were considered

in Chapter 14. The student is urged to review this material. It will be recalled that all metals "above hydrogen," in the order of metal activity (p. 161), react with water more or less readily whereas metals "below hydrogen" do not react, even under most favorable conditions.

Water + Metal (above hydrogen) → Hydrogen + Base (at ordinary temperatures) or Metal oxide (at elevated temperatures)

Water with metal oxides. Metal oxides are sometimes called *basic oxides* because they react with water to make bases.

Water + Metal oxide ⟶ Base

One such reaction has been encountered previously in our study, namely, the reaction of calcium oxide with water to make calcium hydroxide.

$$\text{Water} + \text{Calcium oxide} \longrightarrow \text{Calcium hydroxide}$$
$$H_2O + CaO \longrightarrow Ca(OH)_2$$

These reactions range in extent from being quite marked with a soluble metal oxide to negligible with an insoluble oxide.

$$\text{Water} + \underset{\text{(very soluble)}}{\text{Sodium oxide}} \xrightarrow{\text{extensive reaction}} \text{Sodium hydroxide}$$

$$\text{Water} + \underset{\text{(slightly soluble)}}{\text{Magnesium oxide}} \xrightarrow[\text{reaction}]{\text{slight but appreciable}} \text{Magnesium hydroxide}$$

$$\text{Water} + \underset{\text{(negligibly soluble)}}{\text{Copper oxide}} \longrightarrow \text{Copper hydroxide (in negligible quantity)}$$

Contacts of this variety which are commonly encountered *in everyday use* are: water with iron oxide of iron rust, as found on rusty iron utensils or implements, and water with aluminum oxide of dulled aluminum ware. But because of the insolubility, meaning negligible solubility, of these metal oxides, reactions with water are very slight.

$$\text{Water} + \underset{\text{(negligibly soluble)}}{\text{Ferric oxide}} \longrightarrow \underset{\text{(in negligible quantity)}}{\text{Ferric hydroxide}}$$

$$\text{Water} + \underset{\text{(negligibly soluble)}}{\text{Aluminum oxide}} \longrightarrow \underset{\text{(in negligible quantity)}}{\text{Aluminum hydroxide}}$$

Water with nonmetal oxides. Water reacts with nonmetal oxides to make acids. For this reason nonmetal oxides are sometimes called *acidic oxides.*

$$\text{Water} + \text{Nonmetal oxides} \rightarrow \text{Acids}$$

One such reaction of importance is that between water and carbon dioxide to make carbonic acid.

$$\begin{array}{ccccc} \text{Water} & + & \text{Carbon dioxide} & \rightarrow & \text{Carbonic acid} \\ H_2O & + & CO_2 & \longrightarrow & H_2CO_3 \end{array}$$

Since carbon dioxide is always present in the atmosphere, portions of this gas that get into solution react with some of the water. Thus it is that streams, rivers, ponds, and lakes are very dilute solutions of carbonic acid. *Physiologically*, this reaction is of *vital* significance; it takes place continuously in the body cells, and the carbonic acid thus made within the cells themselves or in the blood is a physiological factor of importance.

Reactions of this sort that are of laboratory and industrial interest include:

$$\text{Water} + \text{Sulfur dioxide} \rightarrow \text{Sulfurous acid}$$
$$\text{Water} + \text{Sulfur trioxide} \rightarrow \text{Sulfuric acid}$$
$$\text{Water} + \text{Phosphorus pentoxide} \rightarrow \text{Phosphoric acid}$$

The reaction between water and sulfur dioxide is of importance because it is one of the means whereby sulfurous acid is obtained for use as a bleaching agent and as a preservative (p. 262); that between water and sulfur trioxide is of consequence because it is necessary for making sulfuric acid by the contact method (p. 48). Because of the marked tendency of water to react with phosphorus pentoxide, this oxide is one of the drying agents used in laboratories for removing water from moisture-laden gases.

Water in direct combination to form hydrates. Water reacts with certain compounds, many of which are salts, to make what are known as hydrates.

$$\textbf{Water} + \textbf{Certain compounds} \longrightarrow \textbf{Hydrates}$$

In hydrates water appears to be held in loose combination with the associated compound, as evidenced by the ease with which hydrates give up water on heating or in a dry atmosphere. The water in combination within a hydrate is always in a definite proportion by weight. These facts are illustrated in the formulas for hydrates, of which *copper sulfate hydrate*, formula $CuSO_4 \cdot 5\ H_2O$, is a typical example.

The hydrate usually forms crystals and sometimes the complex compound exhibits color which is distinctly different from that of

the anhydrous substance. This is illustrated in the behavior of copper sulfate. Anhydrous copper sulfate is a light gray powder; on contact with water a decidedly blue hydrate is made. If water is evaporated at room temperature from a solution of copper sulfate, the blue crystals of the hydrate appear. The reaction for the equation is as follows:

$$\text{Copper sulfate} + \text{Water} \longrightarrow \text{Copper sulfate hydrate}$$
$$CuSO_4 + 5\ H_2O \longrightarrow CuSO_4 \cdot 5\ H_2O$$

An energy product. When an anhydrous salt reacts with water to make an hydrate, *there is always an energy product.* This indicates that the hydrate possesses less chemical energy than did the anhydrous compound and water, inclusively.

A reversible reaction. These reactions are reversible. When heat is supplied, the hydrate decomposes to make the anhydrous compound and water. For example:

$$\text{Copper sulfate hydrate} \longrightarrow \text{Copper sulfate} + \text{Water}$$

Setting of plaster of Paris. Making a plaster of Paris cast involves a reaction of water with a partially hydrated calcium sulfate, known as plaster of Paris, to make gypsum, which is this salt completely hydrated.

$$\text{Water} + \text{Plaster of Paris} \longrightarrow \text{Calcium sulfate hydrate or Gypsum}$$
$$3\ H_2O + (CaSO_4)_2 \cdot H_2O \longrightarrow 2\ CaSO_4 \cdot 2\ H_2O$$

Plaster of Paris is powdery (Fig. 61 A); gypsum is crystalline, and under favorable conditions forms long, interlocking crystals (Fig. 61 B). When a cast is

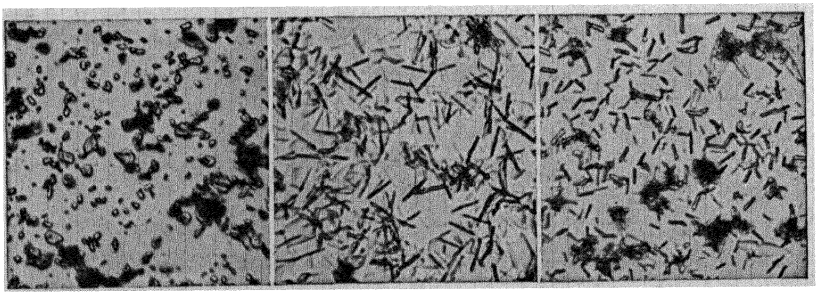


Fig. 61. A. Crystals of plaster of Paris. *B.* Gypsum crystals which were not disturbed during the setting process. Note the compact interlocking of the crystals. *C.* Gypsum crystals which were disturbed during the setting process. Note sparce interlocking of the crystals.

(Luck, J. Vernon: "Plaster of Paris Casts: an Experimental and Clinical Analysis," *J.A.M.A.*, 124:24, [Jan. 1] 1944.)

made, the wet plaster of Paris reacts gradually with water throughout the mass to produce gypsum. Crystals of this hydrate, as they form, push out in every direction; hence, the mass swells so that the material, in setting, occupies a larger volume than the original plaster of Paris and water. If in a confined space a pressure results which thrusts the reacting materials into all cracks, wrinkles, and pockets of any object in its way.

During the reaction between plaster of Paris and water, if the cast in process of development is handled roughly, bent, or twisted, instead of the formation of long, interlocking crystals of gypsum so essential to a satisfactory cast, smaller and shorter crystals appear (Fig. 61 C). This results in a crumbling cast at the points of disturbance. Not until the chemical reaction is complete and all excess water is evaporated can the cast be handled roughly without danger of damage.

As with other reactions to make hydrates, the reaction of plaster of Paris with water is accompanied by a heat product, a fact frequently noted by the individual in direct contact with the cast during the setting process.

Salts are not the only substances which react with water to make hydrates. An outstanding example is the marked tendency of sulfuric acid to react in this manner. It is for this reason that concentrated sulfuric acid is used as a drying agent for gaseous products of reactions that are laden with undesired moisture, since the *concentrated* acid combines with this water, thus removing it most effectively.

Hydrogen sulfate + Water ⟶ Hydrogen sulfate hydrate
(Sulfuric acid)

$$H_2SO_4 + 2\,H_2O \longrightarrow H_2SO_4 \cdot 2\,H_2O$$

A caution: The combination of sulfuric acid with water is accompanied by such an unusually large quantity of heat product that bringing these two

HYDRATES OF COMMON OCCURRENCE	COMMON NAMES	FORMULA FOR MOLECULAR WEIGHT AND MOLECULE
Calcium chloride hydrate		$CaCl_2 \cdot 6\,H_2O$
Calcium sulfate hydrate	Plaster of Paris	$(CaSO_4)_2 \cdot H_2O$
Calcium sulfate hydrate	Gypsum	$CaSO_4 \cdot 2\,H_2O$
Copper sulfate hydrate	Blue vitriol or bluestone	$CuSO_4 \cdot 5\,H_2O$
Ferrous sulfate hydrate	Copperas	$FeSO_4 \cdot 7\,H_2O$
Sodium borate hydrate	Borax (hydrate)	$Na_2B_4O_7 \cdot 10\,H_2O$
Sodium carbonate hydrate	Washing soda (hydrate)	$Na_2CO_3 \cdot 10\,H_2O$
Sodium sulfate hydrate	Glauber's salt	$Na_2SO_4 \cdot 10\,H_2O$
Magnesium sulfate hydrate	Epsom salt (hydrate)	$MgSO_4 \cdot 7\,H_2O$
Potassium aluminum sulfate hydrate	Alum	$KAl(SO_4)_2 \cdot 12\,H_2O$
Hydrogen sulfate hydrate		$H_2SO_4 \cdot 2\,H_2O$

substances together constitutes a hazard. Therefore, when making a dilute solution of this acid from the concentrated supply, the laboratory worker should habitually *pour the denser concentrated acid very slowly into the less dense water* so that, automatically, a greater distribution of acid and water is obtained, and the heat product is thereby distributed.

Water in hydrolysis reactions. ***Hydrolysis defined.*** *Hydrolysis is a double decomposition reaction* (p. 13) *involving water as one of the reacting substances.* In such reactions water functions as *hydrogen hydroxide*, half of its hydrogen constituting a hydrogen radical, the rest of the hydrogen combined with all of the oxygen serving as a hydroxyl radical.

Hydrolysis of salts. Many salts react with water, in double decomposition, to make an acid and a base.[2]

Water (hydrogen hydroxide) + (certain) **Salts** ⟶ **Acid** + **Base**

Water + Sodium carbonate ⟶ Carbonic acid + Sodium hydroxide

$$2\,HOH + Na_2CO_3 \longrightarrow H_2CO_3 + 2\,NaOH$$

Water + Ferric chloride ⟶ Hydrochloric acid + Ferric hydroxide

$$3\,HOH + FeCl_3 \longrightarrow 3\,HCl + Fe(OH)_3$$

A reversible reaction. Such reactions are not completed because the acid and base in the solution set up the reverse reaction to make

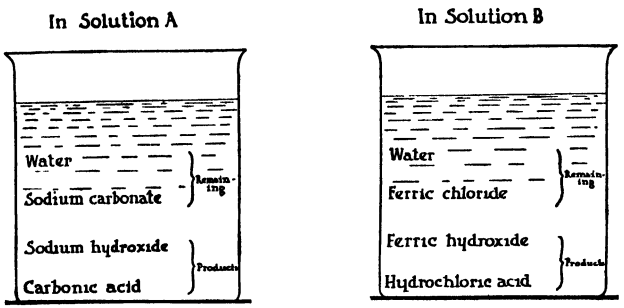


Fig. 62. When salts hydrolyze, four substances are present in the solution.

water and salt. Thus, two opposing reactions are established in the solution.

$$\text{Water (in hydrolysis)} + \text{Salt} \rightleftharpoons \text{Acid} + \text{Base}$$

As a result, there are always four substances in the solution: (1) water, (2) salt, (3) acid, and (4) base (Fig. 62).

[2] The exceptions are salts of strong acids and strong bases; see page 250.

Relative concentrations. The acid and base have a *greater tendency* to react to make water and salt than salt and water have to make acid and base. Consequently, the salt and water are always in relatively high concentration and the *concentrations of acid and base are relatively low in these solutions.*

For example, in a solution of sodium carbonate (Fig. 62 A) only a small portion of this salt seemingly becomes hydrolyzed. Hence, the solution will contain water (the small portion involved in the reaction and the large portion that serves merely as solvent), most of the sodium carbonate, a little sodium hydroxide, and a little carbonic acid. The same conditions hold within a solution of the salt ferric chloride (Fig. 62 B).

Salts of strong bases and weak acids. When a salt is composed of a metal radical from a strong base and an acid radical from a weak acid, it is referred to as a *salt of a strong base and a weak acid.* All salts of this type are subject to hydrolysis. Sodium carbonate, sodium bicarbonate, and potassium acetate are examples of these salts.

$$\text{Water (in hydrolysis)} + \underset{\left(\begin{smallmatrix}\text{strong}\\ \text{base}\end{smallmatrix} \begin{smallmatrix}\text{of}\\ \text{and}\end{smallmatrix} \begin{smallmatrix}\text{weak}\\ \text{acid}\end{smallmatrix}\right)}{\text{Salt}} \longrightarrow \text{Strong base} + \text{Weak acid}$$

Reaction of the solution. When the water solution of such a salt is tested with litmus, the solution will be found to be "*basic in reaction.*" In spite of the presence of both salt and weak acid, the solution behaves chemically like a dilute solution of the base. (For further explanation see p. 249.)

Some such reactions of importance. **1.** The salt, sodium bicarbonate, occurs in considerable quantities in solution in blood and lymph. The hydrolysis of this salt to provide sodium hydroxide in the solution is one of the means whereby these fluids are maintained always a little on the basic side of neutral in the living animal. Thus:

$$\begin{array}{ccccccc} \text{Sodium bicarbonate} & + & \text{Water} & \longrightarrow & \text{Sodium hydroxide} & + & \text{Carbonic acid} \\ \text{NaHCO}_3 & + & \text{HOH} & \longrightarrow & \text{NaOH} & + & \text{H}_2\text{CO}_3 \end{array}$$

2. A water solution of sodium bicarbonate is used frequently as a safe source of sodium hydroxide—"safe" because by this means only a low concentration of this strong base is thus provided. When a basic solution is required for contact with skin or mucous membranes, for instance, to counteract an acid accidentally spilled or spattered on the skin, a solution of sodium bicarbonate is often used to provide the desired base.

3. When using sodium carbonate or sodium phosphate for softening of hard water, neither should be added in excess of quantities necessary to remove

the offending hardness because this excess reacts with the water to make the strong base, sodium hydroxide.

Softening agents (excess)			*Strong base*		*Weak acid*
Sodium carbonate	+ Water	⟶	Sodium hydroxide	+	Carbonic acid
Sodium phosphate	+ Water	⟶	Sodium hydroxide	+	Phosphoric acid

And although this base when made from salt hydrolysis is always in very dilute solution, it can be present in sufficient concentration to produce an irritating effect on the skin, weaken fibers of silk and wool fabrics, and alter colors that are sensitive to such attacks.

4. Salts of soaps (p. 326) also react with water to make strong bases and weak acids. But, although the soap solution is appreciably basic in reaction, so little sodium hydroxide (or potassium hydroxide) is made from soap hydrolysis that the effect on the skin and on the silk and wool of fabrics is slight.

Soaps			*Strong bases*		*Weak acids*
Sodium stearate	+ Water	⟶	Sodium hydroxide	+	Stearic acid
Sodium palmitate	+ Water	⟶	Sodium hydroxide	+	Palmitic acid
Potassium oleate	+ Water	⟶	Potassium hydroxide	+	Oleic acid

Hydrolysis of salts of weak bases and strong acids. When the metal radical of a salt is from a weak base, or if it is the ammonium radical, and the acid radical from a strong acid, the salt is referred to as a *salt of a weak base and a strong acid.* Salts of this type react with water in hydrolysis.

$$\text{Water (in hydrolysis)} + \text{Salt} \left(\begin{matrix}\text{weak} \\ \text{base}\end{matrix} \text{ of } \begin{matrix}\text{strong} \\ \text{acid}\end{matrix}\right) \longrightarrow \text{Strong acid} + \text{Weak base}$$

Examples of these salts are ammonium chloride, copper sulfate, and ferric chloride. Equations representative of their hydrolysis reactions are as follows.

Water (in hydrolysis)	+ Ammonium chloride	⟶	Ammonium hydroxide	+	Hydrochloric acid
HOH	+ NH_4Cl	⟶	NH_4OH	+	HCl
Water (in hydrolysis)	+ Copper sulfate	⟶	Copper hydroxide	+	Sulfuric acid
2 HOH	+ $CuSO_4$	⟶	$Cu(OH)_2$	+	H_2SO_4
Water (in hydrolysis)	+ Ferric chloride	⟶	Ferric hydroxide	+	Hydrochloric acid
3 HOH	+ $FeCl_3$	⟶	$Fe(OH)_3$	+	3 HCl

Reaction of the solution. In the water solution of a salt of this type, while it is true that a base and an acid are both present—as are also a salt and water—the solution, as a whole, is "*acid in reaction.*"

Water in hydrolysis with substances other than salts. Water reacts in double decomposition with many substances which are not salts, and such reactions also are referred to as hydrolytic in character. The following are some such instances.

Hydrolysis of fats. Fats are organic compounds composed of the glyceryl radical in combination with fatty-acid radicals. The following are representative fats.

Glyceryl stearate	$C_3H_5(C_{17}H_{35}CO_2)_3$
Glyceryl palmitate.....	$C_3H_5(C_{15}H_{31}CO_2)_3$
Glyceryl oleate.....	$C_3H_5(C_{17}H_{33}CO_2)_3$

When fats hydrolyze they react with water in double decomposition to make glycerol (glyceryl hydroxide) and fatty acids. This reaction is illustrated in the hydrolysis of glyceryl stearate.

$$\text{Water} + \text{Fat} \longrightarrow \text{Glycerol} + \text{Fatty acid}$$

$$\text{Water} + \text{Glyceryl stearate} \longrightarrow \text{Glycerol} + \text{Stearic acid}$$

$$3\ HOH + C_3H_5(C_{17}H_{35}COO)_3 \longrightarrow C_3H_5(OH)_3 + 3\ HC_{17}H_{35}COO$$

Hydrolysis of disaccharides. Disaccharides include the sugars sucrose, lactose, and maltose. All three of these disaccharides have the same element composition, as is represented in their common disaccharide formula; hence, the same equation will represent the hydrolysis reaction for all of these disaccharides. Thus:

$$\text{Water (in hydrolysis)} + \text{Disaccharide} \longrightarrow 2\ \text{Monosaccharides}$$

$$HOH + \underbrace{C_6H_{11}O_6 \cdot C_6H_{11}O_5}_{C_{12}H_{22}O_{11}} \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

$$\text{Water (in hydrolysis)} + \text{Sucrose} \xrightarrow{\text{sucrase}} \text{Glucose} + \text{Fructose}$$

$$\text{Water (in hydrolysis)} + \text{Lactose} \xrightarrow{\text{lactase}} \text{Glucose} + \text{Galactose}$$

$$\text{Water (in hydrolysis)} + \text{Maltose} \xrightarrow{\text{maltase}} \text{Glucose} + \text{Glucose}$$

More will be said about the hydrolysis of fats and carbohydrates in later chapters which deal with the study of these important classes of compounds.

QUESTIONS

1. What are some of the important uses of water as a solvent?
2. Compare the quantity of heat given off by 1 kg of water in a hot-water bottle at 46° C (about 115° F) with that of a flatiron of the same weight and temperature as each cools to 37° C (98.6° F). Which, therefore, would be the greater source of heat?
3. How much heat must be "absorbed" from the body and the surrounding environment for melting 100 gm of ice within an ice cap? What will be the temperature maintained within the ice cap as long as ice and water are in

contact? In what two ways, then, does an ice cap function as a cooling agent? Which is the more effective?

4. How much heat must disappear as latent heat of vaporization for the evaporation of 1 liter of water of perspiration?

5. Summarize in concise statements the chemical behavior of water in respect to each of the following: metals, metal oxides, nonmetal oxides, formation of hydrates, and salts in hydrolysis. Illustrate each reaction possibility through word and formula equations for typical contacts.

6. What is hydrolysis? Illustrate in reference to the hydrolysis of potassium phosphate and glyceryl oleate—a typical fat.

7. What determines whether the "reaction" of a salt solution will be "acid," or "basic"? Illustrate by reference to solutions of potassium phosphate and ammonium chloride.

8. Why is it impossible to secure a high concentration of sodium hydroxide with a solution of sodium bicarbonate? What practical advantages are taken of this fact?

9. If directions for preparing a solution call for a definite weight of a salt which you find occurs both as a powdery anhydrous salt and as a crystalline hydrate, will it make any difference in the concentration of the resulting solution which of these you select for use? Explain.

10. a. What reaction is involved in the setting of a plaster of Paris cast? How do you account for the disappearance of water as the cast sets? Why is it important that a plaster cast be handled with care during the setting process? Account for the fact that pressure may develop under a circular cast.

    b. At certain stages during the setting of a plaster cast considerable heat may be noted, more especially where the plaster is in close proximity to the skin. Account for this.

    c. On the other hand, while the cast is still wet but with water evaporating at the surface, the cast may feel decidedly cool. Account for this seeming contradiction of fact. (See 10 b, above.)

CHAPTER 16

SOLUTIONS. COLLOIDAL SOLUTIONS. EMULSIONS

True solutions. Substances, when brought in contact with water or other selected liquids, dissolve either completely or in part to form solutions. The process of dissolving is automatic; it proceeds in some instances rapidly, in other instances very slowly, until an even distribution is effected between the liquid and the dispersed substances. As a result (1) every solution eventually becomes homogeneous; that is, the solute or dispersed substance becomes evenly distributed throughout the solvent as the dissolving medium. Furthermore, once the solution is obtained, no matter how long it may stand—whether it be for hours, days, or years—provided the same temperature is maintained and no solvent is allowed to evaporate (2) no tendency toward separation of the solute from solvent becomes apparent even though there may be considerable difference in their density. Thus, cane sugar and water can form a solution, so, likewise, can iodine and alcohol; moreover, they will maintain the condition of solution indefinitely, with no tendency toward a settling out of the denser cane sugar from the water or the denser iodine from the alcohol.

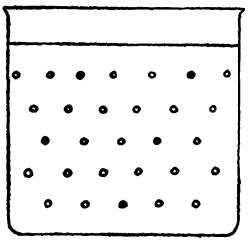
Other facts concerning solutions are that (3) both liquid and dissolved solute are able to pass through a filter very readily, and (4) they diffuse through appropriate membranes. Moreover, (5) the dispersed particles are of such minute dimensions that they cannot be detected even with the aid of an ultramicroscope. It must be concluded, therefore, that the dispersed particles within a true solution are exceedingly small. In fact, their size has been computed to be less than 1 millimicron (1 mμ) in diameter,[1] which means that they

[1] 1 micron (μ) = 0.001 mm. 1 millimicron (mμ) = 0.000001 mm.

are probably single molecules of the solute substances concerned, or ion particles (p. 220).

Explanation. Just why the solvent and solute portions of a true solution effect and maintain an even distribution regardless of the difference in their densities is not known, but there are certain beliefs that seem reasonable.

1. It is believed that within a true solution the dispersed particles of both solute and solvent are single molecules[2] of the substances concerned. Furthermore, it is believed that these molecules are moving about with speeds which vary inversely with their relative weights; that is, the heavier the molecules the less the speeds with which they travel, while the lighter the molecules the greater their speed of movement. Consequently, despite the difference in relative weights of the molecules of solvent and solute, they all move about among each other with the same kinetic energy. Naturally there are frequent collisions among the molecules and against sides of the container, followed by rebounds. In an attempt to reduce collisions to a minimum, the heavier but slowly moving molecules and the lighter but more rapidly moving molecules eventually effect an even distribution (Fig. 63).



o Molecules of solvent
• Molecules of solute

Fig. 63. In true solution, an even distribution of solvent and solute.

2. It is further believed that in many instances there is a tendency for molecules of water or other solvent to get in between and surround dispersed molecules of solute, thereby aiding in maintaining their distribution.

Defined. With these items in mind it becomes possible to define a true solution from two viewpoints.

1. Considering the character of the dispersion, *a true solution is a system in which a substance is in even distribution throughout a liquid, with no tendency toward separation of dispersed substance from dispersing liquids.*[3]

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[2] The term molecule, as used here, applies to both neutral molecules of such substances as sugars and to electrically charged particles, called ions or ion molecules, obtained from acids, bases, and salts when they are in water solution (pp. 222–28).

[3] The solutions with which this text is concerned involve liquid solvents, usually water, hence the above emphasis. Actually, however, the solution phenomenon has a broader scope, because solutions of gases in gases and solids in

2. From the standpoint of the character of the dispersed particles, *a solution is a system in which the dispersed particles are single molecules of the solute in even distribution throughout the liquid solvent.*

As has already been implied, the dispersing liquid is commonly called the *solvent* and the dispersed substance the *solute.* Most frequently, the solute is a solid substance, although it can be a liquid substance, as is true of a solution of alcohol in water; or a gaseous substance, as in the case of a solution of hydrogen chloride in water.

Suspensions. In contrast to true solution, a *suspension* is a dispersion system which can be obtained only through mechanical aid (such as by stirring or shaking) and which is characterized by a marked tendency toward separation of dispersed particles from the dispersion medium. When mixing ceases, separation sets in almost immediately. Familiar examples of such systems are sand and water or raw starch with water. Dispersed particles which are characteristic of suspensions are greater than 0.1 micron (0.1 μ) in diameter or more than 100 times the diameter of the dispersed particles of true solutions. Save in exceptional instances, they cannot pass through a filter, nor are they diffusible through membranes; they can be distinguished either by the naked eye or certainly with the aid of an ordinary microscope. Dispersed particles of a suspension are believed to be made up of many thousands of coherent molecules of the substances concerned.

Colloidal solutions. Dispersions of a third type which range between true solutions and suspensions are called *colloidal solutions* or *colloidal dispersions.* Examples of such dispersions are albumin with water and soap with water.

In dispersions of this type the sizes of dispersed particles are known to vary from 1 mμ in diameter, or larger than those of true solutions, to less than 0.1 μ in diameter, or smaller than those of suspensions. Hence, colloidally dispersed particles are presumed to be aggregates of many coherent molecules (Fig. 64), the number of which can vary from less than 100 molecules in some aggregates to thousands in other aggregates; possibly in some instances colloidal particles may be extremely large, single molecules. It is not surprising, therefore, that properties of colloidal solutions range between those of true solutions and those of suspensions. Thus (1) there is

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solids are possible. Air, for example, may be regarded as a solution of gases, as may also illuminating-gas mixture; and copper with nickel forms a solution of a solid in a solid.

always a tendency for colloidal particles to separate from the dispersing liquid. If the aggregates are composed of relatively few molecules, the separation may not become apparent for a very long time; if composed of thousands of coherent molecules, the particles will

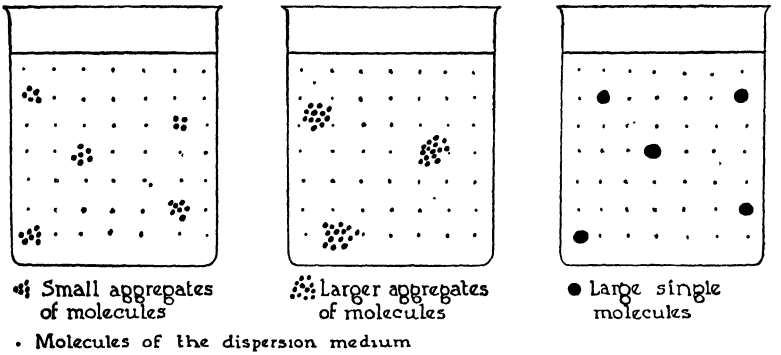


Fig. 64. Particles in colloidal solution.

approach more nearly those within suspensions, and their separation from the dispersions will become apparent within a shorter period of time. (2) Colloidal particles pass through filters more or less readily, depending upon their size. (3) As a rule they do not diffuse through membranes. (4) They are not visible through an ordinary

Distributed particles

TRUE SOLUTIONS	COLLOIDAL SOLUTIONS	SUSPENSIONS
Less than 1 mμ in diameter	1 mμ to 0.1 μ in diameter	Greater than 0.1 μ in diameter
Indistinguishable even with ultramicroscope	Not visible under an ordinary microscope but presence detected by ultramicroscope	Can be distinguished by the naked eye or with the aid of an ordinary microscope
Pass through filter paper, subject to diffusion through membranes	Pass through filter paper but usually do not diffuse through membranes	Do not pass through filter paper and are not subject to diffusion
Dispersion is permanent	Tendency toward separation of dispersed substance more or less delayed	Separation of dispersed material is almost immediate

microscope, but that they are present as discrete particles scattered through the dispersion can be made evident through the aid of the ultramicroscope. Other properties of colloidal dispersion are discussed later in this chapter.

TRUE SOLUTIONS WITH WATER AS SOLVENT

In this section properties of true solutions, other than those presented previously (p. 193), will be discussed as they apply to solutions in water, but the same principles carry over to all true solutions whether with water or other liquids as dissolving media.

Boiling and freezing points of solutions. The presence of a nonvolatile substance[4] in solution in water has the effect of raising the boiling point and depressing the freezing point of the solution in relation to the boiling point and freezing point of water alone. Moreover, the extent of the effect is directly proportional to the concentration of the solute particles in the solution.

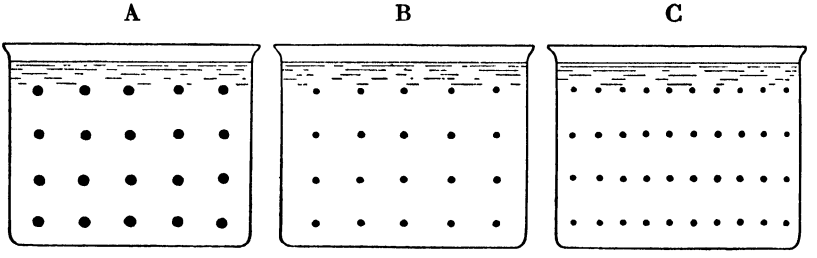


Fig. 65

For example, given two solutions (Fig. 65 A and B), one of which contains 1 gram-molecular weight of sucrose (342.308 gm) and the other 1 gram-molecu-

[4] Volatile substances depress the boiling point of the solvent; for example, a solution of alcohol in water has a boiling point below 100° C.

lar weight of glucose (180.162 gm) each in a liter of water, both solutions will have the same boiling point, 100.52° C, and the same freezing point, −1.86° C. The explanation for the increase of 0.52° C above the boiling point of water and the decrease of 1.86° C below the freezing point of water in both instances is that the molecule concentrations of the solutions were the same in each instance—gram-molecular weights of substances being composed of the same number of molecules (p. 92).

The same condition holds true for all other nonvolatile substances in water solution (with the exception of electrolytes[5]) where the dispersed particles are single molecules. In general, then, *for every gram-molecular weight (or mole) of such nonelectrolytes dispersed in a liter of water, the boiling point of the solution will be increased 0.52° C over the boiling point of water alone, and the freezing point of the solution will be decreased 1.86° C below that of water.* Thus, a solution that contains 2 gram-molecular weights of such a substance dissolved in a liter of water has a boiling point of 2 × 0.52° C higher than 100° C and a freezing point of 2 × 1.86° C lower than 0° C—the freezing point of water.

Boiling points and freezing points of electrolyte solutions. Electrolytes are substances whose water solutions carry an electric current. To be more specific, acids, bases, and salts are electrolytes. Some electrolytes enter water solution as molecules, part of which then separate into positively charged and negatively charged ions. In other instances, the electrolyte is an ionic compound which does not form molecules (p. 126) but which provides positively charged and negatively charged ions in the solution. Each ion, as well as each molecule, constitutes a particle in the solution. It follows, therefore, that a solution of an electrolyte which contains a mole of the compound in a liter of water contains more individual particles than does a solution of a nonelectrolyte of similar concentration. Consequently, such electrolyte solutions show relatively higher boiling points and freezing points than do solutions of nonelectrolyte composition of like concentration.

For example, the salt, sodium chloride, is an electrolyte. The gram-molecular weight of sodium chloride is 58.448 gm. When this quantity of this salt is dissolved in 1 liter of water, the boiling point of the solution is 100.92° C and the freezing point is −7.72° C. Almost twice as great an effect is produced on the solution as is obtained by dissolving 1 mole of glucose, a nonelectrolyte.

Osmotic pressure. It will be recalled that in a true solution molecules of water and those of the solute are continually moving about among each other in their attempt to effect and maintain an even distribution. In so doing they are continuously hitting against

[5] Molecules of nonelectrolytes do not separate into ions (or ion molecules) when in water solution.

each other and against the sides of the container, or any other object in their way, and rebounding, An *inner-solution pressure* thus becomes established which is called *osmotic pressure.* It is proportional to the concentration of dispersed particles of solute; therefore, the higher the concentration of the solute the greater the number of impacts involving solute and water molecules, hence, the greater the osmotic pressure of the solution. And, vice versa, the lower the concentration of the solute the less is this pressure within the solution.

Note. A solution of such a substance as a sugar (a nonelectrolyte) which contains 1 gram-molecular weight of the substance in 1 liter of solution (Fig. 66, A and B) has an osmotic pressure equal to standard atmospheric pressure (p. 3). Therefore, a solution which has twice this concentration has an osmotic pressure of 2 atmospheres.

Osmosis. An important phenomenon that results from osmotic pressure is that of *osmosis,* which is *the diffusion of molecules of water or of water and solute through a permeable membrane* in the attempt to equalize solution concentrations on both sides of the membrane. Obviously, the number of molecules of solute, and of water that succeed in penetrating the membrane from either side will be in direct proportion to the number of their respective impacts against it. Examples, with some consequences stressed, are as follows.

When a permeable membrane encloses a solution of sucrose and is surrounded by another sucrose solution (Fig. 66), some molecules of both water and sucrose hitting against the membrane on both sides will pass through.

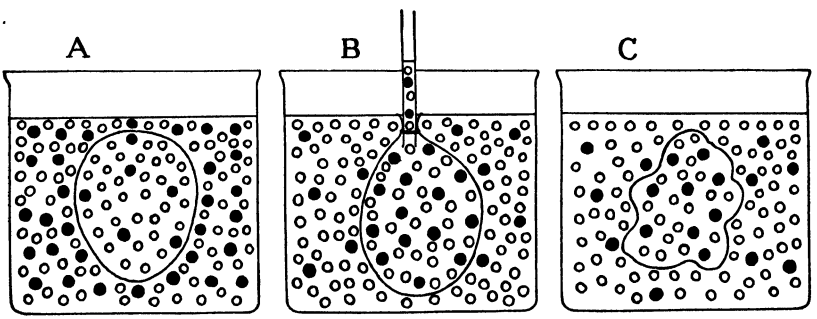


Fig. 66. Unequal diffusions of water and solute molecules through a permeable membrane.

1. If the less concentrated sugar solution is inside the membrane (Fig. 66 A) and the more concentrated is outside, *more sugar molecules* will pass through the membrane from the outer solution to the solution inside the bag than vice

versa. At the same time, *more water molecules* will penetrate the membrane from the inner to the outer solution than vice versa. As a result, the solution inside the bag becomes sweeter but decreases somewhat in volume, while the outer solution decreases in sweetness but will increase slightly in volume.

2. However, if conditions are reversed and the less concentrated sugar solution is outside the membrane bag and the more concentrated inside (Fig. 66 B and C), fewer sugar molecules but more water molecules will penetrate from the outer solution to the inner one, as more sugar but fewer water molecules pass through from the solution in the bag to the outside. Consequently, the outer solution becomes sweeter but decreases in volume while the inner solution loses sugar but increases in volume. If an outlet such as a tube (Fig. 66 B) is provided for the solution inside the bag, the volume increase is indicated by a rise of the solution in the tube. If no such outlet is provided (Fig. 66 C) and the bag was full to begin with, then, with increased volume, the membrane must either stretch continuously or burst.

Importance of osmosis. The phenomenon of diffusion of water or of both water and solute through membranes is of importance in many ways.

In food preparation. The swelling of dried fruits and dried beans when soaked for some time in water, and the shriveling of fresh fruits, such as peaches and pears, when preserved in concentrated sugar solution, likewise the shriveling of cucumbers when soaked in brine—all involve osmosis phenomena, the skins of the fruits and seeds serving as the permeable membranes.

In plants. It is due to diffusion through rootlet membranes that water and soluble salts are able to enter plants from the soil, and that water and soluble compounds are able to enter plant cells from the sap and to leave the cells to join this circulating fluid.

In animals. Osmosis is a functioning factor, even though a minor one,[6] whereby water and soluble products of digestion are absorbed from the intestinal tract into the capillaries of the villi. It is also through the process of osmosis that water and various soluble substances are able to pass from the blood through successive membranes into the cells, and from the cells through various membranes into the blood, either for distribution to other cells or on their way out of the body.

In therapeutic treatment. In general, solutions that are used for irrigation and, usually, those employed for introduction into the blood stream should be "isotonic," that is, solutions of equal osmotic pressure with the blood and the solution enclosed in blood corpuscles.

Water the best-known solvent. Every liquid is a solvent for selected substances: iodine, for example, is soluble in alcohol, fats

[6] That factors other than osmotic pressures function in the control of diffusion of substances across living membranes—such as at intestinal walls, capillaries, tissue cells, and kidneys—is evident because absorption frequently occurs at rates that cannot be explained on the basis of osmotic pressure alone.

are soluble in ether, and gold is soluble in mercury. But water is the best-known solvent because it dissolves more substances to an appreciable extent than does any other liquid. In fact, strictly speaking, no substance is absolutely insoluble in water, "insoluble" being merely a way of saying "soluble only to an exceedingly slight degree."

Solubility of substances usually limited. There is no limit to the solubility of some substances in selected solvents. This is true of ethyl alcohol with water and of glycerol with water, which are soluble in each other in all proportions. But as a rule, a given quantity of water, or of any other liquid solvent, is able to hold in solution varying weights of a given substance *only up to a definite limit* under given temperature conditions. For example, 100 ml of water at 20° C is able to hold in solution varying quantities of sucrose up to the limit of 203.9 gm. From then on, provided the solution is kept at 20° C and even though a considerable excess of the undissolved sugar may be present, the quantity of sucrose in solution is maintained at this constant of 203.9 gm in 100 ml of water.

Saturated solution. *A solution is saturated if, upon contact with some of the undissolved solute, it is unable to take more into solution.* For example, the above-mentioned solution of sucrose (203.9 gm in 100 ml of water) is saturated at the given temperature of 20° C, since, if in contact with an undissolved portion of this sugar, the quantity in solution does not increase. But, when the solution is at 100° C, it requires 487.0 gm of sucrose in 100 ml of water to produce saturation. Quantities of other substances that provide a saturated condition in the specified volume of water at given temperatures are listed in the accompanying table (p. 202).

Unsaturated solution. *A solution is unsaturated when, upon contact with some of the undissolved solute, it is able to take more of the same into solution.* For example, a solution of sodium chloride which at 20° C contains 30 gm of this solute in 100 ml of water is unsaturated (see table) because if some of the solid sodium chloride is introduced more will dissolve. Furthermore, the solution will continue to be unsaturated with this salt at this temperature until it contains 36.0 gm, at which time it will be saturated.

Factors affecting solubility. It is obvious from the foregoing examples, and from solubilities as listed in the accompanying table, that the solubilities of substances in water—meaning the quantities necessary to produce saturation—vary with the substances concerned and with the temperatures of the solution.

SOLID SUBSTANCES	QUANTITY OF SUBSTANCE IN GRAMS TO PRODUCE SATURATION IN 100 ML OF WATER AT THE GIVEN TEMPERATURE	
	AT 20° C	AT 100° C
Aluminum chloride	69.9 (at 15° C)	
Aluminum hydroxide	0.00015	
Aluminum oxide	Insoluble	Insoluble
Barium sulfate	0.00024	0.00039
Boric acid	4.8	28.7
Calcium carbonate	0.0014 (at 25° C)	0.0018 (at 75° C)
Calcium chloride	59.5 (at 0° C)	159.0
Calcium hydroxide	0 165	0.077
Calcium oxalate	0.00068 (at 25° C)	0.0014 (at 95° C)
Calcium phosphate	0.002	
Calcium sulfate	0.1759 (at 0° C)	0.1619
Cupric oxide	Insoluble	Insoluble
Cupric sulfate hydrate	31 6 (at 0° C)	203.3
Glucose (dextrose)	83	
Iodine	0.029	0.078 (at 50° C)
Lactose (milk sugar)	17	
Magnesium oxide	0.0086 (at 30°)	
Magnesium sulfate	26 (at 0° C)	
Mercuric chloride	6.1	61.3
Mercurous chloride	0.5	25.0
Potassium hydroxide	112.0	178.0
Potassium iodide	144.0	208.0
Silicon dioxide	Insoluble	Insoluble
Silver chloride	0.00089 (at 10°C)	0.0021
Silver nitrate	222.0	952.0
Sodium bicarbonate	9.6	16.4 (at 60° C)
Sodium chloride	36.0	39.8
Sodium hydroxide	109.0	347.0
Sodium tetraborate (borax)	2.83 (at 0° C)	201.4
Sucrose (cane sugar)	203.9	487.0
Zinc oxide	0.00016 (at 30° C)	
Zinc stearate	Insoluble	Insoluble

GASEOUS SUBSTANCES	IN 100 ML OF WATER AT GIVEN TEMPERATURE UNDER STANDARD PRESSURE	
Carbon dioxide	179.7 ml at 0° C	90.1 ml at 20° C
Chlorine	310.0 ml at 10° C	177.0 ml at 30° C
Hydrogen	1.93 ml at 0° C	0.85 ml at 80° C
Hydrogen chloride	82.3 gm at 0° C	56.1 gm at 60° C
Oxygen	4.89 ml at 0° C	2.61 ml at 30° C
Nitrogen	2.35 ml at 0° C	1.55 ml at 20° C

Slightly soluble and very soluble substances. These are frequently used expressions, and, with the accompanying table at hand, they have significance. Thus, mercurous chloride (calomel) is only *slightly soluble* in water at 20° C, which is around ordinary temperatures. On the other hand, silver nitrate is comparatively *very soluble* at ordinary as well as at high temperatures.

Effect of temperature. As a rule the solubility of substances which are solids increases with an increase in the temperature of the solution; for example, boric acid, silver nitrate, and sucrose are more soluble in water at higher than at lower temperatures. But, there are a few solid substances that increase in solubility with decreasing solution temperatures; calcium hydroxide and calcium sulfate are more soluble in cold than in warm or hot water.

If the solutes are gaseous substances, they are always less soluble as the temperature of the solution increases, and vice versa. This fact is illustrated in the accompanying table.

Aids in preparation of solutions. The speed with which a substance dissolves is affected by both the area of contact between water and solute and the temperature of the solution.

Effect of area of contact. It is self-evident that the greater the area of contact between water and solute, the greater the speed with which the substance dissolves. For this reason finely divided solids dissolve more rapidly than do the same substances in coarser particles. Stirring or shaking also hastens solution making by producing a more thorough distribution of the solute in contact with water.

Temperature aid. The effect of temperature in bringing about more speedy solution depends upon whether the solubility of the substance increases with increased temperatures or with decreased temperatures. For example (see table of solubilities, p. 202), boric acid dissolves more quickly in hot than in cold water because its solubility increases with increasing temperatures of the solution. But calcium hydroxide dissolves more rapidly in cold than in hot water because its solubility increases with decreasing temperature of the solution. No general rule can be formulated as to the temperature most desirable for making solutions as speedily as possible, but tables of solubilities of substances at different temperatures are helpful in this connection and can be consulted with advantage.

A caution: The dissolving in water of some substances is accompanied by the appearance of considerable heat, called the *heat of solution* of the substance. In such instances it is most unwise to use hot water when making the solution concerned. These substances include sodium and potassium hydroxides, calcium and iron chlorides, iron sulfate, magnesium chloride, magnesium sulfate, and magnesium nitrate.

Supersaturated solution. In some instances, when a solution has been saturated at a high temperature with a solid solute, the

entire solute will remain in solution as the temperature of the solution is lowered, provided no undissolved solute is in contact with the solution. Such solutions at the lower temperatures are supersaturated. *A supersaturated solution,* then, *is one which is holding in solution an excess of the solute above the quantity required for saturation at the given temperature.* For example, if a saturated solution of sucrose is obtained at 100° C (487.0 gm for every 100 ml of water), as the solution cools it will for a time hold this total quantity of sucrose in solution—that is, provided no sucrose crystals are present. Hence, at all temperatures below 100° C, as long as no precipitation occurs, the solution is supersaturated.

But supersaturated solutions are frequently very difficult to maintain since a slight disturbance, such as shaking, stirring, or the introduction of a solid particle, especially if it is a particle of the solid solute itself, will give rise to a precipitation from the solution of the solid solute in excess of saturation at the given temperature.[7]

In cookery. The making of fudge or of boiled frosting provides an example of the transition of a sucrose solution from an unsaturated to a supersaturated solution with the final precipitation of crystals. The hot syrup is removed from the stove as a concentrated but *unsaturated solution.* Then, as the syrup cools, if not disturbed in such a way as to start crystal formation, it becomes slightly *supersaturated.* On further cooling it becomes more heavily supersaturated. The skilled cook learns just when to disturb the supersaturated solution by stirring it in order to bring about precipitation of the desired small crystals.

Dilute and concentrated solutions. Solutions are dilute or concentrated, depending upon whether relatively little or much of the solute is present in a given volume of the solution. Some substances are very soluble in water and therefore are capable of yielding highly concentrated solutions in this solvent. This is true of sucrose, sodium

[7] A supersaturated solution for demonstration purposes can be made with sodium sulfate. A suggested procedure is as follows: Obtain a saturated solution of anhydrous sodium sulfate at 50° C, which requires 50 gm of this salt for 100 ml of water at this temperature. If any excess of the solid persists it should be separated carefully and completely by pouring the solution into a *clean, warm* flask. The flask carrying the solution should then be closed with a loose plug of cotton and cooled. If undisturbed, this solution will continue in a supersaturated condition at lower temperatures for some time. When the time comes for the demonstration of this condition, the plug is removed and a small crystal of sodium sulfate hydrate ($Na_2SO_4 \cdot 10\ H_2O$) is introduced. Presently—often almost immediately—all the excess of the salt above saturation will precipitate. Anhydrous sodium sulfate has the formula Na_2SO_4. One hydrate of this salt has the formula $Na_2SO_4 \cdot 7\ H_2O$; another has the formula $Na_2SO_4 \cdot 10\ H_2O$.

hydroxide, and silver nitrate. Other substances, such as mercuric chloride and calcium hydroxide, are so slightly soluble in water that it is impossible to obtain them in any save very dilute solutions.

Sometimes dilute and concentrated solutions are referred to as weak and strong solutions, respectively. Such expressions used in this connection are confusing because "weak" and "strong" are used with a different and very specific meaning in relation to solutions of acids, bases, and salts (p. 219).

Methods of expressing exact concentrations. Various standards are used for solutions of more or less exact quantitative concentrations. Among those in common use are the following.

Solution concentration on a percentage basis. Solutions are frequently made up on a percentage basis, and their concentrations are expressed as 10 per cent, 50 per cent, 1 per cent solutions, etc. If such solutions are *accurately* prepared, both the solute and solvent must be measured on a common *weight* basis. Thus, on a gram basis with water as solvent, a 10 per cent solution of sodium chloride is one which contains 10 gm of sodium chloride to every 90 gm of water. For convenience, however, when water is the solvent used, although the solute may be measured in grams, the water is frequently measured in milliliters. For example, on this basis, a 10 per cent solution, so-called, would contain 10 gm of solute to 90 ml of water. And a solution so assembled comes very close to being accurate on a percentage basis because, although actually 1 ml of water weighs 1 gm only when at 4° C, in the range of temperatures from 0° C to 100° C this volume (1 ml) of water always weighs very close to 1 gm.[8]

Solutions on a percentage basis have no chemical significance, but they are appropriate for many desired purposes including therapeutic, industrial, and laboratory uses. Solution concentrations which do have a chemical significance are called molar and normal solutions.

Molar solutions. *One mole* of a substance is 1 gram-molecular weight of the substance. With this information at hand we are in a position to define *a molar solution as a solution which contains 1 mole of the solute in 1 liter of solution.* For example, a molar solution of sodium chloride contains 58.448 gm of this solute in 1 liter of solu-

[8] 1 ml of water at
- 0° C weighs 0.99987 gm
- 4° C " 1.00000 gm
- 20° C " 0.99823 gm
- 50° C " 0.98807 gm
- 100° C " 0.95838 gm

tion. A molar solution of silver nitrate contains 169.888 gm of this compound in 1 liter of solution.

Na	Cl	Ag	N	O_3
22.991	35.457	107.88	14.008	3×16
	58.448		169.888	

More concentrated or more dilute solutions can be prepared on this basis as multiples or fractional parts of a molar solution. Thus, a 2-molar solution contains 2 moles or 2 gram-molecular weights of solute in each liter of solution, whereas a one-tenth-molar solution contains one tenth of the gram-molecular weight of the solute in each liter of solution.

A form of shorthand has come into use for representing these concentrations. Accordingly, a solution of molar concentration is represented by 1 *M*, a 2-molar solution by 2 *M*, a solution containing 5 moles of solute per liter of solution by 5 *M*. Similarly, for more dilute solutions, the concentration of a solution which contains one half mole of solute per liter is represented either by 0.5 *M* or by *M*/2, a one-tenth-molar solution is represented by 0.1 *M* or *M*/10, a one-fifth-molar solution by 0.2 *M* or *M*/5, etc. Examples of some of these solution concentrations on a molar basis are as follows:

1 M (molar) solution	***Contains***	
Sodium chloride	58.448 gm	in 1 liter of solution
Silver nitrate	169.888 gm	

2 M (2-molar) solution		
Sodium chloride	116.896 gm	in 1 liter of solution
Silver nitrate	339.776 gm	

0.1 M (one-tenth-molar) solution		
Sodium chloride	5.8448 gm	in 1 liter of solution
Silver nitrate	16.9888 gm	

Solution concentrations on this basis have a chemical significance in that they are made up on a molecular-weight basis, and molecular weights serve as measuring units for substances as they become involved in chemical reactions (p. 89). Consequently, if the ratio of molecular weights of substances mutually involved in a given chemical reaction are known and if solutions of the substances are made up on a molar basis, it is possible to measure out volumes of the solu-

tions respectively concerned to contain the exact weights of the substances for their mutual and complete reaction.

For example, in the reaction between sulfuric acid and sodium hydroxide, the equation provides data as to the molecular-weight ratio that must always be met for exact reacting-weight quantities of these substances. This information, in turn, provides the key to the volumes of their solutions, on the same molar basis, that must be used to contain these weights. Thus:

Sulfuric acid	+	Sodium hydroxide	⟶	Water	+	Sodium sulfate
H_2SO_4	+	2 NaOH	⟶	2 H_2O	+	Na_2SO_4
↓		↓				
1 gram-molecular weight		2 gram-molecular weights				

Sulfuric acid	to	***Sodium hydroxide***
1 liter of *M* solution	to	2 liters of *M* solution
or, 10 ml of *M* solution	to	20 ml of *M* solution
or, 10 ml of 0.1 *M* solution	to	20 ml of 0.1 *M* solution

Molecule concentrations in such solutions. Since 1 gram-molecular weight or 1 mole of every substance is believed to include 6.02×10^{23} molecules of the substance, it follows that 1 liter of a molar solution must contain 6.02×10^{23} molecules of the substance concerned (p. 92), while 1 liter of a one-half-molar solution must contain one half this number of molecules of the substance. Which, if true, means that *equal volumes of solutions of various substances of the same molarity must contain equal numbers of molecules of these substances.*

Normal solutions. Solutions on a normal basis apply only to acids, bases, and salts, and they are concerned with concentrations of the *radicals* provided within these compounds rather than with concentrations of the compounds in themselves. The measuring unit for the solute is the *equivalent weight;* that is, the weight of the compound which provides a 1-valent quantity of each of the constituent radicals. *A normal solution contains 1 gram-equivalent weight of the acid, base, or salt in a liter of the solution.*[9] The following table provides examples.

Solutions of greater or less concentration but still on a normal basis are also frequently used. Shorthand representations for solu-

[9] It is well to note that the isotonic solution of sodium chloride, sometimes referred to as *normal* or *physiological* salt solution, is not a normal solution from a chemical viewpoint. Such a solution, that is, normal from a chemical angle, contains 58.448 gm of sodium chloride per liter of solution, whereas an isotonic solution contains only 9.0 gm of sodium chloride per liter of solution, this being approximately the concentration of the salts normally present in the blood stream.

tion concentrations on a normal basis are as follows: N, 2 N, 5 N, obviously in respect to normal, 2-normal, and 5-normal concentrations; 1/2 N or 0.5 N and 1/10 N or 0.1 N in respect to solutions of one-half-normal and one-tenth-normal concentrations.

A NORMAL SOLUTION OF	CONTAINS IN 1 LITER OF SOLUTION
Hydrochloric acid H^+ Cl^- 1.008 35.457 M.W. (36.465)	1 gram-molecular weight (36.465 gm) of this acid, since this provides for the presence in the solution of a 1-valent quantity of each of the two radicals: 1.008 gm hydrogen radical (H^+) 35.157 gm chloride radical (Cl^-)
Calcium hydroxide Ca^{++} $(OH)_2$ 40.08 2×17.008 M.W. (74.096)	1/2 the gram-molecular weight (37.048 gm) of this base because this contributes to this volume of solution a 1-valent quantity of each of the two radicals: 20.04 gm calcium radical ($Ca^{++}/2$) 17.008 gm hydroxyl radical (OH^-)
Sodium phosphate Na_3^+ $(PO_4)^{---}$ 3×22.991 94.975 M.W. (163.948)	1/3 the gram-molecular weight (54.657 gm) of this salt which contributes to 1 liter of solution a 1-valent quantity of each of the two radicals: 22.991 gm sodium radical (Na^+) 31.325 gm phosphate radical ($PO_4^{---}/3$)

Normal solutions of acids and bases. A normal solution of an acid, or of a base, may also be defined on the basis of the concentration of hydrogen radical, or of hydroxyl radical, respectively, provided in the solution. Thus, *a normal solution of an acid is a solution which contains a 1-valent quantity, or 1.008 gm, of hydrogen radical* (H^+) *in 1 liter of solution;* whereas *a normal solution of a base is a solution which contains a 1-valent quantity, or 17.008 gm, of hydroxyl radical* (OH^-) *in 1 liter of solution.*

Modifications of normal solutions of acids and bases, such as one-half-normal and one-tenth-normal solutions, are of commensurate concentrations.

	1 LITER OF NORMAL SOLUTION CONTAINS	1 LITER OF ONE-TENTH-NORMAL SOLUTION CONTAINS
$H^+NO_3^-$ (63.016)	63.016 gm nitric acid, which includes 1.008 gm (H^+) of hydrogen radical	1/10 of 63.016 gm nitric acid, hence 1/10 of 1.008 gm ($H^+/10$) of hydrogen radical
$H_2^+SO_4^{--}$ (98.082)	1/2 of 98.082 gm sulfuric acid, 1.008 gm (H^+) of hydrogen radical	1/20 of 98.082 gm sulfuric acid, 1/10 of 1.008 gm ($H^+/10$) hydrogen radical
Na^+OH^- (39.999)	39.999 gm sodium hydroxide, 17.008 gm (OH^-) hydroxyl radical	1/10 of 39.999 gm sodium hydroxide, 1/10 of 17.008 gm ($OH^-/10$) hydroxyl radical

Milliequivalent weights. The term *milliequivalent* weight is used frequently for recording the concentration of various elements or radicals contributing to physiological solutions, such as blood or urine. The milliequivalent is simply $\frac{1}{1000}$ of the corresponding gram-equivalent weight; or, it may be interpreted as the equivalent weight of the element or radical recorded in milligrams, rather than in grams. For example: A solution contains 5 meq/liter of calcium (Ca^{++}). This means that there are $\frac{5 \times 0.001 \times 40.08}{2} = 0.1002$ gm of calcium radical in a liter of this solution or 100.2 mg of calcium radical per liter of solution.

COLLOIDAL SOLUTIONS WITH WATER AS DISPERSING LIQUID

Some properties of colloidal solutions in contrast with related properties of true solutions have been considered previously (pp. 193 to 197). It will be recalled that the difference in properties of these two varieties of dispersions is due primarily to the difference in the sizes of their dispersed particles. Those particles in true solutions are single molecules, hence with exceedingly minute dimensions; those in colloidal solutions are molecule aggregates which may vary from clusters of possibly less than 100 molecules to aggregates of thousands of coherent molecules. With these characteristics in mind, the study of colloidal solutions is now continued.

Why colloidal particles remain dispersed. It is a curious fact that relatively heavy colloidal particles do remain dispersed for a

longer or shorter time among single, lightweight water molecules of the dispersion medium. There are several reasons for this phenomenon.

1. Water molecules, although light in weight, are in very rapid vibratory motion, darting about in every direction. Hence, as heavy colloidal particles start downward, they are being continually hit by numerous darting water molecules which drive them first in one direction then another—down, up, sideways, etc. As a result, colloidal particles follow a sort of zigzag path that is referred to as their *Brownian movement.* Obviously, the impacts by water molecules do not check entirely the precipitation of these particles, but they do cause more or less of a delay.

2. The colloidal particles themselves are in more or less vibratory motion which results, on their part, in impacts against water molecules, against each other, and against the sides of the container, and these impacts are accompanied by reboundings into the dispersion.

3. But the most significant factor in the dispersion of colloidal particles is the fact that they usually carry like charges—either positive or negative. As a result, a repulsive effect becomes established between these particles, and in their effort to keep away from each other they tend to remain distributed in the dispersion medium, which is usually water.

What causes their precipitation? Despite the afore-mentioned forces which function to maintain the dispersion of colloidal particles, because of their weight there is always a tendency toward their precipitation. This separation may not become apparent for days, weeks, months, or longer, but the predisposition is forever present. Moreover, it follows that the heavier particles give evidence of precipitation sooner than do the lighter ones.

But a potent precipitating effect is produced by the introduction of an acid, base, or salt, the positive or negative ions from which offset opposite charges on the colloidal particles; therefore, repulsive forces between these dispersed particles being diminished, precipitation begins. For example, the casein component of milk is maintained in colloidal dispersion in fresh milk by negative charges on dispersed casein molecule aggregates, but when milk sours, the presence of positively charged hydrogen ions, contributed by lactic acid, is one factor which makes it possible for the casein aggregates to assemble and precipitate.

Light penetration. True solutions with water as the solvent are transparent, since a light beam passes through them unimpeded by

the tiny dispersed particles which are single molecules. In contrast, colloidal dispersions are from slightly to decidedly translucent. This is due to the fact that light rays, upon penetrating into a colloidal solution, strike against the sizable colloidal particles and are reflected at various angles, or "scattered," throughout the dispersion. This effect is quite conspicuous in a dispersion of albumin in water and in a gelatin-in-water dispersion. [10]

Boiling and freezing points. Substances in true solution have the effect of increasing the boiling point above that of water alone and depressing the freezing point below that of water (p. 197). In contrast, substances in colloidal dispersion produce from very little to no appreciable effects on these properties, with the result that colloidal dispersions in water have boiling points of 100° C, or very little above this temperature, and freezing points of 0° C, or very little below this level. The reason is that these effects are proportional to particle concentrations, and in any colloidal dispersion, while there are many thousands—even millions—of molecules, they are clustered in relatively few molecule aggregates which are the dispersed particles. Thus, for example, a true solution of a sugar has a boiling point definitely above 100° C and a freezing point definitely below 0° C, dispersed particles being millions of single molecules. But a water dispersion of gelatin, being a colloidal dispersion, has a boiling point and a freezing point either very close to or at 100° C and 0° C, respectively, because while there may be millions of gelatin molecules involved, the molecules are concentrated in relatively few particles, or gelatin aggregates.

Colloidal dispersions and osmosis. While dispersed molecules of true solutions are able to diffuse through permeable membranes such as cellophane or animal gut, the dispersed particles, or molecule aggregates, of colloidal solutions are either absolutely incapable of diffusion through such membranes or can do so only to a very slight extent. It is, more especially, the *size* of the particles that is involved. Most colloidal particles are too large to squeeze through the minute pores of the permeable membrane, only such as are made up of relatively few coherent molecules being able, occasionally, to accomplish this penetration. Thus, there is reason to believe that dispersed par-

[10] There are occasional colloidal dispersions which appear to the naked eye to be transparent but, when examined with the ultramicroscope, are shown to be colloidal in character. In such dispersions the colloidal particles are relatively small.

ticles of egg albumin, lactalbumin, and some of the intermediate products of protein digestion are small enough to diffuse through *some* membranes to a slight extent. Herein may lie an explanation for the sensitivity of an occasional person to these proteins in his food since it may be that the intestinal membrane of such an individual is somewhat permeable to these molecules or molecule aggregates.

Dialysis. The difference in diffusion possibility of substances in true solution and those in colloidal solution is taken advantage of for the separation of two such substances when they are mingled in the same water dispersion. This is accomplished by enclosing the dispersion in a bag of permeable membrane which is immersed in water. The substances in true solution are able to pass through the membrane into the surrounding water, but the substances in colloidal solution are not.

This process of separating a colloidal substance from a substance in true solution, by diffusion of the soluble substance through a membrane, is sometimes called *dialysis.*

Biological importance. This difference in diffusion possibilities of substances in true and colloidal solutions is of vital importance to plants and animals. The water of the sap of plants and of the blood of animals holds some substances in true solution and others in colloidal solution, but only the substances in true solution are able to enter the cells. On the other hand, within the cells of both plants and animals there are substances held in colloidal solution that must be kept there if cell activities are to proceed normally, and, fortunately, being colloidal, these substances are incapable of escaping from the cells.

One of the reasons why cooked starch and most proteins of the food mass are not able to pass through the intestinal membrane into the blood, and why glycogen and cell proteins cannot leave the cells by diffusion through cell membranes into the intercellular fluid, is believed to be the inability of their relatively very large single molecules or molecule aggregates to work their way between the molecules comprising the intestinal and cell membranes, respectively.

Colloidal dispersions and gels. The colloidal dispersions referred to previously are *sols*, meaning dispersions which are fluid. This is in contrast to dispersions called *gels*, which are jellylike in character and, although containing considerable water, possess a greater or lesser degree of rigidity. A colloidal gel is possible with a substance which is capable of concentrating great quantities of water

at the surface of its dispersed particles and in so doing swells enormously. Familiar examples of gels are fruit jellies and the more or less rigid dispersions made from gelatin. Incidentally, the term "gel" is derived from "gelatin," which is outstandingly capable of forming this variety of dispersion.

Gels may vary all the way from fluid jellies, which flow on slight pressure, to gels with decided rigidity. The rigidity is believed to be due to a development within the dispersed system of a meshlike structure that is brought about, presumably, by the adherence of some of the colloidal particles to one another in such a manner as to form a network of fibrils which encloses a more dilute colloidal solution.

Procedure. Two methods are in common use for making gels, and both are familiar. One of these consists of allowing a sufficient quantity of a suitable substance, such as gelatin or soap, to soak in contact with water until enough swelling of the colloidal material has occurred to produce a jellylike mass.

The second method consists of first preparing a colloidal sol of the material concerned at an elevated temperature, then lowering the temperature of the dispersion and permitting it to stand and cool, undisturbed, until it gradually "sets" to the gel condition. Familiar examples are the gel formation which occurs during the cooling of a dispersion of cooked starch, and the molded gelatin desserts that follow from the cooling of the gelatin sols.

The aging of gels. In the course of time a gel shows certain characteristic changes, notably what amounts to a squeezing out of some of the liquid from the gel mass. This is accompanied by a concentration, hence, shrinking, of the solid material. The fluid which exudes from the gel is not water alone but water with a dilute solution of components that contribute to the gel. This process is known as *syneresis* and may be regarded as the reverse of the initial process toward gel formation whereby water was concentrated at the surface of dispersed material with consequent swelling.

Examples. The gels of fruit jellies and of gelatin molds have already been mentioned; other gel dispersions are custards and junkets, and various mucilages, glues, and pastes. But, none of these gels can be kept for any length of time without showing characteristic evidence of age: drops of moisture will eventually collect on the surface of jellies, custards will "break," and curds will separate from the whey of junket.

Breadmaking involves obtaining a protein-starch gel of a definite structure, but as bread ages, syneresis, or the characteristic squeezing out of water with dissolved components, occurs. This becomes evident in the moisture that collects on the surface of bread that is kept enclosed in a tight tin box so that evaporation is slow. Moreover, since this moisture was originally part of the structure of the bread, as it is removed, drying out continues, and the whole texture of the bread becomes altered.

The preparation of gelatin and agar slants and culture plates in the bacteriologic laboratory involves gel formation of these materials, and all laboratory

workers are familiar with the syneresis—characterized by the appearance of drops of moisture and the shrinkage of the material within the tubes and plates —that occurs as these culture media age.

Gels are of physiological importance. About 70 per cent of the content of the body is water, the greater part of which is present within the cells of muscle, nerve, and other tissues, But, despite this large supply of water, the content of each cell remains in a semifluid condition. The reason is that most of the water is concentrated at surfaces of the colloidal material present to form a gel which, with its meshlike framework, becomes a factor in cell structure. Moreover, it is claimed by some that certain of the changes which accompany old age, as for instance the changes in blood-vessel walls known as arteriosclerosis, are essentially the result of the aging of the colloidal systems that comprise the cell structures.[11] The clotting of blood involves the formation of a gel; and the subsequent exudation of serum, which is characteristic of the hardening and drying of the clot, is another example of syneresis.

EMULSIONS AND EMULSIFYING AGENTS

What is an emulsion? An emulsion can be defined as a mixture of two mutually insoluble liquids, one of which is dispersed in the other in more or less finely divided droplets. The most commonly occurring emulsions are those of water with fatty oils and water with liquid hydrocarbons, or mixtures of liquid hydrocarbons such as gasoline and kerosene.

The dispersed droplets in an emulsion are usually of suspension dimensions (p. 196), hence, large enough to be discernible to the naked eye or under an ordinary microscope. Such a dispersion is a *suspension emulsion*—most French dressings are of this type. Occasionally, however, the dispersed droplets are colloidal in size (p. 196), in which case the dispersion is a *colloidal emulsion.* The more permanently dispersed systems of some mayonnaise dressings are examples.

Emulsifying agents. Although an emulsion can be obtained easily by mixing and shaking the two liquids together, it is difficult to maintain unless some means is provided to check the marked tendency of the two liquids to separate. Such a means is provided through the agency of selected substances which, when added to the emul-

[11] Gortner, R. A.: *Outlines of Biochemistry.* John Wiley & Sons, Inc., New York, 1949, pp. 242–43.

sion, are capable of prolonging the dispersion period. These substances are known as emulsifying agents or stabilizers. The mixture of an oil with water, first without then with the presence of a stabilizer, is an example. Upon thorough shaking of the oil with water, a suspension is formed, but, if allowed to stand, within a very short time practically all of the oil will be found in a layer on top of the water. However, if a little white of egg is added and the mixture is again thoroughly shaken, a much more lasting emulsion can be obtained with the protein of the egg white functioning as an emulsifying agent.

In general, emulsions are characterized by a "milky" appearance, after the manner of milk and the milky secretions of certain plants, such as the milkweed or the poppy.

Functioning of emulsifying agents explained. The functioning of the emulsifying agent in prolonging the life of an emulsion is believed to be due to its ability to collect in a thin film at the surface areas of the dispersed droplets, thereby preventing them from coalescing to make larger drops. In order that it may function in this way, the emulsifying agent must be a substance which can be concentrated (adsorbed) either by the water or by the dispersed liquid at surface areas where the water and dispersed substance meet—called interfacial areas.

For example, sodium and potassium soaps; resins, and certain gums, such as gum acacia and Irish moss; proteins, such as albumin gelatin, and hemoglobin; dextrins and starches; cholesterol (p. 401) and lecithins (p. 400) are all stabilizers for water and oil emulsions. The effectiveness of these emulsifying agents is attributed to the semisolid films which they form at the interfaces between the two liquid components of the emulsion.

For some emulsions certain finely divided, insoluble solids function as emulsifying agents; and the more finely divided this agent is, the greater is its stabilizing effect. Fuller's earth and kaolin are examples of solid stabilizing agents for emulsions of liquid hydrocarbons suspended in water. Such emulsions are used for insecticidal sprays.

Surface tension a factor in emulsions. A factor which is believed to play an important part in the behavior of emulsions and in the functioning of emulsifying agents is the surface tensions or interfacial tensions of the two participating liquids and the changes which are effected in these surface tensions by the introduction of an emulsifying agent.

A liquid, although conforming to the shape of the container, has definite surface boundary where it meets with an insoluble gas (as is true of water in contact

with air) or with another liquid with which it is insoluble (as at the interfacial areas between water and an oil). At each such surface the liquid behaves as if it were covered by a more or less elastic film or skin maintained under tension. The reason for this effect is that the molecules at the surface of the liquid are drawn together with greater cohesive forces than exist between molecules within the body of the liquid. It is *the marked cohesive effect between molecules at a liquid surface which is called surface or interfacial tension.* Manifestations of this force are the tendency of a liquid to reduce its surface to a minimum, as the result of which individual droplets try to take the form of spheres; and the tendency of droplets coming into contact to coalesce to form larger drops.

Thus, in an emulsion of oil in water, the oil is dispersed in spherical drops, with both water and oil exhibiting their respective surface tensions at their interfacial areas—water having the higher surface tension. Consequently, (1) in order to decrease its considerable surface area, where it surrounds the numerous oil droplets, the water tends to squeeze out the oil. At the same time (2) the oil droplets, upon coming into contact with each other, coalesce to form larger drops in order to decrease their area of contact with the water. Hence, a separation of the two liquids is sooner or later effected.

Therefore, for stabilizing an emulsion it is necessary to overcome to some extent the tensions that are operative at the interfacial areas of the two mutually insoluble liquids. The addition of a substance which lowers the surface tension of either one of the liquids to a marked degree will function toward this end. For example, sodium and potassium soaps markedly lower the surface tension of water; it is for this reason that these substances are effective emulsifying agents for oil-in-water emulsions. Moreover, substances which lower the surface tension of a liquid tend to collect at its surface—at the surface of the liquid and its container, at the liquid-air surface, and at the interfacial surface between the two liquids. It is this collection of the emulsifying agent at the interfacial surface of the two liquids which is believed to account for its distribution in a thin film around the droplets of the dispersed liquid, thus interfering with their coalescence.

Practical uses of emulsions. Emulsions are of importance in a great variety of daily uses of which only a few can be suggested here.

In ordinary cleaning operations the most common agent for the removal of fats and oils is water with soap, the soap being provided to function as an emulsifying agent, since neither fats nor oils are soluble in water. It follows that an important part of the cleaning procedure consists in obtaining a good emulsion, and to accomplish this, the soap must be used in sufficient concentration to produce an effective film around the fat droplets. (It is quite as possible to use too much soap as it is to use too little. Furthermore, the soap that is used in excess of the need not only is wasted but actually can decrease the stability of the emulsion.) The handrubbing or the agitation produced in the washing machine is also important in effecting the desired dispersion of the grease throughout the soapy water. In this manner fats and oils can be removed from the skin, garments, and utensils in an emulsion when this could not possibly be accomplished through the agency of water alone.

Emulsions have an important place *in cookery*. The making of mayonnaise dressing involves obtaining an emulsion of oil with water, the water being provided by the use of either vinegar or lemon juice. The process employed is a familiar one. The two liquids are thoroughly mixed by beating, during which the oil is separated into finer and finer droplets; egg yolk is added, the proteins of which function as emulsifying agents for the dispersion. But the proteins of egg yolk are not the only stabilizers that are possible for mayonnaise. In some commercial preparations of this dressing, starch is introduced for this purpose. In the making of French dressing, gelatin can be used to advantage as an emulsifying agent for the fat and water dispersion. In the preparation of gravies and various food sauces, cooked starch, provided by flour or cornstarch, functions to hold the fat and water in emulsion dispersion. An interesting example of a modern use of emulsification is in the preparation of both sweet milk and cream from appropriate quantities of dried skim milk and butter where fresh milk and cream are not readily available. The mixture is assembled through the aid of a homogenizer.

In pharmacy, also, emulsions have their uses, notably to render certain oily medications, such as mineral oil and cod-liver oil, somewhat more palatable. The emulsifying agents used for this purpose include agar and gum acacia.

Emulsions are of importance physiologically. As will be discussed later (p. 448), the emulsification of fats in the digestive tract is of great importance as a means for bringing fats, water, and digestive enzymes into contact with each other, thereby aiding fat digestion. The emulsion phenomenon is also important as the means provided by nature for maintaining the dispersion of fats in the lymph and blood for transportation to the cells.

QUESTIONS

1. Distinguish between true solutions, colloidal solutions, and suspensions as to each of the following, with water as the dispersion medium: size of the dispersed particles, appearance, permanence, ability to diffuse through a membrane. How, theoretically, are these differences accounted for?

2. Why would a scald occasioned by the spilling of a boiling solution of brine (concentrated sodium chloride solution) be likely to produce greater tissue injury than a similar scald occasioned by boiling water?

3. Of what advantage is it to the plant that the carbohydrates of its sap (chiefly glucose, fructose, and sucrose) are capable of true solution, whereas the starch found in seeds, roots, or tubers is not capable of true solution?

4. When concentrated brine solutions are emptied on growing grass the plants in the area usually die. What may happen to the root cells that would account for this fact?

5. The membranes of the alimentary canal normally are impermeable to magnesium sulfate. How does the administration of a concentrated solution of this salt affect diffusion in respect to this membrane?

6. a. Is it possible to secure a 50 per cent solution of sodium chloride in either cold or boiling water? Reason.
   b. How much sodium chloride must be used per liter of solution if a solution which is saturated at ordinary temperature is required?
   c. How much sodium chloride must be used to make a solution of normal concentration?

7. How much sulfuric acid must be used to provide 1 liter of solution of each of the following: (a) a molar solution, (b) a $M/10$ solution, (c) a normal solution?

8. Is it possible to secure a solution of mercuric chloride of molar concentration? Of glucose? If so, how much of the solute would be required for 2 liters of solution? If not, tell why.

9. How much $M/10$ solution of sodium hydroxide must be used to exactly neutralize 10 ml of $M/10$ solution of hydrochloric acid? Explain.

10. In a specimen of blood, the concentration of sodium is recorded as 320 mg per 100 ml. Record in milliequivalents per liter. The concentration of magnesium in this sample is 3.0 mg per 100 ml. Record in milliequivalents per liter.

11. Why are solutions on either a molar or a normal basis usually preferred, to solutions on a percentage basis, for use in a chemistry laboratory?

12. Under which condition would the blood be capable of holding the higher proportion of oxygen in solution: (a) when the temperature is normal, about 98.6° F? (b) in a febrile condition as when the temperature is 103° F? State the reason for your answer.

13. What is a gel? Give examples.

14. What is an emulsion? Name two factors that must be provided for in order to secure a lasting emulsion and illustrate by reference to some process of cookery or household interest that involves the preparation of an emulsion.

CHAPTER 17

IONS AND IONIZATION

Electrolytes and nonelectrolytes. Acids, bases, and salts are the only compounds whose water solutions conduct an electric current. For this reason they are called *electrolytes*. This is in contrast to many other compounds, such as sugars and alcohols, which are called *nonelectrolytes* because their solutions do not conduct a current.

Chemical activity of electrolytes and their conductivity. Different electrolytes, even in solutions of comparable concentrations, differ as to the degree in which they conduct the current of electricity, and on this basis they are classed as *strong electrolytes* and *weak electrolytes*. It is highly significant, moreover, that strong electrolytes are very active chemically, whereas weak electrolytes are relatively less active chemically. In fact, the chemical activity or "strength" of a given acid, base, or salt is directly related to the

Comparative activities of acids, bases, and salts in one-tenth-normal solution

Strong acids		*Strong bases*		*Strong salts*	
Hydrochloric	92	Potassium hydroxide	91	Potassium chloride	86
Nitric	92	Sodium hydroxide	91	Sodium chloride	84
Sulfuric	60	Barium hydroxide	77	Silver nitrate	81
				Sodium nitrate	79
				(nearly all salts are strong)	
Weak acids		*Weak base*		*Weak salt*	
Oxalic	40.0	Ammonium hydroxide	1.3	Mercuric chloride	1.0
Phosphoric	27.0				
Tartaric	8.5				
Acetic	1.3				
Carbonic	0.17				
Boric	0.01				

degree in which this electrolyte, in solution, conducts the electric current. Some of these relationships are indicated in the table on page 219.

A *strong electrolyte* may be described, therefore, as an acid, base, or salt which is active chemically and, in water solution, gives good conduction of an electric current. By contrast, a *weak electrolyte* is an acid, base, or salt which is not very active chemically and which, in water solution, is a relatively poor conductor of electric current.

Another important observation regarding acids, bases, and salts is that to exhibit electrical conductivity and the associated chemical activity peculiar to these compounds, they must be in solution in water.[1]

An explanation for behavior of electrolytes. Because of these and other phenomena which are peculiar to electrolytes, chemists long ago began to suggest possible explanations in terms of something which happens to acids, bases, and salts in water solution. About 1887, a young Swedish student of chemistry, Svante Arrhenius, proposed a theory which, with modifications, has provided the desired explanation.

Arrhenius proposed that when acids, bases, and salts dissolve in water, part or all of their molecules separate to form independently reacting, electrically charged particles which have come to be called *ions* (meaning wanderers). For example:

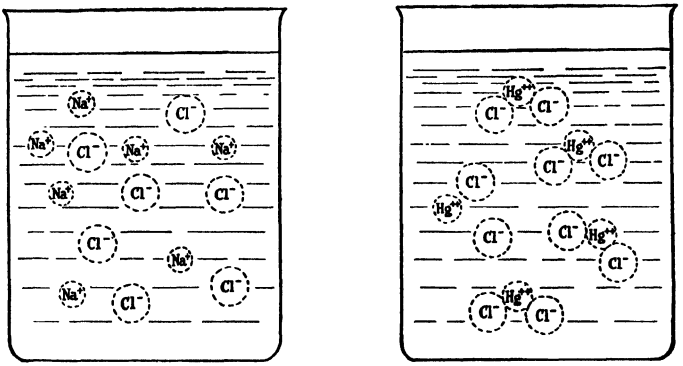
$$NaCl \longrightarrow Na^+ + Cl^-$$
$$Ca(OH)_2 \longrightarrow Ca^{++} + 2\,(OH)^-$$
$$HC_2H_3O_2 \longrightarrow H^+ + C_2H_3O_2^-$$

These ions, rather than the neutral molecules, are the chemically active particles that engage in the reactions peculiar to acids, bases, and salts, and the conduction of the electric current is accounted for by the flow of these charged particles through the solution. The different degrees of activity exhibited by solutions of different electrolytes are explained, according to this theory, by the proportion of active ions to molecules in the solution. Thus, with a strong electrolyte, such as sodium chloride or potassium hydroxide, the proportion of ions in the solution is high—even up to 100 per cent (Fig. 67 A); whereas in solutions of weak electrolytes, such as acetic acid and

[1] Bases and salts in solid form do conduct the electric current slightly. Also liquid ammonia is another solvent in which electrolytes show electrical conductivity.

ammonium hydroxide, the neutral molecules predominate and the proportion of ions is correspondingly low (Fig. 67 B).

The concepts advanced by Arrhenius are still used to explain the behavior of weak electrolytes. But for strong electrolytes, in the light of newer knowledge, certain modifications of this theory must be considered.



In a solution of sodium chloride, a typical strong electrolyte, all of the salt is in the form of ions.

In a solution of mercuric chloride, a typical weak electrolyte, molecules predominate and ion concentration is low.

Fig. 67

The charges carried by ions. While Arrhenius firmly believed, and chemists believe today, in the existence of ions, he was not able to account satisfactorily for the charges carried by these particles. The experimental findings that have led to the modern concept of atom structure, and hence of ion composition, are more recent developments.

The explanation accepted by the modern scientist is that (1) an ion is *positively charged* when the atom concerned has given up one or more of its electrons (Fig. 40, p. 125) to another atom or atom group, and (2) an ion is *negatively charged* when the atom (or atom group) involved has acquired an electron or electrons from some outside source. For example:

the sodium ion (Na^+) is 1-positively charged
because the sodium atom has given up 1 electron

the chloride ion (Cl^-) is 1-negatively charged
because the chlorine atom has 1 excess electron

the sulfate ion (SO_4^{--}) is 2-negatively charged
because the sulfate atom group has 2 excess electrons

BASES AND SALTS

Ionic compounds. Earlier in our study we discussed the concept of molecules as unit-reacting particles of substances. This idea still holds for many types of compounds, including sugars, alcohols, and acids. However, more recent experimental studies of the structures of crystals of bases and salts have led chemists to the conclusion that strong bases and most salts do not form molecules. Instead, they are ionic compounds (p. 126) which are composed of positively charged and negatively charged ions—both in the solid crystalline

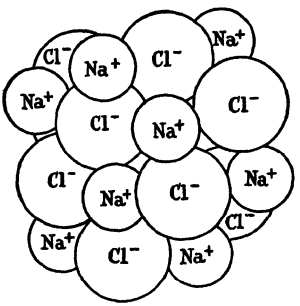


Fig. 68. Diagram of sodium chloride as an ionic compound showing the solid crystal composed of alternate sodium and chloride ions.

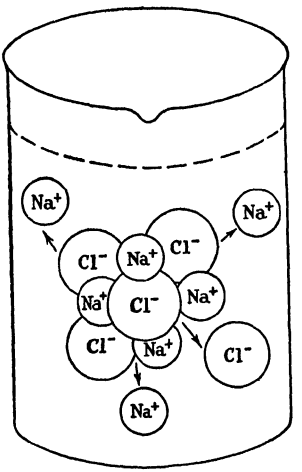


Fig. 69. As a crystal of sodium chloride dissolves in water, sodium ions and chloride ions are set free in the solution.

form and as they exist in solution. These oppositely charged ions are mutually attracted to each other and cluster together in a systematic fashion in the crystalline structure, as is suggested in the diagram for sodium chloride (Fig. 68).

In the solid state, each base and each salt exhibits a characteristic form of crystal. These are built up in such a way that positively

charged ions are surrounded by negatively charged ions and negative ions are surrounded by a zone of positive ions. There are no discrete molecules. The formula for such a compound represents, not the molecule of the substance, but the unit of positive and negative ions that builds the solid crystal.

Free ions the reacting particles. As crystals of salts and bases dissolve in water, the ions previously bound in the crystal are liberated from their fixed positions, probably through an attraction exerted by water molecules, and become free ions in the solution (Fig. 69).

In the crystal		*In solution*
Sodium chloride (solid)	⟶	Sodium ions + Chloride ions
Na^+Cl^-	⟶	$Na^+ + Cl^-$
Potassium hydroxide (solid)	⟶	Potassium ions + Hydroxyl ions
K^+OH^-	⟶	$K^+ + OH^-$

The free ions thus released in the solution are the units which, given suitable conditions, engage in reactions with other ions or molecules with which they come in contact.

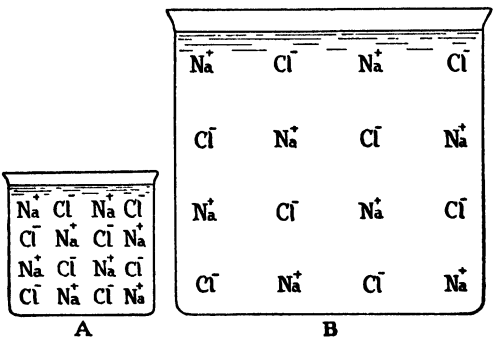


Fig. 70. The attraction between ions is greater in *A* than in *B*.

Interionic attractions reduce ion activity. However, even in solution, these ions are not completely independent because of the mutual attraction of oppositely charged ions. Thus, some of the positively charged ions in the solution become surrounded by negative ions, while some of the negative ions acquire a surrounding zone of positive ions. This is most marked in very concentrated solutions (Fig. 70 A). In more dilute solutions the ions are farther apart; hence, the attraction between ions is diminished (Fig. 70 B). The

figures given on page 219 are indicative of the degree to which the ions of strong bases and salts there mentioned are independent and their movements unrestricted by the attractive forces between them.

In solutions of strong bases and strong salts. Some of the strong bases, notably potassium hydroxide and sodium hydroxide, can provide solutions which are very active chemically, because, being completely ionized and also very soluble in water, these bases can give a high concentration of ions in solution. Other bases, such as calcium hydroxide and magnesium hydroxide, can provide only low concentrations of ions, hence relatively less active solutions. This is due to the tendency of the ions that contribute to such bases to form crystal aggregates and thus to be removed from solution as insoluble material. (See solubility table, p. 202.)

$$\underset{\text{Insoluble portion}}{Ca^{++}(OH)_2^-} \longleftrightarrow \underset{\text{Ions in solution}}{Ca^{++} + 2\ OH^-}$$

Most salts are strong electrolytes and, as such, are believed to be completely ionized; hence, if they are soluble in water, they provide chemically active solutions.

Weak salts and weak bases. A few salts, including mercuric chloride, are weak electrolytes. In these salts the metal and acid radicals are believed to be held in combination through covalent bonds (p. 128). Similarly, in molecules of weak bases—ammonium hydroxide for instance—the metal or ammonium radical is believed to be held in combination with the hydroxyl group. Ionization of these weak electrolytes is accomplished only as the salt or base dissolves in water. Moreover, the ions thus formed in the solution have a marked tendency to recombine into molecules. Consequently, there are always two opposing reactions operating in a solution of a weak base or a weak salt: (a) the ionization reaction, and (b) the recombination of ions to form molecules. For example:

In ammonium hydroxide solution

$$NH_4OH \underset{b}{\overset{a}{\longleftrightarrow}} NH_4^+ + OH^-$$

In mercuric chloride solution

$$HgCl_2 \underset{b}{\overset{a}{\longleftrightarrow}} Hg^{++} + 2\ Cl^-$$

As a result, in these solutions of weak electrolytes, the molecule concentration is relatively high and the ion concentration is correspondingly low. (See table, p. 219.) This helps to account for the slow reactions characteristic of weak electrolytes.

THE IONIZATION OF ACIDS

Acid molecules. Acids, when not in water solution are believed to be made of covalent molecules (Fig. 71).[2] But, as they dissolve in water part or all of their molecules separate to form positively charged and negatively charged ions. With strong acids, practically all of the molecules are believed to ionize; with weak acids, a larger proportion remains un-ionized.

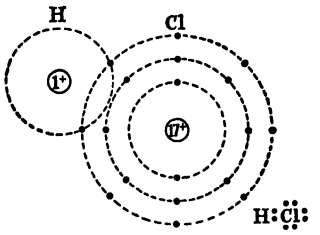


Fig. 71. Hydrogen and chlorine atoms combined through 1 pair of shared electrons (covalent bond) in the molecule of hydrogen chloride.

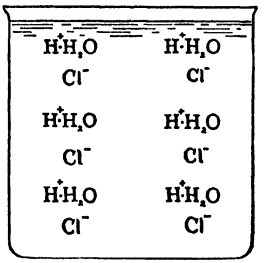


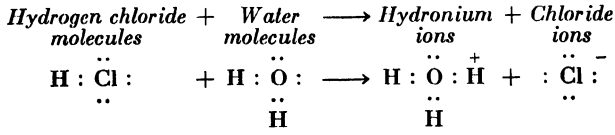
Fig. 72. In water solution, hydrochloric acid is dispersed in the form of hydronium ions ($H^+ \cdot H_2O$) and chloride ions (Cl^-).

The ionization reaction. Arrhenius proposed that on entering water solution some of the acid molecules simply dissociate (fall apart) into positively charged hydrogen ions and negatively charged acid radical ions. But, chemists are now convinced that ionization of molecules of acids is not thus easily accomplished. Water molecules are believed to take an active part in attracting the positively charged hydrogen atoms away from the acid molecules, thus leaving negatively charged acid radicals in the solution. The reaction of acid

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[2] The distinction between ionic compounds and compounds which form covalent molecules should not be regarded as hard and fast. It is attributed to different degrees of attraction exhibited by different ions. Some ion pairs appear to maintain independence even in concentrated solutions, as in solutions of sodium hydroxide and potassium hydroxide. Other ion pairs are more strongly attracted to each other and, except in very dilute solutions, assemble in ionic crystals which precipitate as insoluble material. Still other ion pairs come together in the more intimate structure of the covalent molecule and in these solutions all three particles occur together—molecules, positive ions, and negative ions. Weak acids, such as acetic acid and phosphoric acid, exemplify this type.

molecules with water is illustrated in the following equation with both ions and molecules represented by structural formulas.



This representation for the reaction illustrates the belief that, when in water solution, the *hydrogen ion* (H^+), which is a single proton, is attached to a molecule of water, thus forming what is known as the *hydronium ion*[3] (formula H_3O^+). This particle may be regarded as hydrogen-ion hydrate and be so represented by the formula $H^+ \cdot H_2O$ (Fig. 72). Equations for the ionization of hydrochloric and sulfuric acids are given below.

$$\underset{\text{Hydrochloric acid molecules}}{HCl} + \underset{\text{Water molecules}}{H_2O} \longrightarrow \underset{\text{Hydronium ions}}{H^+ \cdot H_2O^*} + \underset{\text{Chloride ions}}{Cl^-}$$

$$H_2SO_4 + H_2O \longrightarrow H^+ \cdot H_2O + \underset{\text{Hydrogen sulfate ions}}{HSO_4^-} \quad \left.\right\} \text{In concentrated solution of the acid}$$

$$H_2SO_4 + 2\,H_2O \longrightarrow 2\,H^+ \cdot H_2O + \underset{\text{Sulfate ions}}{SO_4^{--}} \quad \left.\right\} \text{In dilute solution of the acid}$$

* Other shorthand devices that are used for representing hydronium ions are H_3O^+ and $H^+(H_2O)$.

Some acids ionize in steps. Acids whose molecules contain two or more replaceable hydrogen atoms ionize in steps. Thus, *in moderately dilute solutions* one or more of the replaceable hydrogen ions may remain in combination with the acid radical, as is suggested in the equations below.

$$H_2CO_3 + H_2O \longrightarrow H^+ \cdot H_2O + HCO_3^- \text{ (hydrogen carbonate ions)}$$
$$H_2SO_4 + H_2O \longrightarrow H^+ \cdot H_2O + HSO_4^- \text{ (hydrogen sulfate ions)}$$
$$H_3PO_4 + H_2O \longrightarrow H^+ \cdot H_2O + H_2PO_4^- \text{ (dihydrogen phosphate ions)}$$
$$H_2PO_4^- + H_2O \longrightarrow H^+ \cdot H_2O + HPO_4^- \text{ (monohydrogen phosphate ion)}$$

The so-called acid salts such as sodium hydrogen carbonate ($NaHCO_3$) and the sodium hydrogen phosphate salts (represented by the formulas NaH_2PO_4 and Na_2HPO_4) are typical acid salts with acid radicals of this type.

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[3] The term *oxonium ion* is also used and preferred by some chemists.

In more dilute solutions, a further ionization may take place:

$$HCO_3^- + H_2O \longrightarrow H^+ \cdot H_2O + CO_3^{--} \text{ (carbonate ions)}$$
$$HSO_4^- + H_2O \longrightarrow H^+ \cdot H_2O + SO_4^{--} \text{ (sulfate ions)}$$
$$HPO_4^- + H_2O \longrightarrow H^+ \cdot H_2O + PO_4^{---} \text{ (phosphate ions)}$$

Hydrogen ions the active agents. Although the positively charged ions that are common to acid solutions are, presumably, hydronium ions, their active constituents are the *positively charged hydrogen atoms* or *hydrogen ions* (or *protons*). Therefore, to avoid unnecessary complications, usually we shall refer only to the hydrogen ions. At the same time there should always be the mental reservation that these ions are hydrated, that is, combined with water molecules.[4]

In solutions of strong acids. When strong acids are in water solution, practically all of their molecules ionize to form hydrogen (or hydronium) ions and acid radical ions. But, as in solutions of strong salts and strong bases, the activity of these ions is influenced

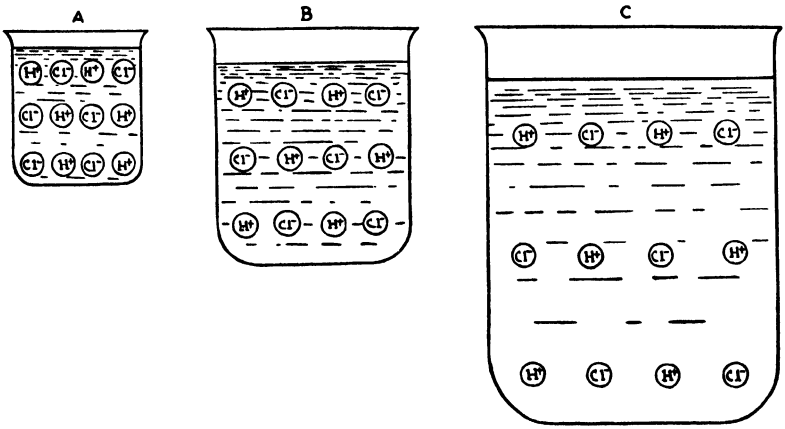


Fig. 73. With decreasing attractive forces between hydrogen ions and chloride ions, their freedom to engage in reaction increases.

by interionic attractions between negatively and positively charged ions. And again, these interionic attractions are most marked in highly concentrated solutions and decrease as the ions get farther apart with dilution of the acid. This condition is suggested in Figure 73.

[4] The practice of ignoring combined water in hydrate molecules is not unusual. Ions other than hydrogen are probably hydrated, but emphasis is not commonly placed on this condition. Also the hydrate state of many salts is frequently ignored; for example, copper sulfate hydrate ($CuSO_4 \cdot 5H_2O$), in which both cupric and sulfate ions are presumed to be hydrated, is frequently referred to simply as copper sulfate ($CuSO_4$).

In solutions of weak acids. Solutions of weak acids are less active chemically than are solutions of strong acids. It is assumed, therefore, that in these solutions the concentrations of ions are relatively low. According to Arrhenius' theory, which is still accepted for weak electrolytes, when weak acids enter water solution a relatively low proportion of the molecules (always less than half) ionize. Such solutions must contain, therefore, three varieties of particles: hydrogen (or hydronium) ions, acid radical ions, and molecules of the acid. For instance, in a solution of acetic acid there are hydrogen ions, acetate ions, and molecules of acetic acid—with the molecules always in predominance (Fig. 74).

The high proportion of molecules in solutions of weak acids is explained by the tendency of the acid radical ions contributing to such acids to recombine to form molecules. This is in contrast with the acid radicals of strong acids which show little tendency to reform molecules as long as they remain in solution. The two opposing reactions which operate in a solution of a weak acid are illustrated below with reference to acetic and tartaric acids.

$$\underset{\text{Acetic acid molecules}}{HC_2H_3O_2} \rightleftharpoons \underset{\text{Hydrogen ions}}{H^+} + \underset{\text{Acetate ions}}{C_2H_3O_2^-}$$

$$\underset{\text{Tartaric acid molecules}}{H_2C_4H_4O_6} \rightleftharpoons \underset{\text{Hydrogen ions}}{2\,H^+} + \underset{\text{Tartrate ions}}{C_4H_4O_6^{--}}$$

Note. As said previously (p. 225), water molecules probably aid in the ionization of acids by pulling away positively charged hydrogen atoms (protons) from the acid molecules to form hydronium ions, thereby releasing the negatively charged acid-radical ions. Such reactions are represented below.

$$HC_2H_3O_2 + H_2O \rightleftharpoons H^+{\cdot}H_2O + C_2H_3O_2^-$$

$$H_2C_4H_4O_6 + 2\,H_2O \rightleftharpoons 2\,H^+{\cdot}H_2O + C_4H_4O_6^{--}$$

EQUILIBRIUM WITHIN SOLUTIONS OF WEAK ELECTROLYTES

Two opposing reactions. When a weak electrolyte, whether acid, base, or salt is in solution in water, two opposing reactions are in mutual operation: (1) molecules dissociate to form ions, and (2) ions combine to form molecules. These opposing reactions continually aim to establish equilibrium; that is, a condition in which the

number of molecules ionizing during any given time is equal to the number of combinations between ions to remake molecules. For example:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

In a solution of acetic acid, two reactions are taking place: acetic acid molecules are ionizing to make hydrogen ions and acetate ions; at the same time some of these ions are combining to make molecules of acetic acid. When the acid first enters solution, the reaction to make ions is the faster. But, as more and more ions are made, the combination of ions to make molecules speeds up and the ionization reaction slows down. If undisturbed, the time will come when the speeds of the two reactions will be equal and the condition of equilibrium attained.

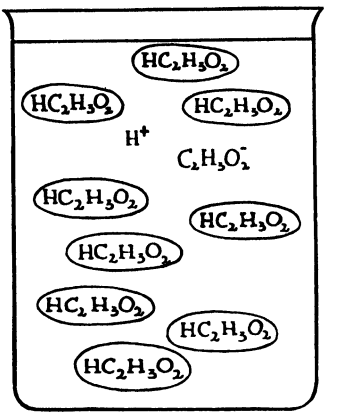


Fig. 74. When acetic acid, a weak electrolyte, reaches equilibrium in water solution, the concentration of molecules always exceeds the concentration of ions.

Concentration relations at equilibrium. When the weak electrolyte system has attained equilibrium between the two opposing reactions, *the concentration of molecules always exceeds the concentration of ions.* In the following equation this situation is represented by means of opposing arrows; the heavier arrow is directed toward the molecules to indicate that they are in higher concentration.

$$H_2C_4O_6 \rightleftharpoons 2\ H^+ + C_4H_4O_6^{--}$$

Interpretation. Two reactions are taking place: (1) ionization to make hydrogen ions and tartrate ions and (2) combination between these ions to make molecules of tartaric acid. When these two reactions are at equilibrium, there is a higher concentration of tartaric acid molecules than of hydrogen ions and tartrate ions.

Percentage of molecules ionized. The percentage of molecules ionized, hence, the degree of activity of weak electrolytes, *varies with electrolytes themselves.* Figures indicating the percentage of ionization for various weak acids, bases, and salts (in a one-tenth-normal solution) are given on page 219.

The *concentration of the acid, base, or salt* in solution is another factor which affects the proportion of molecules that are ionized;

the more dilute the solution the higher the proportion of ions.[5] For example, for **acetic acid:**

In normal solution the two reactions are at equilibrium when:		*In* 0.1 *normal solution* the two reactions are at equilibrium when:	
$HC_2H_3O_2$	$H^+ + C_2H_3O_2^-$	$HC_2H_3O_2$	$H^+ + C_2H_3O_2^-$
99.6% of the acid is in neutral molecules	0.4% of the acid is in the form of ions	98.7% of the acid is neutral molecules	1.3% of the acid is in the form of ions

Response to a disturbance of equilibrium. When a weak electrolyte has attained equilibrium, the two reactions continue at equal speed until some disturbing factor enters the field. This disturbance might be:

1. *Concentration of the solution by evaporation of water.* As the volume of the solution decreases, the ions become more concentrated. This favors combination of ions to make molecules, and this reaction will be favored as long as the disturbance continues.

2. *Dilution by adding more water.* This lowers the concentration of the electrolyte, hence of the ions in the solution, and favors the ionization reaction.

3. *If one variety of ion is being removed,* thus tending to lower the concentration of ions in the solution, the ionization reaction will be favored over the combination reaction as long as ion removal continues. For example:

Given a solution of ammonium hydroxide in which the two opposing reactions are at equilibrium, the introduction of an acid will disturb this equilibrium because hydrogen ions will combine with hydroxyl ions to make molecules of water. This lowers the concentration of hydroxyl ions, and more of the ammonium hydroxide molecules will ionize in order to restore the ion concentration of the solution.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$+$$

$$H^+ \text{ Hydrogen ions introduced}$$

$$\downarrow$$

$$H_2O$$

4. *If one of the ion substances is added to the solution* from another electrolyte without adding any of the partner ion, combination be-

[5] Temperature of the solution is also a factor that determines the percentage of molecules of a weak electrolyte that is ionized, but the effect is variable. The figures given here are for ionization in solutions at 18° C.

tween ions will be favored over ionization as long as this disturbance continues. Thus:

Again, given a solution of ammonium hydroxide in which the two reactions are at equilibrium, if ammonium ions are introduced by adding an ammonium salt, the equilibrium will be disturbed. Since the concentration of ions is thus increased, the combination of ammonium ions and hydroxyl ions will be favored over the ionization as long as ammonium ions continue to be thus added to the solution.

Ammonium ions introduced
from another source
↓

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

In general, when the equilibrium of a weak electrolyte is disturbed, nature favors the reaction—either ionization or combination between ions—which will be most effective in restoring the condition of equilibrium.

Electrolyte equilibrium of biological importance. The aim of weak electrolytes to attain their equilibriums and their sensitivity to disturbances plays an important part in laboratory studies and also in reactions of importance to plants and animals.

The presence of carbonic acid, lactic acid, phosphoric acid, and other weak acids within cells and circulating fluids of animals is of physiological significance. Each of these electrolytes continually aims at establishing equilibrium. But disturbing factors are continually present such as (1) the entrance into the blood from the intestine of various ions and the molecules of weak acids; (2) the removal from the blood by absorption into the cells of various ions and the return of other ions to the blood and lymph; (3) the selective removal of ions from the blood by the kidneys. With all of these disturbing factors operating can these weak electrolytes ever achieve equilibrium? Probably not, save transiently! Indeed, it is probable that should all weak electrolytes within the animal body ever attain their equilibrium aims, the life of the animal would cease. Some of these vitally important reactions will be considered more fully in Chapter 32.

REACTIONS BETWEEN ELECTROLYTES

When two electrolytes, which contribute different ions, come in contact within the same solution, four varieties of ions intermingle in the solution. Even so, *no reaction takes place unless a product is*

formed which captures some of the free ions and removes them from the solution (Fig. 75). This is accomplished when the ions are "caught" in a product which is (1) an insoluble compound, either gaseous or solid; (2) an unstable compound, which decomposes; or (3) a very weak electrolyte, especially water.

Reactions of this type have been discussed previously (p. 153); the difference is that now we have progressed to the belief that the reacting particles are the free ions. The following are examples.

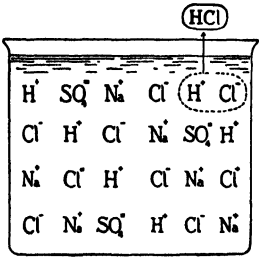


Fig. 75. No reaction; ions merely continue to move about in the solution, unless ions of one product are carried out as by evaporation of hydrogen chloride gas.

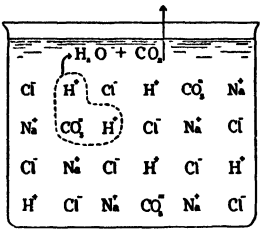


Fig. 76. Hydrogen ions and carbonate ions combine to make carbonic acid, which decomposes to produce water and the slightly soluble, gaseous carbon dioxide.

1. ***Ions form an insoluble compound.*** When sodium chloride and silver nitrate come together in solution, silver ions, nitrate ions, sodium ions, and chloride ions mingle in the solution. But as silver ions and chloride ions encounter each other, they tend to fall into fixed positions in crystals of silver chloride which precipitate from the solution. In this way the reaction between these ions is carried forward to completion, so that the only free ions left in solution are sodium ions and nitrate ions.

$$[Na^+ + Cl^-] + [Ag^+ + NO_3^-] \longrightarrow AgCl\downarrow + Na^+ + NO_3^-$$

2. ***Ions may combine to make molecules of an unstable compound.*** In a solution of sodium carbonate and hydrochloric acid the free ions are sodium ions, carbonate ions, hydrogen ions, and chloride ions. This means that the ions that contribute to carbonic acid and sodium chloride are also present. But carbonic acid is unstable; therefore there is a continuous combination of hydrogen ions and carbonate ions to form molecules of this weak acid which, in turn, decompose to make water and carbon dioxide. The latter, being only slightly soluble in water, bubbles out of the solution (Fig. 76):

$$[2\,Na^+ + CO_3^{--}] + 2[H^+ + Cl^-] \longrightarrow \underset{\uparrow CO_2 + H_2O}{\overset{\downarrow}{H_2CO_3}} + 2\,Na^+ + Cl^-$$

3. ***Hydrogen and hydroxyl ions combine to make water.*** In the contact between acetic acid and sodium hydroxide, hydrogen ions, made by the ionization of acetic acid molecules, combine with the hydroxyl ions coming from the base to make water molecules. The ionization of acetic acid and the combination of hydrogen ions with hydroxyl ions continue until the reaction has been practically carried to completion to make water and sodium acetate as products.

$$\begin{matrix} HC_2H_3O_2 \\ \uparrow\downarrow \\ [H^+ + C_2H_3O_2^-] + [Na^+ + OH^-] \longrightarrow H_2O + Na^+ + C_2H_3O_2^- \end{matrix}$$

Or, to use the more conventional form for the ionic equation:

$$HC_2H_3O_2 + Na^+ + OH^- \longrightarrow H_2O + Na^+ + C_2H_3O_2^-$$

Ionic equations. The ionic equations, such as those used above, serve to illustrate the concept that *ions in the solution are substances in their own right.* In assembling ionic equations the following conventions are observed:

1. Strong, soluble electrolytes are represented by their free ion constituents.
2. Weak electrolytes (with molecules in predominance in the solution), also nonelectrolytes, are represented by formulas for the molecules.
3. The removal of substances from solution, whether as ion pairs or as molecules of nonelectrolytes, is represented by the formula for the whole substance. A small downward arrow ↓ denotes a precipitate; an upward arrow ↑ indicates an escaping gas.

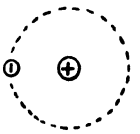
HYDROGEN IONS AND HYDROXYL IONS

Acid and base defined. Acids and bases are frequently defined in terms of the common and characteristic ions that each provides when in water solution.[6] From this standpoint, *an acid is a substance which reacts with water to provide hydrogen ions in the solution.* It will be recalled that these hydrogen ions are believed to be hydrated, that is, in combination with water molecules, and as such are known as *hydronium ions.*

A base may be defined as a substance which, in water solution, provides free hydroxyl ions.

[6] For discussion of acids as "proton donors" and of bases as "proton acceptors," the student is referred to more comprehensive chemistry texts.

Hydrogen ions. A hydrogen ion is an atom of hydrogen which, in breaking away from a molecule of acid, has left behind its 1 electron and thereby has acquired a positive charge. A hydrogen ion is, therefore, a proton or the nucleus of a hydrogen atom (Fig. 77). Inasmuch as the weight of an electron is negligible, the *weight of the hydrogen ion* is that of the hydrogen atom, or relatively 1.008.

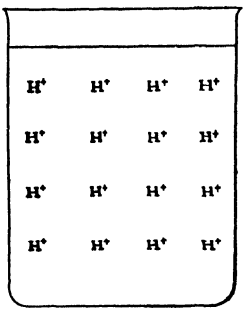


Hydrogen atom, complete with its nuclear proton and 1 planetary electron, is neutral.

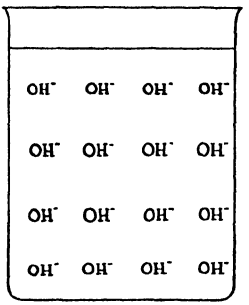


Hydrogen atom without its planetary electron is a hydrogen ion or a nuclear proton.

Fig. 77



6.02×10^{23} hydrogen ions weigh *inclusively* 1.008 gm



6.02×10^{23} hydroxyl ions weigh *inclusively* 17.008 gm

Fig. 78

Mole of hydrogen ions. Because of the very important roles which hydrogen ions play in various concerns, it has become necessary to establish means for measuring these ions in appreciable quantities. And, because other substances are measured on a molar basis, hydrogen ions also are measured on this basis. Accordingly,

1 mole of hydrogen ions weighs 1.008 gm and includes 6.02×10^{23} individual hydrogen ions (Fig. 78).

Hydroxyl ions. A single hydroxyl ion is composed of 1 hydrogen atom and 1 oxygen atom, in close combination, which have acquired 1 extra electron; the hydroxyl ion, therefore, carries the ultimate

negative charge of 1 electron. Disregarding the negligible weight of the electron, *the weight of a hydroxyl ion* is the inclusive weight of these 2 atoms, or relatively 17.008.

Mole of hydroxyl ions. Because a mole of hydroxyl ions is composed of 1 atomic weight of oxygen and 1 atomic weight of hydrogen,

1 mole of hydroxyl ions weighs 17.008 gm and includes 6.02×10^{23} individual hydroxyl ions (Fig. 78).

Reactions of hydrogen ions and hydroxyl ions. Whenever an acid and a base enter the same solution, the *hydrogen ions* provided by the acid and the *hydroxyl ions* provided by the base, on coming in contact with each other, combine to make molecules of water, leaving ions of the salt product in solution. For example, when nitric acid and potassium hydroxide are brought together in the same solution practically all of the hydrogen ions and hydroxyl ions combine to make water molecules, and the ions of potassium nitrate remain in the solution.

$$[H^+ + NO_3^-] + [K^+ + OH^-] \longrightarrow H_2O + K^+ + NO_3^-$$

Or, ignoring the ions contributing to the salt:

$$H^+ + OH^- \longrightarrow H_2O$$

Because of this reaction the introduction of hydrogen ions serves as an excellent means for decreasing the concentration of hydroxyl ions,

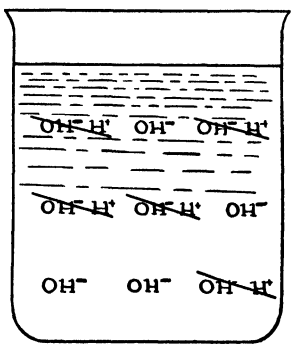


Fig. 79. To decrease the concentration of hydrogen ions, introduce hydroxyl ions.

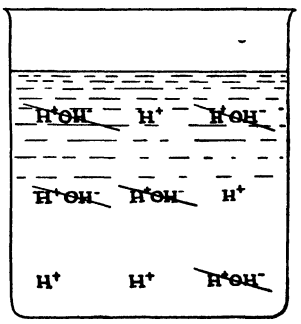


Fig. 80. To decrease the concentration of hydroxyl ions, add hydrogen ions.

and vice versa (Figs. 79 and 80). Hence, the reaction of hydrogen ions with hydroxyl ions to make water is known as *neutralization.*

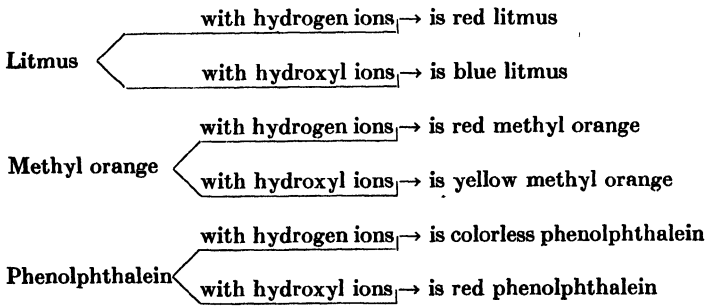
Other properties of hydrogen ions and hydroxyl ions. ***Hydrogen ions are sour.*** Water solutions of all acids are more or less sour, so it seems reasonable to attribute this taste to their common hydrogen-ion component. This accounts for the sourness of vinegar, (which contains acetic acid), of fruits with their various acids, and of gastric contents with its hydrochloric acid.

Hydroxyl ions feel slippery. When the fingers come in contact with solutions of sodium or potassium hydroxide, they detect a slippery feeling. The same is true of solutions of household ammonia—of which ammonium ions and hydroxyl ions are components. It is assumed that this feeling is due to the presence of hydroxyl ions. The slipperiness of solutions of sodium carbonate and sodium bicarbonate is also attributed to the hydroxyl ions produced through the hydrolysis of these salts.

$$[2\ Na^+ + CO_3^{--}] + 2\ HOH \longrightarrow 2\ Na^+ + OH^- + H_2CO_3$$
$$[Na^+ + HCO_3^-] + HOH \longrightarrow Na^+ + OH^- + H_2CO_3$$

Affect the color of some dyes and pigments. It is a matter of common knowledge that acids in contact with some colored substances produce color changes, and it seems certain that hydrogen ions are responsible for these effects. Then there are colored substances which undergo color changes on contact with bases, and such changes are attributed to hydroxyl ions.

Useful to chemists. Chemists make use of color changes in selected pigments and dyes to detect the presence of these ions in solutions. Color effects with litmus, methyl orange, and phenolphthalein are examples.



There are other dyes which show a gradation of color changes in solutions of different hydrogen-ion or hydroxyl-ion concentrations.

Such dyes are employed for detecting the presence of these ions in *specific concentrations.* The use of such dyes is discussed in the next chapter.

In the study of microorganisms. Litmus and sometimes other dyes that are sensitive to hydrogen ions are added to culture media to help in identifying acid-forming microorganisms. For instance, a shift in color from blue to red accompanies the growth of *Escherichia coli* in litmus milk or litmus lactose agar and identifies this organism as an acid producer.

Frequently a nuisance. Some of the stains which are produced by the spattering of acids, from foods and other sources, on fabrics used for clothing and other purposes are due to the effects of hydrogen ions. Similarly, some of the changes in tints and colors observed during laundering may be caused by hydroxyl ions provided through the hydrolysis of washing soda (sodium carbonate) or of laundry soaps.

Attack on fabrics. Protein fibers, silk and wool, can be attacked by either hydrogen ions or hydroxyl ions. If the ions are in high concentration, destruction of the fabric is rapid. This may be a laboratory experience if either acid or base comes in contact with clothing. Prolonged contact with even dilute solutions of hydroxyl ions, such as is provided by ammonia water or washing soda, will weaken the fibers of silk and wool. Although apparently less sensitive to hydroxyl ions than are protein fibers, the cellulose fabrics such as cotton, linen, and rayon are also attacked by these ions.

Attack on living tissues. Either hydrogen or hydroxyl ions, if in sufficiently high concentration, can be irritating—even destructive—to living tissues. Solutions containing either of these ions, if spilled on the skin, spattered into the eye, or even swallowed, will react with proteins of the cells—sometimes with serious injury. Every year, among the reported causes of death among young children, there are instances of tissue injury caused by children swallowing lye, a commercial product containing sodium hydroxide. This and other potential sources of hydroxyl or hydrogen ions should be stored with care out of reach of inquisitive children or careless adults.

Treatment of injuries caused by these ions. In general, the first treatment for injuries by either hydroxyl or hydrogen ions is to *flush the affected area with water* to dilute and carry away the destructive ions.

If further treatment is necessary, the injurious agent can be neutralized. (1) Hydrogen ions can be destroyed by hydroxyl ions, but these

must be provided in low concentration to avoid further injury to tissue.[7] (2) Hydroxyl ions can be neutralized by applying hydrogen ions, but low concentrations should be used.

Safe sources of these ions. Strong acids, like hydrochloric and sulfuric acids, are excellent sources of hydrogen ions, as sodium and potassium hydroxide are of hydroxyl ions, but it requires both knowledge and careful attention to technics to obtain the ions from these sources in safe concentrations for ordinary use. How then can solutions of these ions be obtained with reasonable assurance of safety for the user?

Reliable *sources of low concentrations of hydrogen ions* are the weak acids such as those in fruit juices or acetic acid in vinegar. These are frequently recommended for use in emergencies. Boric acid yields an even lower concentration of these ions, but deaths have resulted from swallowing this acid.

Hydroxyl ions in low concentrations can be obtained from the weak base ammonium hydroxide, in household ammonia; this could be used on clothing. Calcium hydroxide in limewater and magnesium hydroxide in milk of magnesia, although strong electrolytes, can provide hydroxyl ions only in low concentrations because of their limited solubility in water. They are sometimes used medicinally as antacids. Another safe source of hydroxyl ions is by hydrolysis of salts of weak acids and strong bases—such as sodium bicarbonate, sodium carbonate, or salts of soap mixtures (p. 190).

QUESTIONS

1. What is an electrolyte? What substances, in general, behave thus? Differentiate between strong electrolytes, weak electrolytes, and nonelectrolytes. Give examples.
2. Summarize in your own words the basic concepts of the ionization theory.
3. Given water solutions of silver nitrate and mercuric chloride, in equal concentrations:
   a. Which solution should show the greater chemical activity? Explain in terms of the ionization theory.
   b. How would this difference in activity be exhibited on contact of these salt solutions with metals under similar conditions?
4. Explain, in terms of the modern concept of ionization, what happens to a crystal of sodium chloride, or other strong salt, when it dissolves in water.
5. What reaction takes place, according to the modern concept of ioniza-

[7] For injury to eye tissue it is undesirable to use hydroxyl ions even in low concentration.

tion, as hydrogen chloride gas dissolves in water? What chemically active substances are present in a solution of hydrochloric acid?

6. What is a hydronium ion? What relation does it bear to a hydrogen ion?

7. Set up an ionic representation to show the effect of introducing a soap, sodium stearate, into "hard water" containing calcium sulfate. Account for both the appearance of a precipitate and the fact that a considerable quantity of soap must be used before a suds can be obtained.

8. When is equilibrium attained by a weak electrolyte in solution?
   a. How do concentrations of ionized and un-ionized portions of weak electrolytes at equilibrium differ in relation to each other?
   b. Interpret each of the following expressions:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$HgCl_2 \rightleftharpoons Hg^{++} + 2\ Cl^-$$

9. What is the effect on a lactic acid system previously at equilibrium of:
   a. The evaporation of part of the water?
   b. The introduction of hydrochloric acid?
   c. The removal of some of the lactate ions?

10. a. From the standpoint of the ionization theory what are the following: (1) an acid, (2) a base, (3) a hydrogen ion, and (4) a hydroxyl ion?
    b. To what are the properties that are common to solutions of all acids supposedly due? The properties common to solutions of all bases?

11. Solutions of hydrogen ions are frequently caustic to tissues and fabrics. What would you do to diminish such an injury should a few drops of a strong acid solution accidentally become spattered on your hand? On your clothing? State the reason for each step in your procedure.

12. Sodium and potassium hydroxides should be stored where neither children nor careless persons will accidentally come in contact with them. Why is this an important precaution? From what sources can safe concentrations of hydroxyl ions be secured for ordinary household purposes?

13. State why each of the following can function as a direct or indirect source of hydroxyl ions: limewater, milk of magnesia, sodium bicarbonate, calcium oxide, soap. Represent by equations the reactions involved in each case to provide the hydroxyl ions.

CHAPTER 18

WATER AS AN ELECTROLYTE. BUFFERED SOLUTIONS

An ultrapoor electrolyte. Although water is commonly looked upon as a medium in which substances dissolve and in which electrolytes dissociate to give free ions, the fact remains that water is in itself a weak electrolyte. As such, some water molecules are continuously dissociating into hydrogen ions[1] and hydroxyl ions, and at the same time some of these ions are combining to remake water molecules. Even in the presence of acids, bases, and salts, water itself as a weak electrolyte is aiming at establishing an equilibrium condition. However, water is such an extraordinarily poor electrolyte that only a minute portion of its molecules is ever ionized. Hence, when the two opposing reactions do attain equilibrium, the concentration of the undissociated molecules is exceedingly high (represented by a ← heavy arrow) and that of the ions is very low (represented by a → light arrow).

$$H_2O \rightleftharpoons H^+ + OH^-$$

Hydrogen-ion and hydoxyl-ion concentrations. *Can vary as to each other.* The concentrations of hydrogen ions and hydroxyl ions within the ionized portion of water can vary in relation to each other and still have the two opposing reactions of the water at equilibrium. These two concentrations can be equal, as they always are when water is the only electrolyte present. Or the concentration of hydrogen ions can be greater than that of hydroxyl ions, as must be the case when an acid is present.

[1] As with hydrogen ions from acids (p. 225) these ions obtained from water are believed to be hydrated in the form of hydronium ions. With this in mind the ionization of water is represented as follows.

$$HOH + H_2O \longrightarrow H^+ \cdot H_2O + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

Or, vice versa, the concentration of hydroxyl ions can be greater than that of hydrogen ions, as when a base predominates in the solution.

$$H_2O \rightleftharpoons H^+ + OH^-$$

Measurement of their concentrations and shorthand representation. Hydrogen and hydroxyl ions are measured in terms of their molar quantities (pp. 232 to 233) in 1 liter of the solution, and the shorthand characters used to represent measurements on this basis are $[H^+]$ and $[OH^-]$. For example:

$[H^+] = 0.25$ means that 1 liter of solution contains 0.25 mole of hydrogen ions.

$[H^+] = 0.001$ means that 1 liter of solution contains 0.001 mole of hydrogen ions.

$[OH^-] = 0.125$ means that 1 liter of solution contains 0.125 mole of hydroxyl ions.

$[OH^-] = 0.0003$ means that 1 liter of solution contains 0.0003 mole of hydroxyl ions.

Product of ion concentrations a constant. Although the concentrations of hydrogen ions and hydroxyl ions can vary in respect to each other, when the two opposing reactions on the part of water are at equilibrium, the concentration of hydrogen ions (measured in moles in 1 liter of solution) multiplied by the concentration of hydroxyl ions (measured on the same bases) is always equal to the exceedingly small value of 0.00000000000001.[2] Thus, briefly:

$$[H^+] \times [OH^-] = 0.00000000000001 \text{ or } 10^{-14}*$$

* Just as values of more than 1 can be represented in terms of positive powers of 10, so values of less than 1 are sometimes represented in terms of negative powers of 10. Ten with a whole-number negative power can be translated without difficulty into the decimal value represented: for example, $10^{-4} = 0.0001$. But the translation of 10 to a negative power that is not a whole number, such as $10^{-4.5}$, presents difficulties unless one's training in mathematics has included the use of logarithms. This text does not presuppose this training. Therefore, for use here a value such as $[H^+] = 10^{-4.5}$ will mean that the molar concentration of hydrogen ions is between 10^{-4} (0.0001) and 10^{-5} (0.00001).

$1000 = 10^3$
$100 = 10^2$
$10 = 10^1$
$1 = 10^0$

$0.1 = 10^{-1}$
$0.01 = 10^{-2}$
$0.001 = 10^{-3}$

[2] The term *hydrogen-ion activity* is considered to be more accurate than hydrogen-ion concentration. However, in dilute solutions of acids and bases, there is a close relation between the activity of the ion and its concentration in the solution.

For example:

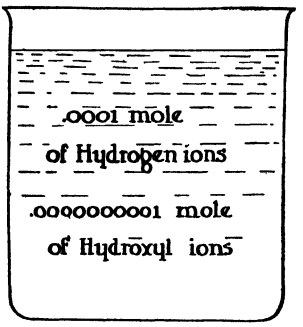
1. If within a given solution (Fig. 81)

$$[H^+] = 0.0001 \text{ or } 10^{-4}$$
$$[OH^-] = 0.0000000001 \text{ or } 10^{-10}$$

the water, as an electrolyte, is at equilibrium since

$$\underset{\text{mole of hydrogen ions}}{10^{-4}} \times \underset{\text{mole of hydroxyl ions}}{10^{-10}} = 10^{-14}$$

Concentration of hydrogen ions is greater than that of hydroxyl ions.



One liter of solution

Fig. 81

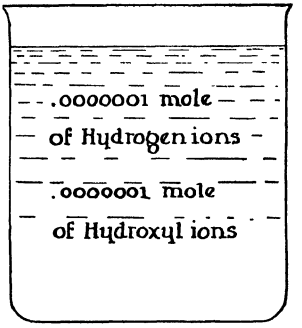
2. If within another solution (Fig. 82)

$$[H^+] = 0.0000001 \text{ or } 10^{-7}$$
$$[OH^-] = 0.0000001 \text{ or } 10^{-7}$$

the water system is likewise at equilibrium since

$$\underset{\text{mole of hydrogen ions}}{10^{-7}} \times \underset{\text{mole of hydroxyl ions}}{10^{-7}} = 10^{-14}$$

Concentration of hydrogen ions is equal to that of hydroxyl ions.



One liter of solution

Fig. 82

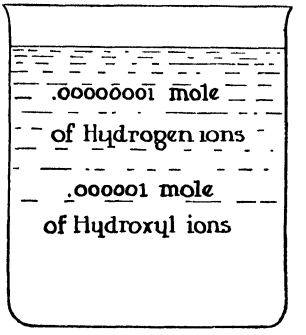
3. If within still another solution (Fig. 83)

$$[H^+] = 0.00000001 \text{ or } 10^{-8}$$
$$[OH^-] = 0.000001 \text{ or } 10^{-6}$$

water, as an electrolyte, is again at equilibrium since

$$\underset{\text{mole of hydrogen ions}}{10^{-8}} \times \underset{\text{mole of hydroxyl ions}}{10^{-6}} = 10^{-14}$$

Concentration of hydroxyl ions is greater than that of hydrogen ions.



One liter of solution

Fig. 83

Necessary to specify only the hydrogen-ion concentration of the solution. Because the relationship between the concentrations of hydrogen ions and hydroxyl ions is fixed and definite, it is necessary to specify only the concentration of hydrogen ions (or only that of hydroxyl ions) in the solution, regardless of whether the solution is acid, basic, or neutral in reaction. In other words, a given molar concentration of hydrogen ions means automatically a definite molar concentration of hydroxyl ions. For example:

1. If the $[H^+]$ of the solution is $10^{-2.3}$ or between 0.01 and 0.001 mole of hydrogen ions in 1 liter of solution,	then the $[OH^-]$ of the solution must of necessity be $10^{-11.7}$ or between 10^{-11} and 10^{-12} mole of hydroxyl ions in 1 liter of the solution.
2. If the $[H^+]$ of a solution is 10^{-8} or 0.00000001 mole of hydrogen ions in 1 liter of solution.	then the $[OH^-]$ must be 10^{-6} or 0.000001 mole of hydroxyl ions in 1 liter of solution.

pH notations. Inasmuch as molar concentrations of hydrogen ions are, for convenience, recorded on the basis of 10 expressed in appropriate negative powers, chemists have adopted the practice of representing these values simply by the power notations concerned. The term given to such a notation is *p*H.[3] Thus:

1. *p*H 2 is the shorthand notation which means that within the solution the $[H^+] = 10^{-2}$ and the $[OH^-] = 10^{-12}$.
2. *p*H 3.7 is the shorthand notation which means that within the solution the $[H^+] = 10^{-3.7}$ and the $[OH^-] = 10^{-10.3}$.
3. *p*H 8 means that the $[H^+]$ of the solution is 10^{-8} and the $[OH^-]$ is 10^{-6}.

***p*H notations**

$[H^+] = 10^{-1}$	*p*H 1.0
$[H^+] = 10^{-1.5}$	*p*H 1.5
$[H^+] = 10^{-2}$	*p*H 2.0
$[H^+] = 10^{-3}$	*p*H 3.0
$[H^+] = 10^{-3.7}$	*p*H 3.7
$[H^+] = 10^{-8}$	*p*H 8.0
$[H^+] = 10^{-8.6}$	*p*H 8.6
$[H^+] = 10^{-9}$	*p*H 9.0
etc.	etc.

[3] In this text *p*H notations are defined as the negative powers on a basis of 10 (or the negative logarithms) of the $[H^+]$ values of solutions. More frequently, however, *p*H is defined as the positive power on a basis of 10 (or the positive logarithm) of the reciprocal of the $[H^+]$ of the solution. But the *p*H value under either definition is the same. Thus:

$[H^+] = 10^{-5}$.....*p*H = 5 $\qquad \frac{1}{[H^+]} = \frac{1}{10^{-5}} = 10^5$.....*p*H = 5

The reason for the more usual concept is that computations for most $[H]^+$ values of solutions are more readily made from figures given on the basis of 10 to positive powers than from figures on the basis of 10 to negative powers. Therefore, the computation is made in terms of the reciprocal of the $[H^+]$ of the solution, then converted to the actual $[H^+]$ value.

Summary tabulation. The accompanying table shows concentration relationships between hydrogen ions and hydroxyl ions in 13 solutions. It also gives the *p*H notations for these solutions.

IN 1 LITER OF SOLUTION

MOLES OF HYDROGEN IONS [H^+]		*p*H NOTATION	MOLES OF HYDROXYL IONS [OH^-]	
↑	0 1	1	0 0000000000001	10^{-13}
Solutions	0.01	2	0 000000000001	10^{-12}
are	0.001	3	0.00000000001	10^{-11}
increasingly	0.0001	4	0.0000000001	10^{-10}
acid	0 00001	5	0.000000001	10^{-9}
↑	0.000001	6	0.00000001	10^{-8}
Neutral solution →	0.0000001	7	0 0000001	10^{-7}
↓	0 00000001	8	0.000001	10^{-6}
Solutions	0.000000001	9	0.00001	10^{-5}
are	0.0000000001	10	0.0001	10^{-4}
increasingly	0.00000000001	11	0 001	10^{-3}
basic	0.000000000001	12	0.01	10^{-2}
↓	0 0000000000001	13	0.1	10^{-1}

It should be noted that *p*H notations decrease for solutions of increasing acidities, hence, of decreasing alkalinities; and, of course, the reverse follows.

Solutions neutral in reaction. It is only when a solution has a *p*H notation of 7, which means that 1 liter contains 0.0000001 mole of hydrogen ions, $[H^+] = 10^{-7}$, and 0.0000001 mole of hydroxyl ions, $[OH^-] = 10^{-7}$, that the *solution is neutral in reaction.* There is always a neutral condition if water is the only electrolyte present, because, when obtained from water itself, hydrogen ions and hydroxyl ions are made in equal numbers as represented in the following equation.

$$H_2O \longrightarrow H^+ + OH^-$$

But a solution can also contain such proportions of acids, bases, and salts that concentrations of hydrogen ions and hydroxyl ions are equal.

Solutions acid in reaction. Solutions are acid in reaction when their $[H^+]$ values are from ever so slightly more than 10^{-7} mole of

hydrogen ions up through 10^{-1} mole per liter, and the corresponding $[OH^-]$ values are from ever so slightly less than 10^{-7} down through 10^{-13} mole per liter.

Solutions basic in reaction. Solutions are basic in reaction in which $[H^+]$ values are ever so slightly less than 10^{-7} mole down through 10^{-13} mole per liter, whereas the corresponding $[OH^-]$ values are from ever so slightly more than 10^{-7} mole up through 10^{-1} mole per liter.

Practical importance of hydrogen-ion concentration. The relative concentrations of hydrogen ions and hydroxyl ions have very important roles in the many and various activities of man. The following are some instances.

It is a well-known fact that the hydrogen-ion concentration of the medium helps to determine *exact colors and shades of various dyes.* The electrochemist has learned that the hydrogen-ion concentration of the solution in contact with a metal is one factor which determines the extent of *corrosion;* also that the concentration of hydrogen ions must be reckoned with in the *effectiveness of metal electroplating.* Sanitary engineers have discovered that hydrogen-ion concentration is a factor to be considered in *effective water purification and in sewage disposal.* Agriculturists have learned that the control of the hydrogen-ion concentration of the soil can be *an important factor in the successful growth of crops.* Different crops frequently require different conditions in this respect.

Food chemists know that the hydrogen-ion—hydroxyl-ion relationship is a potent factor in cookery. The hydrogen-ion concentration of fresh milk is almost neutral, but with an increase in this concentration, the casein that is held in colloidal dispersion in fresh milk precipitates. This is the familiar phenomenon that occurs as milk sours, and it is important in the making of cheese. During cooking, the stability of vitamins and colors of pigments of fruits and vegetables are affected by the hydrogen-ion concentration of the medium. For example, ascorbic acid is relatively stable in a medium in which the concentration of hydrogen ions is somewhat greater than that of hydroxyl ions; hence, when fruits with their acid components and acid vegetables, such as tomatoes, are heated there is little destruction of this vitamin. Vegetables that carry either red or yellow pigments retain their colors when cooked in a medium in which there is an excess of hydrogen ions over hydroxyl ions. This is not the case, however, with the green vegetables whose pigment is chlorophyll;

this pigment turns brown when boiled for any length of time in the presence of plant acids.

Microbiologists have learned that the hydrogen-ion concentration of the media is one factor which determines the life activities of microorganisms. Some organisms can tolerate a wide range; others have very specific hydrogen-ion requirements. Moderate variations may result in modification of some cultural characteristic. More extreme variations may check reproduction or kill the organism. Most microorganisms that are pathogenic to man have requirements not far from neutral and can meet this requirement in the human body—in the mouth, gastrointestinal tract, blood, or tissue cells. The high hydrogen-ion concentration of gastric juice is one of nature's safeguards against invasion by microorganisms entering with the food.

Hydrogen-ion concentrations favorable to growth of typical microorganisms*

	OPTIMUM	RANGE FOR GROWTH
Mycobacterium tuberculosis	pH 6 8–7 2	pH 4 0–8 6
Eberthella typhosa	pH 6.5–7 2	pH 4.5–8 0
Escherichia coli	pH 6.0–7.0	pH 4 4–9.0
Diplococcus pneumoniae	pH 7.8	pH 7.0–8.3
Streptococcus pyogenes	pH 6 4–8.5	pH 6 3–9 2
Yeasts	pH 4 0–5 8	pH 2 5–8 0
Molds	pH 3.8–6 0	pH 1 5–8 5

* Porter, John R.: *Bacterial Chemistry and Physiology.* John Wiley & Sons, Inc., New York, 1946, p. 85.

The physiological chemist has discovered that hydrogen-ion concentration plays a part in determining whether chemical reactions proceed normally along the digestive tract, in the cells, and in the blood. Practically all reactions in living cells are under enzyme control and it is known that enzymes are sensitive to even slight changes in hydrogen-ion concentration. The table shown at the top of page 247 records some reported findings in this connection.

Measurement of hydrogen-ion and hydroxyl-ion concentrations. The discovery that hydrogen- and hydroxyl-ion concentrations play such an important part in many phenomena has led to a search for experimental means for measuring them. One method[4] is

[4] For another method—called potentiometric method—for measuring hydrogen-ion concentrations of solutions, the student is referred to more comprehensive texts on inorganic or general chemistry.

Optimum hydrogen-ion concentrations in humans

Blood and lymph	*p*H 7.33–7.51	
Urine	*p*H 4.8 –8.4	
Whole saliva	*p*H 5.75–7 05	frequently about 6.8
Ptyalin functioning	*p*H 6 0 –7.0	(Inactive at *p*H 8, destroyed at *p*H 4)
Pepsin functioning	*p*H 1.5 –2.5	
Sucrase functioning	*p*H 6.2	
Maltase functioning	*p*H 6 1	
Pancreatic amylase functioning	*p*H 6.7 –7.0	
Steapsin functioning	*p*H 8 0	

called the colorimetric method and depends upon the fact that solutions of definite hydrogen-ion concentrations produce definite color and shade effects with selected dyes called indicators. For example, a dye called LaMotte Yellow functions, through characteristic color effects produced, for detecting the hydrogen-ion concentrations of solutions which have *p*H notations of from 2.6 to 4.2.

Some of the dyes that are used for this purpose are listed in the accompanying table. Each of these dyes produces revealing color

THE DYE	*p*H NOTATIONS FOR THE $[H^+]$ RANGE WITHIN WHICH THE DYE FUNCTIONS	
Meta Cresol Purple	1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8	Red to yellow
LaMotte Yellow	2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2	Red to yellow
Bromphenol Blue	3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6	Yellow to blue
Bromcresol Green	3.8— 5.4 Yellow to blue	Each of these indicators, as with the three foregoing dyes, functions for nine solutions in its *p*H range with 0.2 *p*H difference ($[H^+]$ $10^{-0.2}$) between successive solutions.
Bromcresol Purple	5.2— 6.4 Yellow to purple	
Bromthymol Blue	6.0— 7.6 Yellow to blue	
Cresol Red	7.2— 8.8 Yellow to red	
Thymol Blue	8.0— 9.6 Yellow to blue	
LaMotte Oleo Red B	8 6—10.2 Yellow to red	
LaMotte Purple	9.6—11.2 Purple to red	
LaMotte Sulfo Orange	11 0—12.6 Yellow to orange	

and shade effects when introduced, in measured amounts, into solutions whose hydrogen-ion concentrations lie within the range in which the dye specifically functions.

Procedure for measuring hydrogen-ion concentrations. 1. *Use of test papers to find approximate p*H *of solution.* There are various test papers which carry dyes that give different colors with solutions of different *p*H values. One

such test paper carries the dye *Hydrion B* which is red in a solution of *p*H 1, orange in a solution of *p*H 3, yellow in one of *p*H 5, and blue-green in one of *p*H 7.[5] The approximate hydrogen-ion concentration of a given solution can be obtained by dipping a strip of such test paper into the solution and noting the color effect produced. If, for example, the test paper employed carries *Hydrion B* and the color produced is yellow with just a suggestion of orange, it tells that the *p*H of the solution is somewhere near *p*H 5.

2. *Use of an indicator dye in a series of solutions of known* pH. When the approximate *p*H of the solution is known, a more accurate measurement can then be made by using an indicator dye which shows evident variations in color with changes in the hydrogen-ion concentrations of solutions within this limited range. Thus, if the approximate *p*H is somewhere near *p*H 5, Bromcresol Green which shows color changes between *p*H 3.8 and 5.4 is an appropriate choice.

To make the measurement, a series of test tubes of uniform bore is set up, as indicated in Figure 84. Each tube contains 10 ml of a standard solution of

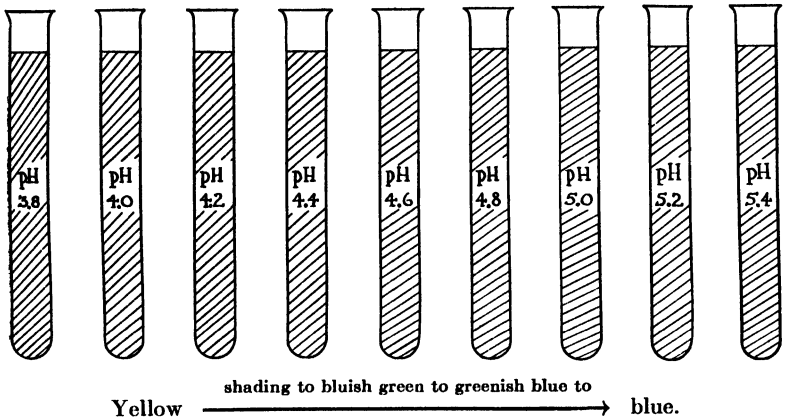


Fig. 84. Bromcresol Green as the indicator in solutions from *p*H 3.8 to *p*H 5.4 serves for measuring hydrogen-ion concentration within this range.

known *p*H, and within the series there is a graduated range of *p*H corresponding to the range of the selected indicator dye. To each tube in the series, 5 drops of the selected dye, in this case Bromcresol Green, are added. When the dye in each tube has diffused evenly, there should be a graduated change in color throughout the series corresponding to the variations in hydrogen-ion concentrations of the standard solutions. This series of solutions is now ready for comparison with the solution to be tested.

3. Introduce 10 ml of the solution under test into a test tube similar to those used for setting up the standard. Add 5 drops of the same indicator dye and mix well. Compare the color of the solution in this tube with the colors obtained with the same dye in the series of standard tubes. The *p*H of the solution under

[5] Nitrazine dye is sometimes used in urinalysis, giving color changes which range from yellow at *p*H 4.5 to blue at *p*H 7.5.

test will be closest to the *p*H of the standard solution which gives the best color match. For example, should the best match be obtained with the standard tube of *p*H 4.8, the solution tested is likewise of *p*H 4.8.

In laboratories where such measurements are made frequently, all of the standard solutions with their respective indicators included are likely to be kept set up ready for use. With this outlay, only two steps are necessary. They are (1) introduction of the test paper into the solution under test for finding its approximate *p*H, and (2) taking a 10-ml sample of this solution, introducing 5 drops of the appropriate indicator (see table, p. 247), and matching the color obtained in the solution under test with colors in the series of standard solutions containing this indicator.

What the *p*H notation tells. With the *p*H notation of a solution known, the following information relating to the solution can be obtained: (1) the concentration in moles of hydrogen ions $[H^+]$; (2) the concentration in moles of hydroxyl ions $[OH^-]$; (3) the concentration in grams of both hydrogen and hydroxyl ions; and (4) the relative acidity or alkalinity of the solution.

HYDROLYSIS OF SALTS

When salts react with water in hydrolysis, water is functioning as an electrolyte. Both the hydrogen ions which contribute to the acid and the hydroxyl ions which contribute to the base are provided through reactions which favor the ionization of water.

Hydrolysis of salts of strong bases and weak acids. When a salt that is derived from a weak acid and strong base—such as sodium acetate, sodium carbonate, or sodium bicarbonate—is dissolved in water, a limited amount of hydrolysis of the salt occurs and *the solution becomes slightly alkaline* because of the very dilute solution of the strong base (p. 189). The explanation, with sodium acetate as an example, is as follows.

Sodium acetate in water solution is entirely ionized. But because hydrogen ions from water are in the presence of acetate ions and because acetic acid is a weak electrolyte, hydrogen ions and acetate ions begin to combine with each other to make neutral molecules of acetic acid.

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$C_2H_3O_2^- + Na^+$$

$$\uparrow\downarrow$$

$$HC_2H_3O_2$$

Or, as represented in an ionic equation:

$$[Na^+ + C_2H_3O_2^-] + HOH \rightleftharpoons HC_2H_3O_2 + Na^+ + OH^-$$

This disturbs the equilibrium of the water, and water compensates for the withdrawal of hydrogen ions by favoring further ionization. Thus, hydrogen ions are produced and removed, while free hydroxyl ions are produced but not removed—sodium hydroxide remaining always completely ionized. Consequently, when the two opposing reactions of water and the two opposing reactions of acetic acid attain their respective equilibriums—which will be before very much of the water is in the form of ions—*the concentration of the hydroxyl ions, while low, will be greater than that of the hydrogen ions.*

Hydrolysis of salts of weak bases and strong acids. Hydrolysis also occurs with salts, such as copper nitrate, ammonium chloride, and ferric chloride, which are derived from weak bases and strong acids. *The resulting solution is always slightly acid in reaction.* For example, with ferric chloride as the salt, water is present in the form of neutral molecules (chiefly) and hydrogen ions and hydroxyl ions (to some extent); ferric chloride is entirely in the form of ferric ions and chloride ions. But ferric hydroxide is a weak electrolyte; hence, hydroxyl ions and ferric ions begin to combine to make molecules of ferric hydroxide.

$$3\ H_2O \rightleftharpoons 3\ H^+ + 3\ OH^-$$

$$3\ Cl^- + Fe^{+++} \uparrow\downarrow Fe(OH)_3$$

Or, represented in an ionic equation:

$$FeCl_3 + 3\ HOH \rightleftharpoons 3\ H^+ + 3\ Cl^- + Fe(OH)_3$$

The response of water to the removal of hydroxyl ions is to favor its further ionization. Therefore, hydrogen ions enter the solution but are not removed and hydroxyl ions are introduced but are in part removed. When the two opposing reactions of water and those of ferric hydroxide are at equilibrium, *the concentration of hydrogen ions, although low, will be greater than that of hydroxyl ions.*

No hydrolysis of salts of strong bases and strong acids. Like practically all salts, a salt of this character is entirely in the form of its ions when in water solution. The water is slightly ionized. But, no combination occurs between hydrogen ions from water and acid-

radical ions nor between hydroxyl ions from water and metal ions; hence, the equilibrium of the two reactions as to water is not disturbed. Concentrations of hydrogen ions and hydroxyl ions continue to be equal, and *the solution is neutral.* For this reason such salts are frequently referred to as neutral salts.

This is illustrated with sodium chloride, which appears in water solution entirely as sodium ions and chloride ions. Water, of course, is ionized to a slight degree. But no combination between hydrogen ions and chloride nor between hydroxyl ions and sodium ions occurs, because both hydrochloric acid and sodium hydroxide are strong electrolytes.

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$Cl^- + Na^+$$

No combination between these ions — No combination between these ions

BUFFERS AND BUFFERED SOLUTIONS

When an acid is put into water, there is an increase in the hydrogen-ion concentration of the solution; when a base is introduced, there is an increase in its hydroxyl-ion concentration. But, there are solutions of some substances into which it is possible to introduce considerable, although limited, amounts of either an acid or a base without producing a marked change in the hydrogen-ion concentration of the solution. These are referred to as *buffered solutions*, and the components of the solution that are responsible for this effect are called *buffers.* In general, two component substances are necessary to provide the buffer action. They are usually (1) *a weak acid*, and (2) *a salt which provides the same acid radical* as that present in the companion buffer. Sometimes, as with the phosphate salts, an acid salt replaces the weak acid. Still another possibility of a buffer pair of substances is a weak base with a companion salt. Examples of typical *pairs of buffer substances* are represented below.

Weak acid	$HC_2H_3O_2$	$H \cdot HCO_3$	$Na \cdot H_2PO_4$
Salt	$NaC_2H_3O_2$	$Na \cdot HCO_3$	$Na_2 \cdot HPO_4$

When hydrogen ions enter the solution. In order to gain some insight into the functioning of a buffered solution, suppose that a

small amount of hydrochloric acid is introduced into a beaker containing a buffered solution, for instance, one containing acetic acid and sodium acetate. The hydrogen ions enter and cause a momentary increase in the hydrogen-ion concentration of the solution. But immediately, some of the acetate ions, supplied by sodium acetate salt, combine with some of the hydrogen ions to make molecules of acetic acid.

$$[H^+ + Cl^-] + [Na^+ + C_2H_3O_2^-] \longrightarrow Na^+ + Cl^- + HC_2H_3O_2$$

Highly ionized acid — Slightly ionized acid

By this means, as long as acid-radical ions are available in the solution for combination with hydrogen ions, the reaction to make undissociated molecules of the weak acid will continue. In this way the hydrogen-ion concentration of the solution is lowered to almost its original level. When the supply of acetate ions becomes exhausted, the buffer action will be at an end.

When hydroxyl ions enter the solution. If a strong base invades the buffered solution, thus providing additional hydroxyl ions, it is the acid of the buffer pair which functions. As hydrogen ions in the solution are used up by combining with hydroxyl ions to make molecules of water, the weak acid ionizes and supplies hydrogen ions to the solution.

$$[Na^+ + OH^-] + [H^+ + C_2H_3O_2^-] \longrightarrow Na^+ + C_2H_3O_2^- + H_2O$$

$HC_2H_3O_2$ (the weak acid, a source of hydrogen ions, in equilibrium with $[H^+ + C_2H_3O_2^-]$)

Highly ionized base — Weak acid a source of hydrogen ions — Very slightly ionized

It will be recognized that the control of hydroxyl ions in the solution can continue only as long as there is a reserve of the weak acid to provide hydrogen ions for this reaction.

Buffered solutions have various uses in the laboratory. They may be used when it is important to prevent marked fluctuations in hydrogen-ion concentration of the material in the course of chemical reaction. The pharmaceutical chemist finds that a buffered solution must be used in certain drug preparations to prevent undesired changes—for example, to keep insulin in solution. Nature has always used buffers. Fruit juices, for instance, are buffered and, con-

sequently, less sour than might otherwise be the case. The hydrogen-ion concentration of blood is maintained with remarkable constancy, normally between *p*H 7.33 and 7.51. This is largely controlled by buffer action, notably of the carbonic acid–bicarbonate salt system. The hydrogen phosphate salts also function in this capacity. For further discussion of the physiological importance of buffers see Chapter 32.

QUESTIONS

1. Explain why water is regarded sometimes as a nonelectrolyte, and sometimes as a weak electrolyte.

2. What, in general, is the relation between the hydrogen-ion and the hydroxyl-ion concentrations when the solution is (a) acid, (b) basic, (c) neutral? What is the $[H^+]$ in a neutral solution? What is the *p*H of such a solution?

3. The $[H^+]$ of a given solution is 0.0001. What does this expression mean? What is the $[OH^-]$ of this solution? Why? What does this $[OH^-]$ tell? How many grams of hydrogen ions are present within 1 liter of this solution? How many grams of hydroxyl ions? What electrolyte system other than water must be present? Why?

4. The normal $[H^+]$ of whole saliva is about $10^{-6.8}$. What is the $[OH^-]$ of this secretion? Which of these ions predominates? What is the *p*H of the saliva? What is the *p*OH?

5. The best yield of jelly is obtained when the reaction of the jelly mass is about *p*H 3. What is the $[H^+]$ of the mass? The $[OH^-]$? How many grams of hydrogen ions would be present in 5 liters of this material? How many grams of hydroxyl ions? What electrolyte system other than water must be present?

6. Certain common molds grow best in a medium of about *p*H 4. Interpret this expression in terms of both the $[H^+]$ and the $[OH^-]$ of the medium. Is this environment acid or basic? Why?

7. Most pathogenic bacteria grow best in an environment of about *p*H 7.4. What information is provided by this statement? Interpret as fully as you can.

8. Upon what principle does the colorimetric system for measuring the hydrogen-ion concentration of a solution depend?

9. From the standpoint of ionization, account for the basic reaction of a solution of sodium bicarbonate in water. Why is it impossible to obtain a very high concentration of hydroxyl ions from such a solution?

10. Account for the neutral reaction which is characteristic of a solution of magnesium sulfate in water.

11. Define *buffered solution*. What, in general, are the essential components of a buffered solution? Illustrate. Represent by means of equations the reactions that take place in a selected buffered solution on entrance of (a) hydrogen ions from a strong acid, (b) hydroxyl ions from a strong base, and tell how each reaction affects the hydrogen-ion concentration of the solution.

12. Saliva is a buffered solution in which the hydrogen phosphate buffer system functions importantly. On the basis of this information, account for the relatively constant hydrogen-ion concentration maintained in saliva in spite of (a) entrance of acid foods, and (b) use of alkaline mouthwashes.

CHAPTER 19

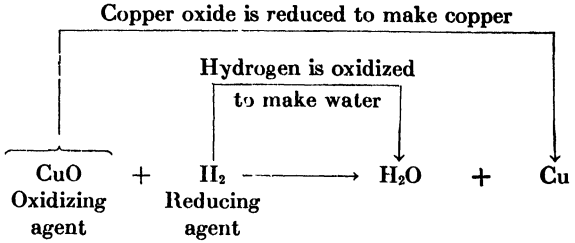
OXIDATION-REDUCTION

The term *oxidation* has long been used with reference to chemical changes in which the substance oxygen reacts with other substances. The term has also been applied to the so-called oxidation-reduction reactions in which oxygen element is supplied to other substances from oxygen-containing compounds. These usages are easily understood. More recently the term *oxidation*, and the associated term *reduction*, have acquired a new meaning; they are used with reference to the exchange of electrons that is believed to account for the previously mentioned oxidations. Moreover, the newer terminology has a wider use; it can be applied to other types of reaction, some of which do not involve the element oxygen.

The older usage is still significant and sometimes most helpful, especially for the study of reactions where the exchange of electrons may be difficult for the inexperienced student to follow. We propose, therefore, to consider briefly the older interpretation of the terms oxidation and reduction, then to turn our attention to the more modern usage.

OXIDATION-REDUCTION: OLDER VIEWPOINT

As complementary processes. ***Oxidation*** *is the making of a substance with a higher proportion of oxygen than that within the substance from which it originates.* ***Reduction*** *is the simultaneous making of a substance with a lower proportion of oxygen than is present in the original substance.* These complementary processes are illustrated in the reaction between copper oxide and hydrogen to make water and copper.



The *oxidation* in this reaction is the making of water from hydrogen. The copper oxide which provides the oxygen is the *oxidizing agent*. The *reduction* is the making of copper from copper oxide. Hydrogen substance, which provides the element responsible for taking oxygen away from copper oxide, is called the *reducing agent* (Fig. 85).

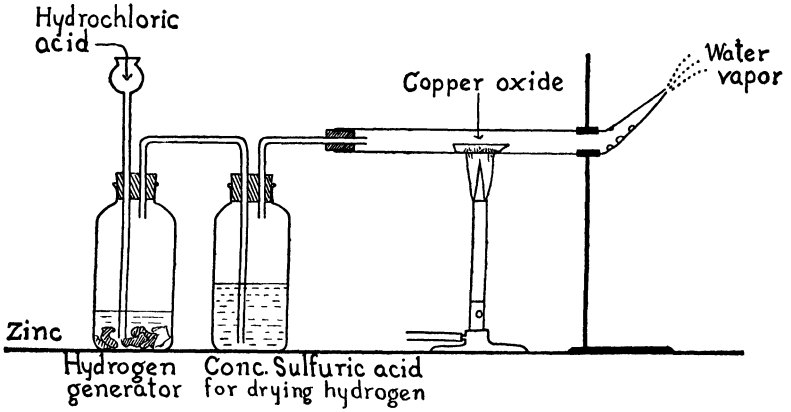
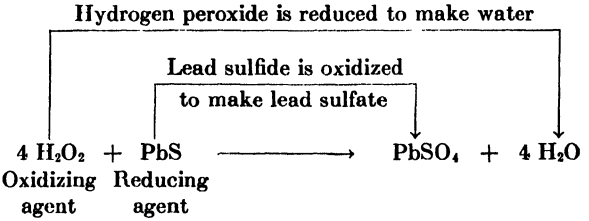


Fig. 85. The reduction of copper oxide by hydrogen.

A stream of hydrogen is passed over copper oxide (contained by the boat) and heat is applied to the materials in the combustion tube because this reaction is appreciable only at elevated temperature. Then, as the hot hydrogen passes over the copper oxide, a reaction can be observed whereby water is made and leaves the tube as water vapor. At the same time, black copper oxide goes out of existence and reddish brown copper substance collects in the boat and on the walls of the combustion tube.[1]

[1] *A caution.* Before heating, it is important to make sure that the apparatus is filled with hydrogen, not a mixture of hydrogen and oxygen. For this purpose, a small test tube full of the escaping gas should be collected and tested by burning. If the collected gas burns *explosively*, the test tube contained a mixture of hydrogen and oxygen; if the gas burns quietly—the top layer first, then successive layers—evidence has been obtained that the combustion tube is now full of hydrogen. Two successive satisfactory tests are desirable.

Another oxidation-reduction reaction is involved when lead sulfide reacts with hydrogen peroxide to make lead sulfate and water.



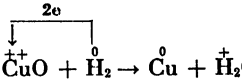
In this reaction, making lead sulfate from lead sulfide is *oxidation;* hydrogen peroxide, which gives up oxygen, is the *oxidizing agent.* Making water, with a lower proportion of oxygen, from hydrogen peroxide is *reduction;* lead sulfide, which pulls oxygen away from the hydrogen peroxide, is the *reducing agent.*

Oxidizing agents. The *oxidizing agents* that function in these reactions *are oxygen-containing compounds that can give up oxygen element* to combine with the element, or elements, provided by the reducing agents. All oxygen compounds are possible oxidizing agents; however, they vary greatly as to the ease with which they function. Compounds such as water, carbon dioxide, and silicon dioxide are poor oxidizing agents because they give up oxygen reluctantly. Hydrogen peroxide, hydrochlorous acid, potassium chlorate, and potassium permanganate are excellent oxidizing agents because they release oxygen readily to appropriate reducing agents.

Reducing agents. The reducing agents functioning with such oxidizing agents *are substances which contain an element or elements that will combine with oxygen but which are not already satisfied in this respect.* The substances carbon and hydrogen, for example, are good reducing agents because the elements carbon and hydrogen readily form compounds with oxygen. Carbon monoxide is an excellent reducing agent because the carbon element in this compound is only partially satisfied with oxygen. Other commonly used reducing agents are sulfurous acid, which is oxidized to make sulfuric acid, and oxalic acid, which is oxidized to make carbon dioxide and water.

The electron exchange. Let us now examine the reaction of hydrogen with copper oxide to discover the exchange of electrons which underlies the observed *oxidation-reduction* reaction. This mutual oxidation and reduction is accomplished through the transfer of elec-

trons from hydrogen atoms to copper atoms, as is suggested in the accompanying equation.



Thus, each positively charged copper atom which receives two electrons is reduced to form a neutral atom of copper. The electrons for this reduction come from hydrogen atoms, and, as a neutral hydrogen atom releases its electron, it is oxidized and becomes 1-positive. Two such hydrogen atoms combine with an oxygen atom to form a molecule of water.

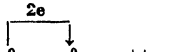
In assigning charges to atoms of elements within covalent molecules or radicals, the relative tendency of the atoms to attract, or release electrons, is considered. Oxygen, because of its marked attraction for electrons, is usually the more negative element in such combinations and is so represented: the companion element is regarded as the positive constituent. The extent of charge on elements, as represented in oxidation-reduction reactions, is consistent with the valence of the atom. However, the term used in this connection is *oxidation number* or the oxidation state of the element. For instance, in the compound water, and in fact in most oxygen compounds, oxygen element exhibits the oxidation number of 2-negative.

The second example of oxidation-reduction (p. 256), the reaction of hydrogen peroxide and lead sulfide (previously cited), is more complex as to electron exchange and will not be discussed at this time (see p. 261).

OXIDATION-REDUCTION: MODERN VIEWPOINT

The modern concept of oxidation-reduction reactions, as has already been stated, relates to the electron exchange between elements. This was illustrated in the example discussed above. Used in this sense ***oxidation*** *involves the removal of 1 or more electrons from an atom or atom group, thereby effecting an increase in the positive state of an element.* Conversely, ***reduction*** *involves the acceptance of 1 or more electrons by an atom or atom group, thereby reducing the positive state (or increasing the negative state) of an element.* And again, these processes are complementary because, as one element is reduced, another element is oxidized. This will be evident in the following examples of reactions, all of which have been considered previously in other settings.

1. In the direct combination of mercury and iodine, the element mercury is oxidized from neutral, in mercury substance, to 2-positive in mercuric iodide. At the same time, iodine element is reduced, from neutral in iodine substance, to 1-negative in the iodide.



This change is brought about through a loss of electrons by mercury atoms and a complementary gain of electrons by iodine atoms.

2. The decomposition of potassium chlorate presents another such reaction. The oxygen element has an oxidation number of 2-negative in potassium chlorate and, during the reaction is oxidized to neutral in oxygen substance. Chlorine has an oxidation number of 5-positive in the chlorate but is reduced to 1-negative in the chloride.

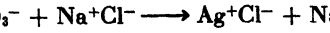


Each of the 3 oxygen atoms within the chlorate ion loses 2 electrons, leaving neutral atoms of oxygen which combine to make oxygen molecules. These electrons are accepted by the 5-positive chloride atoms within the chlorate ions, reducing them to chloride ions with the oxidation number of 1-negative.

3. Displacement reactions (p. 13) are typical oxidation-reduction reactions. This is illustrated by the valence changes that occur during the reaction of copper with silver nitrate.



It will be noted that oxidation-reduction reactions do not necessarily involve oxygen, and, even when present, oxygen may not be one of the elements directly involved in the electron exchange. Nor should it be assumed that every reaction involves the exchange of electrons, hence, falls into the category of oxidation-reduction reactions. Double decomposition reactions, for instance, are not of this classification.



IMPORTANT PROCESSES INVOLVING OXIDATION-REDUCTION REACTIONS

Making metal substances from metal oxides. Only a few metal substances occur ready-made in nature. For the most part metal elements are found in compounds, components of the ores recovered from earth's crust. Thus, iron, zinc, and tin to be used for metal construction must be made by reducing the metal element in a compound to obtain the metal substance.

To obtain iron, iron oxide is mixed with coke (for the sake of the carbon component) and oxygen is admitted. The furnace is charged with the mixture in such a way that carbon monoxide is first obtained as the desired reducing agent since it is a better reducing agent than carbon and, being gaseous, is able automatically to make excellent contact with the ore. For some uses of iron, chiefly laboratory uses, a very finely powdered grade is desired; this can be better made through the use of hydrogen as the reducing agent. For making tin from tin oxide a different sort of furnace is used, and carbon of powdered coal is commonly selected as the reducing agent. Equations for some of these reactions are as follows.

From hematite:

$$2\,\overset{+++}{Fe_2}O_3 + 3\,\overset{0}{C} \longrightarrow 4\,\overset{0}{Fe} + 3\,\overset{++}{CO_2}$$

$$\overset{+++}{Fe_2}O_3 + 3\,\overset{++}{CO} \longrightarrow 2\,\overset{0}{Fe} + 3\,\overset{++}{CO_2}$$

From stannic oxide:

$$\overset{++}{SnO_2} + \overset{0}{C} \longrightarrow \overset{0}{Sn} + \overset{++}{CO_2}$$

The chief zinc compound found in earth's crust is zinc sulfide. To make zinc, this compound is first treated to obtain zinc oxide. This material, in turn, is reduced by carbon in powdered coal.

$$2\,\overset{++}{ZnO} + \overset{0}{C} \longrightarrow 2\,\overset{0}{Zn} + \overset{++}{CO_2}$$

Hydrogen also can be used for reducing oxides of the less active metals from the platinum oxides up to and including the iron oxides (p. 161).

Oxidation-reduction and bleaching. Bleaching takes place when colored substances are destroyed and colorless substances are

made. In order to obtain snowy-white cotton, linen, and silk, our grandmothers removed the brownish pigment—made in plants along with cotton and flax fibers and in silkworms along with silk fibers—by bleaching, and it is removed now by bleaching. Stains on white fabrics that are resistant to washing out, such as iron-rust stains, ink stains, fruit stains, and stains caused by some drugs, in many instances are removed by bleaching. In modern industries bleaching is resorted to for various purposes. Rags and wood are bleached as part of the process to which they are submitted in the making of white paper; fruits are sometimes bleached and then redyed with desired colors. Certainly, neither the red of the maraschino cherries, nor the green color of the same cherries used for St. Patrick's Day food decoration, is the color that nature made this fruit.

Bleaching by oxidation of pigment. Some colored compounds are attacked by substances which function as oxidizing agents with the colored compounds themselves acting as reducing agents. When only colorless products are obtained, bleaching has occurred.

One of the most generally used oxidizing agents is hypochlorous acid. It is a very weak acid, even weaker than carbonic acid. On reduction it yields the more stable compound hydrochloric acid. Unless the composition of the substance bleached is known, it is impossible to follow the reaction in detail, but the element responsible for the reduction is a constituent of the colored compound.

XYZ	+	$H\overset{+}{C}lO$	⟶	$H\overset{-}{C}l$	+	XYZO
The colored substance		Hypochlorous acid		Hydrochloric acid		Compound or compounds with a higher proportion of oxygen than the colored substance. If colorless, bleaching has occurred.

In the course of the reaction, the oxidation state of chlorine element has changed from 1-positive in the hypochlorite radical to 1-negative in the chloride.

Hypochlorous acid is used extensively in industrial bleaching of cotton, linen, and wood pulp, all of which are associated with yellowish pigments in the plants from which they are obtained. This oxidizing agent can be made in several ways, as follows.

Ways for making hypochlorous acid for use in bleaching

1. Hypochlorous acid is sometimes made from the reaction of chlorine with water. In this case the materials to be bleached are moistened with water and

suspended in the atmosphere of chlorine so that the hypochlorous acid will be made in direct contact with the colored substances.

$$Cl_2 + H_2O \longrightarrow HClO + HCl$$

2. Sometimes it is made from hypochlorite salts, such as sodium hypochlorite: (a) in low concentration by hydrolysis of the salt; (b) in higher concentration by reaction with an acid. If the latter method is used, the hypochlorous acid is made in direct contact with the colored substance by dipping the materials first into a solution of the hypochlorite salt and then into the acid solution.

a. $NaClO + HOH \longrightarrow HClO + NaOH$
b. $NaClO + HCl \longrightarrow HClO + NaCl$

3. Another method for making hypochlorous acid is through the use of bleaching powder, sometimes called chloride of lime, which is a complex hypochlorite salt. For such purpose the bleaching powder can be treated with *any* acid, but the acid that frequently functions is carbonic acid. Thus, bleaching may be produced by dipping the colored material into the solution of bleaching powder and then exposing the moist fabric to contact with carbon dioxide in the air.

$$\underset{\text{(From air)}}{CO_2} + \underset{\text{(On wet fabric)}}{H_2O} \longrightarrow H_2CO_3$$

$$\underset{\text{(Bleaching powder)}}{2\,CaCl(ClO)} + H_2CO_3 \longrightarrow 2\,HClO + CaCO_3 + CaCl_2$$

Hydrogen peroxide is also used as a bleaching agent for oxidizing the pigments in silk, wool, and feathers. It is the active agent in some of the laundry bleaches recommended for the protein fabrics and is obtained through the reaction of water with sodium peroxide.

The reaction of hydrogen peroxide with lead sulfide (p. 256) may be considered as a bleaching reaction because lead sulfide is a black substance and lead sulfate is colorless. This reaction will now be used to illustrate the functioning of hydrogen peroxide as an oxidizing agent.

The composition of the peroxide group is believed to be as follows: $\left[\begin{matrix} \cdot\cdot & \cdot\cdot \\ :O:&:O: \\ \cdot\cdot & \cdot\cdot \end{matrix} \right]^{--}$ or O_2^{--}; therefore, each oxygen atom contributing to this group has an oxidation number of 1-negative. When hydrogen peroxide is reduced to make water, the oxygen atom is reduced to its usual oxidation number of 2-negative, as represented below.

$$\overset{\overset{8e}{\downarrow}}{Pb\overset{-2}{S} + 4\,H_2\overset{-1}{O}_2 \rightarrow Pb\overset{+6}{S}O_4 + 4\,H_2\overset{-2}{O}}$$

The sulfur atom in lead sulfide is oxidized from 2-negative to 6-positive in the sulfate group.

This is a reaction which is used for the restoration of old oil paintings when the original white paint contained a lead carbonate. Through reaction with hydrogen sulfide in the air, lead sulfide was made, darkening the area. The reaction of lead sulfide with hydrogen peroxide restores a white compound to the surface.

Potassium permanganate is an excellent oxidizing agent to use for removing stains on white fabrics. Any excess of this purple potassium permanganate, or the brown manganese compound which follows its use, can be easily removed with a solution of oxalic acid, followed, of course, by thorough rinsing with water.

Bleaching by reduction of pigment. Sulfurous acid has been used for centuries for bleaching certain colored substances. According to the writings of Pliny, a Roman of the first century A.D., the ancients treated wool with "burning sulfur" to render it white and fluffy. And wool is bleached today in the same manner; so also is silk, either to obtain the desired whiteness, or preliminary to redying or recoloring.[2] Certain dried fruits are prepared in an atmosphere of sulfur dioxide, obtained by burning sulfur, thus maintaining the light color of the flesh. As the gas comes in contact with water the sulfurous acid is made in direct contact with fruit. The series of reactions is as follows:

$$S + O_2 \rightarrow SO_2 \qquad SO_2 + H_2O \rightarrow \underset{\text{Sulfurous acid}}{H_2SO_3}$$

Because sulfurous acid is a good reducing agent and because the pigments associated with wool and silk fibers and the pigments that give color to plants and fruits are probably oxygen compounds, there is reason to believe that reactions involved may be somewhat as follows:

$$\underset{\text{Pigment}}{H_2SO_3 + ABCO} \longrightarrow H_2SO_4 + \underset{\text{Pigment remains, compound or compounds containing a lower proportion of oxygen than in the original pigments}}{ABC}$$

[2] Hartsuch, Bruce E.: *Introduction to Textile Chemistry.* John Wiley & Sons, Inc., New York, 1950, p. 276.

Another compound which is effective for the removal of certain stains—especially those of iron rust, ink, and fruits—is oxalic acid. This compound is a reducing agent which, on oxidation, yields carbon dioxide and water.

$$\underset{\text{Oxalic acid}}{H_2C_2O_4} + \underset{\text{Pigment}}{ABCO} \rightarrow H_2O + 2\,CO_2 + ABC$$

Incidentally, it should be noted that in most of these common bleaching procedures an acid is present either as the bleaching agent or as another party to the reaction. Consequently, the possibility of an accompanying attack of hydrogen ions on the fabric should be anticipated. And the fact is that silk, wool, and rayon fibers are indeed very sensitive to destructive attacks by hydrogen ions; cotton fibers are more resistant, but even these fibers are gradually weakened through such continued contact. In order to minimize this attack, the fabric, after treatment for bleaching, should be rinsed thoroughly, first with a solution of soap, washing soda, ammonium hydroxide, or some other agent capable of providing a low concentration of hydroxyl ions, and then with plenty of water.

Disinfection by oxidizing and reducing agents. The actual nature of the reactions that result in the death of microorganisms is to a large extent still unknown. However, among the substances known to be effective in destroying these organisms there are both good oxidizing agents and good reducing agents. It is certain that many organic compounds within living cells are subject to oxidation, reduction, or both. Therefore, it is reasonable to conclude that when good oxidizing agents are effective in destroying microorganisms they may function by oxidizing, and thereby destroying, compounds which are essential for the life of the organism. Similarly, the germicidal effectiveness of the strong reducing agent may be related to the reduction of compounds vitally important to the microorganism.

Oxidizing agents as disinfectants. Some of the oxidizing agents used in bleaching are also good disinfectants. These include hypochlorous acid, potassium permanganate, and hydrogen peroxide.

An outstanding instance of such disinfectant action is the chlorination of water supplies and the use of sodium hypochlorite in swimming pools. Dakin's solution and its various modifications, which are used in wound disinfection, are essentially sodium hypochlorite. As shown in the discussion of bleaching (p. 260), the active agent obtained from all of these disinfecting agents is hypochlorous acid. Presumably, the chemical behavior of these substances as disinfectants is similar to their action on organic compounds in bleaching

reactions.[8] Potassium permanganate is used to some extent as a disinfectant and deodorant for wound dressings and irrigations, but the stain left is objectionable, and the manganese compounds produced may be toxic. These disadvantages limit its use.

Reducing agents as disinfectants. The practice of exposing fruits, during the drying process, to sulfur dioxide gas helps to preserve them by killing molds, fungi, and other microorganisms involved in decay. It is probable that as sulfur dioxide comes in contact with the moist fruit sulfurous acid is made and functions to reduce certain compounds—enzymes, or other cells components—which are essential to the life of the microorganisms.

Formaldehyde has long been known as an effective disinfectant. It is gaseous and therefore penetrating. It is a powerful reducing agent; hence, its germicidal effect is presumed to be due, at least in part, to the reduction of compounds of vital importance to the organism. (See also p. 307.)

Physiological importance. Many of the reactions that are constantly going on within both plant and animal cells in the process of metabolism are oxidation-reduction reactions. Some of these reactions will be considered in our subsequent study.

QUESTIONS

1. Define oxidation and reduction from the standpoint of oxygen involvement. Why are they said to be complementary processes? Illustrate with reference to some specific oxidation-reduction reaction.
2. From the standpoint of oxygen involvement:
   a. What is an oxidizing agent? What happened to it during the reaction?
   b. What is a reducing agent? What happens to it?
3. From the standpoint of electron involvement, define:
   a. oxidation, b. reduction. Show that these are complementary processes by reference to a specific example selected from reactions not discussed in this chapter.
4. The corrosion of metal is essentially an oxidation process. Explain what is meant by this statement, illustrating by reference to some well-known corrosion reaction.
5. Locate the mutual oxidation and reduction involved in:
   a. The reaction of chlorine with water (p. 261)
   b. The reaction of sulfur with oxygen (p. 262)

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[8] Another destructive attack on microorganisms may be due to a direct reaction of chlorine with proteins of these cells. Chlorine can be made from hypochlorous acid by reactions represented as follows:

$$2\,HClO \rightarrow 2\,HCl + O_2 \qquad HClO + HCl \rightarrow Cl_2 + H_2O$$

6. From the standpoint of electronic interchange, indicate which of the following reactions include oxidation-reduction reactions. State which elements undergo oxidation and which are reduced, with reasoning.
   a. The reaction of zinc with hydrochloric acid
   b. The decomposition of mercuric oxide
   c. The hydrolysis of cupric sulfate
   d. The reaction of aluminum with water

7. How does hypochlorous acid function in oxidation-reduction reactions? Suggest two sources from which this compound can be made, representing the reactions by which it is obtained. When used as a bleaching agent, what happens to the pigment? To the hypochlorous acid? Why is the fabric weakened on prolonged exposure to this bleach? How can the destructive attack be minimized?

8. What is the principle involved in removal of potassium permanganate stains? Suggest two possible agents that can function for this purpose. What happens to the compound which thus removed the stain?

9. Remembering that many pigments are subject to either reduction or oxidation, how would you proceed in attempting to remove a stain of uncertain origin?

10. From the standpoint of oxidation-reduction reactions, account for:
   a. The disinfection of swimming pool water by use of sodium hypochlorite
   b. The destruction of fungi and molds by drying in sulfur dioxide fumes

CHAPTER 20

AN INTRODUCTION TO ORGANIC CHEMISTRY

Organic and inorganic compounds. Compounds have been classed as organic and inorganic ever since the earliest days of the science of chemistry, but for many years the differentiation was confused and far from satisfactory. Then, in the early 1820's, it was pointed out by the great chemist Berzelius,[1] that since all so-called organic compounds known at the time were made *only in living cells* of plants and animals they might possess a "vital" or "living force" which it would be impossible for man to duplicate. Thereupon this classification assumed a new and more definite significance, and chemists came to believe in organic compounds as compounds possessed of this inherent vital capacity which rendered it impossible for man to make them in the laboratory. Among such compounds were included urea, proteins, carbohydrates, and fats. All other compounds were labeled inorganic, as suggestive of the lack of this vital force; to be sure, these included certain compounds made in living cells—such as water, carbon dioxide, and hydrochloric acid—but possible also for man to make in beakers and test tubes. The experimental achievement which cast the first shadow of doubt upon this cherished notion was the making of *urea* in the laboratory in 1828 by a German chemist, Friedrich Wöhler.

Wöhler had been heating two inorganic compounds, ammonium sulfate and potassium cyanate, in the hope of obtaining ammonium cyanate, likewise inorganic; but the product which was actually made was *urea!*[1] Since urea was among the compounds admittedly made in living cells and hitherto supposed possible only as a product of animal metabolism, this was a disturbing discovery. As time went on, other compounds classed as organic were made in laboratories,

[1] Moore, F. J.: *A History of Chemistry.* McGraw-Hill Book Company, Inc., New York, 1931, p. 135.

with the result that chemists were forced eventually to surrender their notion that organic compounds possessed "vital force." Hence, there arose a need for another basis of classification.

In this new classification the original class labels, organic and inorganic, were retained but with a different significance. *Organic* came to apply only to compounds that contain *carbon* as one contributing element, while nearly all other compounds, by elimination, came to be labeled *inorganic*. This modern classification basis, then, has only arbitrary significance and it admits inconsistencies in that a *few carbon compounds* which previously had been conceded to be inorganic are still, for convenience, classed as such; among these are carbon dioxide, carbon monoxide, carbon disulfide, carbonic acid, and the carbonates.

Importance of organic compounds. The importance of organic compounds begins to be recognized when it is realized that they include many *substances of biological importance* such as carbohydrates, fats, and proteins; vitamins, enzymes, and hormones; urea and other metabolic products. Organic compounds also include important drugs, disinfectants, and antibiotics, together with thousands of materials of commercial importance such as perfumes, flavors, dyes, soaps, synthetic detergents, natural fibers of silk, wool, and cotton as well as rayons, nylons and plastics, also fuels—such as gasoline—and other compounds too numerous to mention.

In fact, knowledge pertaining to organic chemistry and the synthesis of new compounds has increased so rapidly that the organic substances now known to man greatly outnumber those of the inorganic variety.

Elements found in organic compounds. To build these many and varied substances, nature draws upon a relatively small number of elements; chiefly carbon, hydrogen, oxygen, and nitrogen; frequently sulfur and phosphorus. There are also compounds containing chlorine, bromine, iodine, and occasionally other elements. But, on the whole, the number of elements contributing to organic compounds appears to be limited.

FACTS AND THEORIES CONCERNING ORGANIC COMPOUNDS

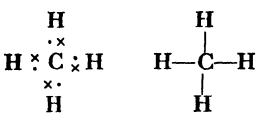
Classification of organic compounds. Many organic compounds fall into distinct classes which are recognized by typical

group behaviors. Some of these classes are shared with inorganic compounds; thus, organic acids and organic salts engage in reactions similar to those of inorganic acids and salts. In addition there are other classes peculiar to organic compounds; among these are hydrocarbons, alcohols, aldehydes, ketones, carbohydrates, and proteins. Compounds within each group exhibit certain chemical reactions peculiar to the group. Studies of some of these characteristic class reactions will become an important part of our work.

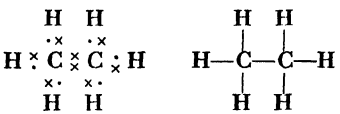
Speed of reactions. Reactions of organic compounds, in contrast with those of inorganic compounds, are usually slow. In some instances they are inappreciable unless favored by a catalyst. Consequently, catalysts play an important part in reactions involving carbon compounds.

Although some organic compounds, notably salts and acids, ionize to an appreciable degree, most carbon compounds do not form ions, hence, are regarded as nonelectrolytes (p. 219). This is one factor that accounts for the slow reactions of organic compounds.

Covalent compounds. Because organic compounds are for the most part nonelectrolytes or weak electrolytes, it is believed that carbon element forms covalent compounds. It will be recalled that carbon has the atomic number 6; hence, the carbon atom is believed to have 4 electrons in its valence shell (p. 127). Consequently, this atom shows little or no tendency to lend or borrow electrons but enters into combination in molecules of compounds through sharing electrons with an adjoining carbon atom or with atoms of other elements. This is illustrated in the accompanying covalent formulas for molecules of methane and ethane. Electrons provided by carbon atoms are represented by x's; those provided by hydrogen atoms by dots.



Methane



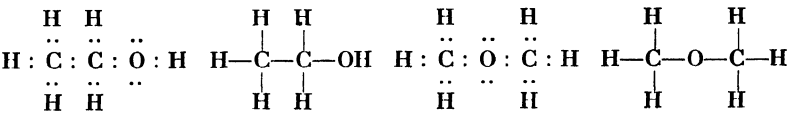
Ethane

A pair of electrons mutually shared by 2 atoms constitutes a single bond between the atoms, as is represented above.

Isomers. There are many instances of the occurrence of two or more organic compounds which have the same element makeup and the same empirical composition, hence, the same molecular weight. Therefore, although such compounds are different substances since

they exhibit different physical and chemical properties, their compositions can be represented by the same empirical formula. An example of this phenomenon, with which the student is already somewhat familiar, occurs with the sugars glucose, galactose, and fructose. The formula for the molecular weights of all three of these compounds is $C_6H_{12}O_6$, and yet they are different substances and have different degrees of solubility and of sweetness. They also show some differences in chemical behavior. *This phenomenon of two or more compounds that have identical empirical composition,* so seldom encountered among inorganic compounds, *is known as isomerism, and the compounds mutually involved are called isomers.* Glucose, fructose, and galactose, accordingly, are isomers of each other. Ethyl alcohol and methyl ether are also *isomeric compounds.* Both have the same composition quantitatively, hence, the same molecular weight, as represented by their common empirical formula C_2H_6O, but they are different substances. They differ in some physical properties, and they behave differently in some of their chemical reactions.

To account for the existence of isomeric compounds the chemist assumes that, although molecules of isomers must have identical composition as far as varieties and numbers of their atoms are concerned, *the arrangement of atoms within the molecules of isomers is probably different.* For instance, molecules of both ethyl alcohol and methyl ether are composed of identical numbers of atoms, as represented in their common empirical formula C_2H_6O, yet they form molecules of different compounds. It is assumed, therefore, that their atoms have different placements in their respective molecules. This is represented in their structural formulas.



Ethyl alcohol ***Methyl ether***

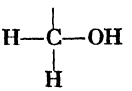
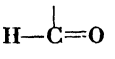
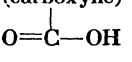
Ethyl alcohol exhibits certain properties that indicate the presence of a hydroxyl group in its molecule and this is represented in its structural formula. Methyl ether, on the contrary, does not behave as might be expected from a compound containing a hydroxyl group; consequently, the atoms must be arranged so as to include an oxygen atom that is not in combination with a hydrogen atom. These examples illustrate a significant use for structural formulas—to indicate samenesses and differences among isomers.

The structural formula and its use. The organic chemist makes extensive use of structural formulas; in fact, they practically replace the simpler type of formula used by the inorganic chemist.

A *structural formula* is really a diagrammatic representation of the placement of atoms within the molecule of the substance. It shows the atoms of the contributing elements arranged in significant groupings, based on the known behavior of the compound. It also shows the valence, or combining capacity, of each atom within the molecule. One type of structural formula has been introduced previously, namely the representation of the covalent molecule showing the distribution of valence electrons. However, an older, and simpler type of formula is usually used by the organic chemist in which a single line represents a valence bond mutually shared by two atoms and a double bond represents a 2-valent situation. This practice has been illustrated in the formula representations for methane and ethane (p. 268), in formulas for ethyl alcohol and methyl ether (p. 269), and many other instances will be encountered as the study progresses.

Structural formulas also provide a means for showing wherein compounds within the same class group are alike—for example, wherein all alcohols of the same variety are alike; wherein all aldehydes are alike; wherein organic acids are alike—and, therefore, why compounds belonging to the same class exhibit certain common chemical behavior.

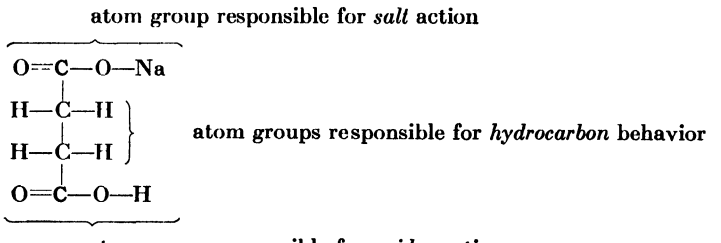
Thus, the chemist believes that molecules of all primary alcohols (p. 292) contain atom groups of specific composition. Similarly, there is a characteristic atom group within molecules of all aldehydes (p. 303). And, still another distinctive atom group must be present within molecules of all organic acids of the type called carboxylic acids (p. 314). These three different and characteristic atom groups are represented structurally as follows.

Primary-alcohol atom group	*Aldehyde atom group*	*Organic acid atom group* (carboxylic)
		

It is important that *structural formulas for compounds within each specific class should indicate the presence within their molecules of atom groups identical in composition and structural placement,* thereby explaining why the molecules, hence, the compounds, behave alike chemically.

The complexity of organic compounds. Many organic compounds, by comparison with inorganic compounds, are quite complex in both composition and chemical behavior. In some instances this is evidenced by very large molecular weights; with other compounds, by the complexity of their chemical reactions. For example, a compound which reacts as an acid, a base, and a salt might reasonably be considered as complex; a compound which exhibits the chemical behavior of a hydrocarbon, an acid, and an aldehyde might likewise be regarded as complex. This chemical complexity of some organic compounds often presents difficulties in obtaining desired results in experimental work, because side reactions, due to certain structural features, go on simultaneously with the reaction which the chemist may be attempting to bring into prominence at the time. Or in the study of drugs and their action, it is not unusual to find a compound which, because of a characteristic structural feature, is capable of a reaction to produce a desired effect but is limited in its usefulness because of undesired side reactions associated with other aspects of its chemical composition.

To explain the complexity of a compound the chemist looks to the *placement of atoms* within its molecule and sees therein as many different atom groups as there are different chemical behaviors exhibited by the compound. For instance, if a compound reacts as an acid, a salt, and a hydrocarbon, it is reasonable to assume that there should be at least three specific atom groups respectively responsible for these reactions. Such a possibility is represented in the following structural formula for the compound concerned.



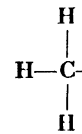
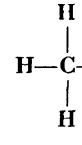
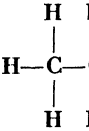
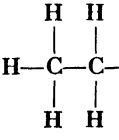
Some compounds are very complex indeed. Hence, it seems reasonable to suppose that the placement of atoms within their molecules must resolve into corresponding complexities; which means, in turn, that formulas that have been developed to represent structural features within such molecules must likewise be complex. (See p. 352.)

Two basic assumptions. Two assumptions underlie the whole theory in relation to organic compounds.

1. The *tetravalency* of the carbon atom, which is in accordance with the fact that the atomic weight of carbon does exhibit a valence of 4. One exception occurs in carbon monoxide, in which carbon has a valence of 2.

2. The *tendency of carbon atoms to combine with each other* within molecules of compounds.

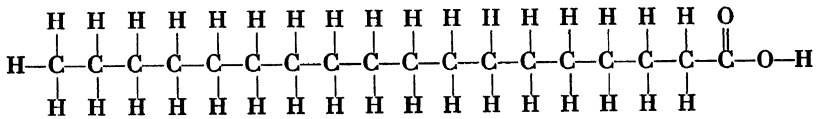
These beliefs are illustrated in the structural formulas already given; the following are other examples.

	EMPIRICAL FORMULA FOR MOLECULAR WEIGHT AND MOLECULE	STRUCTURAL FORMULA FOR MOLECULE	OBSERVATIONS
Methane	CH_4		All 4 valence bonds on the carbon atom are satisfied with hydrogen atoms.
Methyl chloride	CH_3Cl		One valence bond on the carbon atom is satisfied with a chlorine atom, the other three with hydrogen atoms.
Ethane	C_2H_6		The 2 carbon atoms are "chained" by one each of their valence bonds; the other valence bonds are satisfied by hydrogen atoms.
Propyl hydroxide or propanol	C_3H_7OH		The 3 carbon atoms are "chained" by single bonds; the other valence bonds are satisfied as indicated.

Carbon atoms chained through single, double, or triple valence bonds. There is much experimental evidence to support the belief that in molecules of many organic compounds carbon

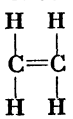
atoms are "chained" (combined) with each other in *single-bond formation.* Such is the case in molecules of ethane and propyl hydroxide. as is represented in their foregoing structural formulas. In these molecules the 2 atoms of carbon in ethane molecule and 3 atoms of carbon in propyl hydroxide molecule are combined in this single-bond structure. In molecules of some organic compounds *many* carbon atoms may be chained thus one to another by single bonds. For example, in the molecule of stearic acid there are 18 carbon atoms, as is indicated in the empirical formula ($C_{17}H_{35}COOH$) for this compound, and it is believed that the valences of these carbon atoms are in part satisfied through this variety of combination as is represented in the following manner.

Structural formula for the molecule of ***stearic acid.***



But within molecules of other organic compounds 1 or more pairs of *carbon atoms are believed to be held in combination with each other, in some instances through 2, in other instances through 3 of their 4 valence bonds.* Molecules of ethylene (ethene), propene, and butene serve as examples of the first variety of compounds, while molecules of acetylene (ethyne), propyne, and butyne serve as examples of the second variety of compounds, and their structural formulas indicate these conditions.

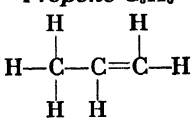
Ethylene or ***ethene*** C_2H_4



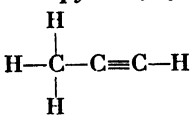
Acetylene or ***ethyne*** C_2H_2



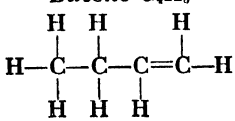
Propene C_3H_6



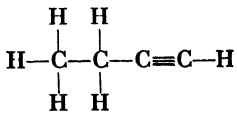
Propyne C_3H_4



Butene C_4H_8

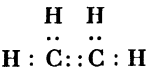


Butyne C_4H_6



The explanation for the double and triple valence bonds thus represented in these molecules lies in the electron distribution (p. 128). Whereas a single bond represents 1 pair of electrons shared between 2 carbon atoms, a double bond represents 2 pairs of mutually shared electrons, and a triple bond indicates that 3 pairs of electrons are thus shared. This is represented below in the formulas for *ethylene* and *acetylene* molecules.

Ethylene

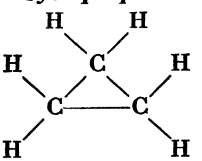


Acetylene

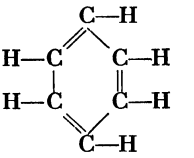


Open- and closed-chain structures. Carbon atoms may combine within molecules to form either "open" or "closed" chains. Examples already cited illustrate molecules of the open-chain type. The simplest of the closed-chain structures is that of the hydrocarbon *cyclopropane*, with the empirical formula C_3H_6. The structural formula for the cyclopropane molecule shows 3 carbon atoms combined, through single bonds, to form a cyclic or closed-chain structure.

Cyclopropane



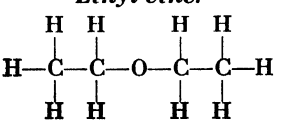
Benzene



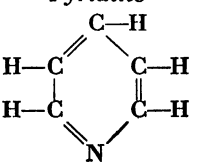
One of the best known and most important of the cyclic, or closed-chain, compounds is *benzene*, with the empirical formula C_6H_6. The structural formula for benzene is represented above. It will be noted that, with the proportion of hydrogen to carbon as indicated by its empirical composition, it becomes necessary to assume that double bonds alternate with single bonds between carbon atoms in order to account for the valence of 4 of carbon atoms.

Elements other than carbon in the chain. Atoms of elements other than carbon, notably nitrogen and oxygen atoms, can occur in the chain. This is indicated in the structural formulas for ethyl ether and pyridine.

Ethyl ether



Pyridine



Functioning of structural formulas. The structural formula is, therefore, a valuable aid to the student of chemistry because it provides, at a glance, significant information regarding the compound concerned. In using the structural formula it should be kept in mind that it is only a *tool*, albeit an important one, to be used as a means for attaining better understanding of the compounds under study. It should be accepted and used as a diagrammatic expression by means of which chemists indicate the placement of atoms of the various elements within molecules of compounds, thereby indicating the properties that are characteristic of the compound.

QUESTIONS

1. What is the modern basis for the classification of compounds as organic or inorganic? What was the previous basis for such classification?
2. Prepare a list of materials in common use: (a) which you know to be naturally occurring organic compounds, (b) which have come into common use as a result of the development of the science of organic chemistry.
3. Mention several ways in which the development of organic chemistry has affected our modern standard of living.
4. Contrast the speed of reactions involving organic compounds with those commonly encountered among inorganic compounds. How is this difference accounted for? Name one means by which this difficulty is frequently overcome.
5. What are isomers? How is this phenomenon explained?
6. What information concerning a compound is provided by the empirical formula? What is the function of the structural formula? State two reasons why the structural formula has such an important place in the study of organic compounds.
7. State: (a) one basic assumption that *must* be complied with in structural formulas of all organic compounds; (b) the second basic assumption that may be considered. Look through the following pages of this text and select structural formulas for at least five compounds. Note in each instance how these two basic assumptions are represented.
8. From the standpoint of the electron distribution of the valence electrons, why do carbon compounds form covalent formulas? What constitutes a single bond? A double bond? Illustrate.
9. How, theoretically, do organic compounds known as "cyclics" differ from those of the "straight-chain" variety? Cite two examples of each, together with their structural formulas.

CHAPTER 21

HYDROCARBONS AND HALOGEN DERIVATIVES

The first class of organic compounds to be studied is the *hydrocarbons*. These substances, as their name implies, are composed of only the two elements hydrogen and carbon. There are many hydrocarbons some of which are encountered frequently, either individually or in mixtures, as important materials in everyday use. Their names, however, do not indicate their hydrocarbon nature.

Some important hydrocarbons. Methane, ethylene, and acetylene are well-known hydrocarbons. *Methane* is a gaseous substance made in nature from the decay, under anaerobic conditions, of certain organic compounds, notably celluloses. It is sometimes called "marsh gas" because it bubbles up through the water in swamps, having been made by bacterial action on cellulose of submerged plants. Coal miners long ago named it "fire damp" (fire vapor) because, made from organic compounds in soft coal and collected in pockets in mines, it was a dread fire hazard in the days before mines were electrically lighted. Methane is also the principal component of "natural gas" and commercially prepared "illuminating gas."

Ethylene may also be present in illuminating gas mixtures. It has been in use since 1923 as a general anesthetic.[1] It is used in the fruit industry to hasten the ripening of citrus and other fruits. The fruit can be picked for shipment while it is still firm and green; then, through contact with ethylene, it is ripened in transit. The ethylene hastens both the development of the natural color of the fruit and the chemical changes of starches to sugars.

[1] Luckart, A. B., and Lewis, Dean: "Clinical Experiences with Ethylene-Oxygen Anesthesia," *J.A.M.A.*, 81:1851–57, 1923.

Acetylene is another frequent component of illuminating gas. When this hydrocarbon burns with oxygen, a great deal of heat is produced. It is the fuel used with commercial supplies of oxygen, through the agency of the oxyacetylene torch, for obtaining the necessary high temperatures—as high as 3500° C—for welding and cutting steel, aluminum, copper, and other metals that are used in modern construction (p. 64). Both ethylene and acetylene are in demand, also, for making some of the modern plastics (pp. 285 to 286).

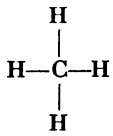
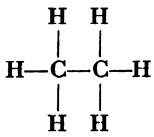
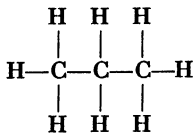
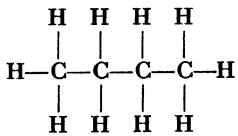
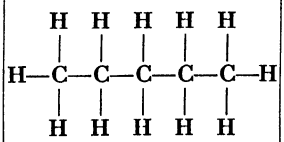
Hydrocarbon mixtures are encountered even more frequently than isolated hydrocarbon substances. Among the hydrocarbon mixtures in common use are benzine[2] used in cleaning; various gasolines, kerosenes, and fuel oils; also mineral oils, petroleum jellies, and paraffins used for a variety of purposes. The principal source of hydrocarbon mixtures is from naturally occurring petroleum oils.

Two major classes. Hydrocarbons fall into two major classes from the standpoint of differing chemical behavior, hence, different molecule structure. Those with open chains are known as *aliphatic* hydrocarbons; those which form closed chains are referred to as *cyclic* or *aromatic* hydrocarbons. There is also a small group known as the cycloparaffins which form a ring structure but in chemical behavior resemble the aliphatic hydrocarbons rather than the aromatic. Cyclopropane (p. 274) belongs to this group. Our present study is concerned with the aliphatic compounds; the cyclic compounds are treated in Chapter 25.

Open-chain hydrocarbons, three classes. *The alkanes*. The most frequently encountered hydrocarbons belong to the *alkane series*. It is known, also, as the *methane* series, because methane is the first member of the group, and as the *paraffin* series, because of the relative chemical inactivity of the members. Formulas for the first five members of the series are presented in the table on page 278.

In studying the table, it will be noted that each member of the series differs from the preceding members by the addition of one or more —CH_2— groups; otherwise their formulas are identical. This is what is known as a *homologous series*, and it is significant because all members of a homologous series exhibit markedly similar chemical behavior. This is characteristic of many types of organic compounds and greatly facilitates their study.

[2] The student should be careful to differentiate between *benzine* and *benzene*. Benzine is a mixture of hydrocarbons of the open-chain variety. Benzene is a single closed-chain hydrocarbon; its formula is given on p. 274.

NAME OF HYDROCARBON	EMPIRICAL FORMULA	STRUCTURAL FORMULA FOR MOLECULE	SEMISTRUCTURAL FORMULA FOR MOLECULE
Meth*ane*	CH_4		
Eth*ane*	C_2H_6		$CH_3—CH_3$
Prop*ane*	C_3H_8		$CH_3—CH_2—CH_3$
But*ane*	C_4H_{10}		$CH_3—CH_2—CH_2—CH_3$
Pent*ane*	C_5H_{12}		$CH_3—CH_2—CH_2—CH_2—CH_3$

The ***semistructural formula*** is an abbreviation of the structural formula which is more convenient for use on the printed page. In this representation the atom groupings are indicated, but the valence bonds designated are only those between connecting carbon atoms, or between carbon and other significant atoms.

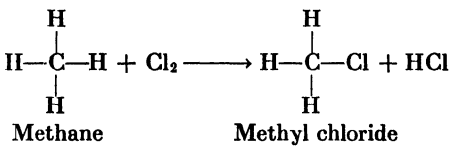
Saturated hydrocarbons. Hydrocarbons of the alkane series are *saturated* hydrocarbons, so called because they engage only in substitution reactions. That is, they cannot combine with any other element without first dropping some of their hydrogen. Thus, meth-

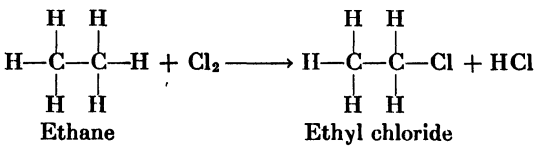
ane and ethane must drop some of their hydrogen before they can combine with chlorine.

$$\underset{\text{Methane}}{CH_4} + Cl_2 \longrightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$\underset{\text{Ethane}}{C_2H_6} + Cl_2 \longrightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl} + HCl$$

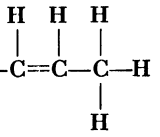
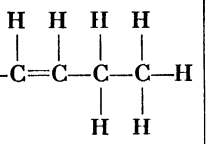
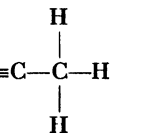
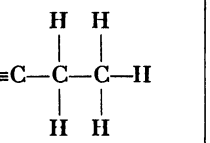
The theoretical explanation for this fact is indicated in the structural formulas (p. 278) which suggest that within molecules of these hydrocarbons all 4 valence bonds of each carbon atom are completely satisfied, either by hydrogen atoms, as in methane, or in part by hydrogen atoms and in part by 1 or more carbon atoms. Hence, there are no available valence bonds on the carbon atom or atoms for reaching out to "pick up" other atoms. Thus, when molecules of methane and ethane are in reaction with chlorine:





Alkene and alkyne series of hydrocarbons. The *alkene* hydrocarbons are also known as the *ethylene series*, named after the first member, or the *olefin* series, because of their oily characteristic. The first three members of this series are *ethylene* or *ethene*, *propene*, and *butene* represented by formulas shown in the table on page 280. It will be noted that at least 2 carbon atoms in each molecule are represented as joined by a *double valence bond;* also, that these compounds form a homologous series.

The *alkyne* or *acetylene* series is also composed of homologous compounds. They differ from the alkenes in that at least 2 carbon atoms in each molecule are represented as joined by 3, that is, *triple valence bonds.*

NAME OF HYDROCARBON	EMPIRICAL FORMULA	STRUCTURAL FORMULA FOR MOLECULE	SEMISTRUCTURAL FORMULA FOR MOLECULE
Ethylene or alkene series			
Ethylene or Eth*ene*	C_2H_4		$CH_2{=}CH_2$
Prop*ene*	C_3H_6		$CH_2{=}CH{-}CH_3$
But*ene*	C_4H_8		$CH_2{=}CH{-}CH_2{-}CH_3$
Acetylene or alkyne series			
Acetylene or Eth*yne*	C_2H_2		$CH{\equiv}CH$
Prop*yne*	C_3H_4		$CH{\equiv}C{-}CH_3$
But*yne*	C_4H_6		$CH{\equiv}C{-}CH_2{-}CH_3$

Unsaturated hydrocarbons. In contrast to hydrocarbons of the methane series, hydrocarbons of both the ethene and ethyne series are *unsaturated;* that is, they are able to enter into direct combination with more hydrogen, or other selected elements, without dropping any of the hydrogen already present therein. When they en-

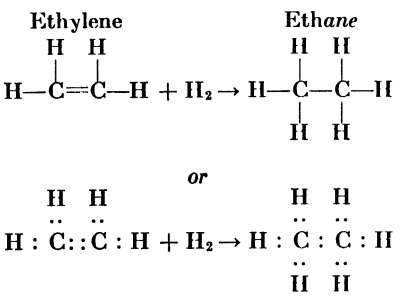
gage in such reaction, the products are either of the saturated or more nearly saturated variety. Such possibilities are represented as follows.

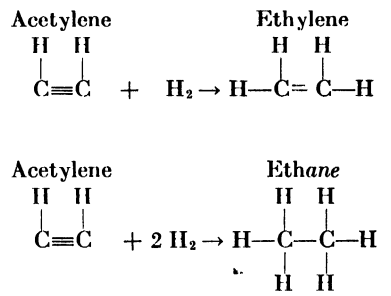
Ethylene + Hydrogen ⟶ Ethane
C_2H_4 + H_2 ⟶ C_2H_6
(Unsaturated) (Saturated)

Acetylene + Hydrogen ⟶ Ethylene
C_2H_2 + H_2 ⟶ C_2H_4
(Unsaturated) (More nearly saturated)

Acetylene + Hydrogen ⟶ Ethane
C_2H_2 + $2\,H_2$ ⟶ C_2H_6
(Unsaturated) (Saturated)

The explanation for the chemical behavior of unsaturated hydrocarbons is believed to lie in the presence of the double or triple valence bonds between adjoining carbon atoms. This means that, in addition to the 1 pair of shared electrons essential for a valence bond, such molecules have one or more bonds where carbon atoms are held by 2 pairs of shared electrons (in the alkenes) or 3 pairs of shared electrons (in the alkynes). In these positions there are electrons which can easily be made available for combinations with other elements. Such reactions are represented in the following equations.





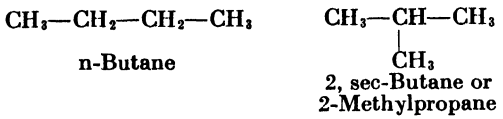
Introduction to naming customs. ***Distinctive endings for names of hydrocarbons of each series.*** Before proceeding further with the study of hydrocarbons it will be well to become better acquainted with the customs that have been developed for naming various classes of hydrocarbons.

The members of the *alkane or methane series* are distinguished by the ending *ane* attached to the stem name. Thus, as has been mentioned previously, the first four members of the series are meth*ane*, eth*ane*, prop*ane*, and but*ane*. Beginning with pent*ane*, the fifth member of the series, the stem designates the number of atoms of carbon which are believed to be present in the molecule; namely, hex*ane* (C_6H_{14}), hept*ane* (C_7H_{16}), oct*ane* (C_8H_{18}), etc.

For hydrocarbons of the *alkene or ethylene series*, the stem name is used with either the ending *ene* or *ylene*, as in eth*ene* or eth*ylene*. Hydrocarbons of the

alkyne or acetylene series are distinguished by the ending *yne* used with the stem name.

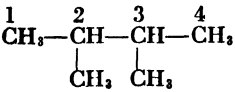
Isomers. There are also *isomeric compounds* in each of these series, and these must be distinguished by names and formulas. For example, there are two butanes, each having the formula C_4H_{10}. These are represented semistructurally as follows.



n-Butane

2, sec-Butane or
2-Methylpropane

The straight-chain hydrocarbon is known as normal (n-) butane; the one with the branched chain as secondary (sec-) butane. The system which is recommended by the Committee of the International Union of Chemistry for naming branched hydrocarbon isomers involves selecting the longest hydrocarbon chain, numbering the carbon atoms in that chain consecutively, and designating the number and position of the branched group, or groups. This method is illustrated in naming the isomer of normal hexane, the formula of which is given below.



2,3-Dimethylbutane

Physical properties of hydrocarbons. The *physical states* of hydrocarbons at ordinary temperatures are related, in general, to their molecular weights. Those with low molecular weights, including methane, ethane, propane, and butane, also ethylene and acetylene, are gaseous. With increasing molecular weights there appear, first, hydrocarbons that are volatile liquids like those in benzine, gasolines, and kerosenes; next, hydrocarbons that are still less volatile liquids, such as those in fuel oils; then others with still higher molecular weights that are semisolid, including the hydrocarbons of petroleum jelly; finally, there appear hydrocarbons in the highest range of molecular weights, such as those present in paraffins, which are solids.

As for *solubilities*, hydrocarbons are not soluble in water. They form solutions with other hydrocarbons, as is evidenced by their natural occurrence as hydrocarbon mixtures. They also form solutions with a variety of other compounds closely related to the hydrocarbons in composition as: alcohols, ether, chloroform, carbon tetrachloride, and halogen derivatives (p. 286). The insolubility of hydrocarbons in water explains why water is so ineffective for remov-

ing stains on linens or clothing if caused by mineral oil, petroleum jelly, or paraffin from dripping candles. With benzine, ether, or carbon tetrachloride as the solvent, such stains disappear as by magic.

Physiological effect. The gaseous and more volatile hydrocarbons have an anesthetic effect on inhalation. This effect is more pronounced with the unsaturated hydrocarbons than with those of the saturated variety. The less volatile members—heavy liquid, semisolid, and solid hydrocarbons—are physiologically inert, probably because they can neither be inhaled nor penetrate membranes.

Chemical behavior of hydrocarbons. ***Chemical activity.*** Comparatively speaking, *saturated hydrocarbons are inactive.* Methane and other members of the alkane series do not usually react with acids and bases. They are slow to react with oxidizing agents, even at high temperatures. *Unsaturated hydrocarbons*, on the other hand, react *more or less readily* with such compounds even at ordinary temperatures.

With oxygen. All hydrocarbons, given favorable conditions, will react with oxygen at burning speed. With an *adequate oxygen supply* the products are carbon dioxide and water, as represented below.

Methane + Oxygen ⟶ Carbon dioxide + Water

$$2\,CH_4 + 4\,O_2 \longrightarrow 2\,CO_2 + 4\,H_2O$$

But with *inadequate oxygen* a third product, namely, carbon, is made.

Methane + Oxygen ⟶ Water + Carbon dioxide + Carbon

$$2\,CH_4 + 3\,O_2 \longrightarrow 4\,H_2O + CO_2 + C$$

The more inadequate the oxygen supply the greater will be the carbon yield, as is illustrated by the following equations representing reactions with acetylene and oxygen in varying proportions.

With adequate oxygen $2\,C_2H_2 + 5\,O_2 \longrightarrow 2\,H_2O + 4\,CO_2$

With oxygen supply limited $2\,C_2H_2 + 4\,O_2 \longrightarrow 2\,H_2O + 3\,CO_2 + C$

With oxygen still more limited $2\,C_2H_2 + 3\,O_2 \longrightarrow 2\,H_2O + 2\,CO_2 + 2\,C$

The carbon deposit that sometimes appears on beakers in the laboratory and on kettles in the kitchen when one burns the hydrocarbons of illuminating gas, indicates that the oxygen provided through the burner is inadequate.

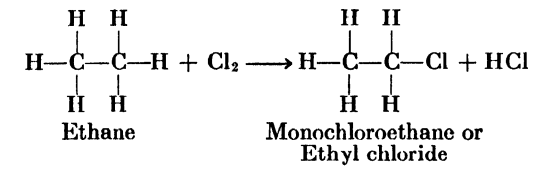
Although in reactions of hydrocarbons and oxygen the *energy product* usually appears as heat and light, it should be kept in mind

that gaseous hydrocarbons, also the more volatile liquids, in reaction with oxygen are able, under appropriate conditions (p. 81), to produce the kinetic energy of explosive mixtures. The explosive reactions which take place in the cylinders of the automobile engine and serve to propel the car should be recalled in this connection, also the necessity for safeguarding against inadvertently establishing the conditions for explosive reactions in the oven of a gas stove, or in the operating room where ethylene or cyclopropane anesthesia is in use. (See pp. 80 to 82.)

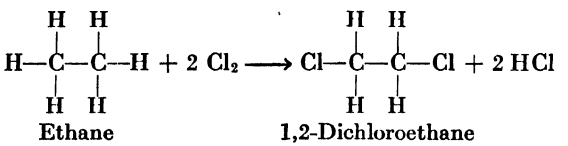
With chlorine and bromine. To the chemist, the tendency of hydrocarbons to react with chlorine and bromine is of great importance. The halogen derivatives thus obtained provide parent substances from which many other organic compounds can be made.

Saturated hydrocarbons react with chlorine and bromine *through substitution reactions.* The halogen element displaces part or all of the hydrogen from the hydrocarbon, thus forming halogen derivatives of the hydrocarbon and hydrochloric or hydrobromic acid. A general statement of such reactions with chlorine and equations for typical reactions are given below. Reactions with bromine follow the same pattern.

Alkane hydrocarbon + Chlorine ⟶ Chloroalkane + Hydrochloric acid



Ethane — Monochloroethane or Ethyl chloride

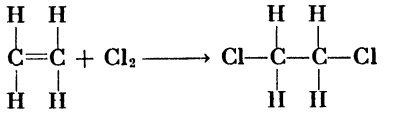


Ethane — 1,2-Dichloroethane

But, *unsaturated hydrocarbons react readily in direct combination* with chlorine and bromine. With hydrocarbons of the alkene series, the products of such reactions are known to be chloro and bromo derivatives of alkane or saturated hydrocarbons. This means, theoretically, that double bonds between pairs of carbon atoms in the molecules affected give way to single bonds upon combining with

the chlorine or bromine. Thus:

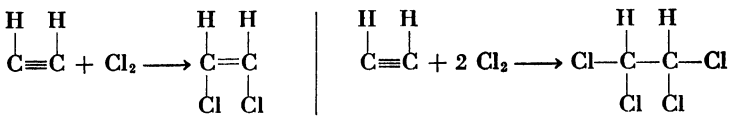
Alkene hydrocarbon + Chlorine ⟶ Chloroalkane



Ethylene or Ethene — 1,2-Dichloroethane

When hydrocarbons of the alkyne series engage in such reactions the products are halogen derivatives of the corresponding alkene or of the alkane hydrocarbons, depending in part upon the proportion of chlorine or bromine engaging in the reaction. From a theoretical angle, then, this would mean that triple bonds between carbon atoms give way to double valence bonds in making alkene derivatives and to single bonds in making alkane derivatives. A general statement for reaction with chlorine and examples are as follows.

Alkyne hydrocarbon + Chlorine ⟶ Chloroalkene or Chloroalkane



Acetylene or Ethyne — 1,2-Dichloroethene | Acetylene or Ethyne — 1,1,2,2-Tetrachloroethane

Polymerization of unsaturated hydrocarbons. The unsaturated hydrocarbons can form *polymers*, that is, compounds whose molecular weights are multiples of the molecular weight of the original compound. Thus, polyethylene, a polymer of ethylene, is represented by the formula $(CH_2—CH_2)_n$. It is believed that polymerization is brought about through the direct combination of one molecule with another. The reaction takes place at the double bonds where electrons are available to form new combinations. The equations given below for the polymerization of acetylene also illustrate this type of reaction.

The polymerization of unsaturated hydrocarbons, carried out under the influence of catalysts, has yielded a variety of synthetic plastics, including polyethylene and synthetic rubber. *Polyethylene,*

made from ethylene, is a tough, flexible plastic material. It is frequently encountered as a substitute for glass in containers, also in some of the flexible tubings—for instance, in intravenous sets. Two of the polymerization reactions that occur in the process of making *neoprene*, a rubber substitute—by reactions of acetylene with hydrochloric acid—are represented below as typical of polymerization reactions in general.

$$\text{Acetylene} \xrightarrow{\text{copper salt}} \text{Vinyl acetylene}$$

$$2\ HC{\equiv}CH \xrightarrow{\text{polymerizes}} H_2C{=}\underset{\displaystyle H}{\underset{|}{C}}{-}C{\equiv}CH$$

$$\text{Vinyl acetylene} + \text{Hydrogen chloride} \longrightarrow \text{Chloroprene}$$

$$H_2C{=}\underset{\displaystyle H}{\underset{|}{C}}{-}C{\equiv}CH + HCl \longrightarrow H_2C{=}\underset{\displaystyle H}{\underset{|}{C}}{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH_2$$

$$\text{Chloroprene} \xrightarrow{\text{polymerizes}} \text{Neoprene (a rubber substitute)}$$

Rubber. The major component of natural rubber is a hydrocarbon called caoutchouc, formula $(C_5H_8)_n$, which would seem to be a polymer of another hydrocarbon called isoprene, formula C_5H_8. Isoprene has been made in the laboratory and polymerized to make synthetic rubber having 800 times the molecular weight of isoprene.

Isoprene	*Caoutchouc*
C_5H_8 or $H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}\underset{\displaystyle H}{\underset{|}{C}}{=}CH_2$	$(C_5H_8)_n$

Chemists have long known of the possibility of producing substitutes for natural rubber for many of the uses made of this material; but, the cost of production seemed too great to do much about it. However, the inaccessibility of natural rubber during World War II greatly stimulated research in this field, and various materials have been produced with properties that are even better adapted to some of the uses made of rubber than is the natural product itself.

Natural rubber varies greatly as to its properties, often in unpredictable ways, owing to many factors that affect the growth of the trees from which it is obtained. But as the result of laboratory researches synthetic substitutes for rubber can now be designed for specific uses with uniform properties adapted to these uses.

HALOGEN DERIVATIVES OF HYDROCARBONS

Important derivatives. A few halogen derivatives of hydrocarbons are met with more or less commonly. *Methyl chloride* derived

from methane, and *ethyl chloride* derived from ethane, are both used as local anesthetics. The reason for this use lies in the fact that they are very volatile; consequently, when sprayed on the skin, in changing rapidly from liquid to vapor, they absorb heat very rapidly from the areas treated, thus chilling and producing numbness in the region.

Chloroform, or trichloromethane, is a sweet-smelling liquid with anesthetic properties. Although it is now seldom used for this purpose, having been replaced by newer and safer anesthetics, chloroform will always be of interest as one of the first compounds used to produce general anesthesia. One of its advantages lies in the fact that it is not flammable; however, it does react with oxygen slowly in the presence of light, and the poisonous gas phosgene is one of the products.

$$\begin{array}{cccccccc} \text{Chloroform} & + & \text{Oxygen} & \longrightarrow & \text{Phosgene} & + & \text{Hydrochloric acid} \\ 2\ CHCl_3 & + & O_2 & \longrightarrow & 2\ COCl_2 & + & 2\ HCl \end{array}$$

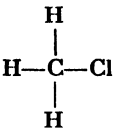
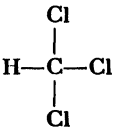
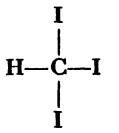
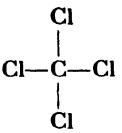
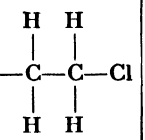
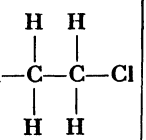
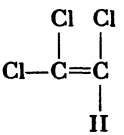
Because of this undesirable reaction, chloroform is stored in brown bottles in dark, cool places.

Iodoform, or triiodomethane, is a yellow solid with a penetrating odor. It has been used as an antiseptic in dressing wounds. The active agent is probably not iodoform itself but iodine which is made gradually upon contact of iodoform with protein.

Carbon tetrachloride is an excellent solvent for fats and resins. It is used as a dry-cleaning agent both commercially and in the household, and for this purpose has an advantage over hydrocarbon mixtures because it does not burn. It is also the fluid contained in certain types of fire extinguishers. This substance cannot be used with safety in an unventilated room because of its physiological effect. It has an anesthetic action, and exposure to carbon tetrachloride vapor produces severe headaches and sometimes more serious toxic effects. Medicinally, it is used to some extent in the treatment of hookworm.

Trichloroethylene or 1,1,2-trichloroethene is a derivative of the unsaturated hydrocarbon ethylene. It is an anesthetic which has proved to be especially effective for the relief of the severe pain of trifacial neuralgia.

Physiological effects. Various chlorinated hydrocarbons are used in industry as solvents for fats and rubber. These include methyl chloride, dichloromethane, carbon tetrachloride, and tetrachloroethane. Prolonged exposure to these agents constitutes a serious problem in industry because of the hazard to the health of the worker

EMPIRICAL FORMULA	STRUCTURAL FORMULA	NAME SPECIFYING HYDROCARBON FROM WHICH DERIVED	NAME STRESSING THE TWO RADICALS	COMMON NAME
Methane derivatives				
CH_3Cl		Monochloro*methane*	Methyl chloride	
$CHCl_3$		Trichloro*methane*		Chloroform
CHI_3		Triiodo*methane*		Iodoform
CCl_4		Tetrachloro*methane*		Carbon tetra-chloride
Ethane derivatives				
C_2H_5Cl		Monochloro*ethane*	Ethyl chloride	
$C_2H_4Cl_2$		1,2-Dichloro*ethane*		
Ethene derivative				
C_2HCl_3		1,1,2-Trichloro*ethene*		

owing to the physiological effects of such compounds.[3] When inhaled, these derivatives produce anesthetic effects similar to those of their parent hydrocarbons. The introduction of chlorine (or bromine) into the hydrocarbon molecule increases the hypnotic and narcotic effect, but at the same time a more toxic compound is produced. The toxic effect is most evident in damage to liver and kidneys.

More concerning naming customs. One-valent radicals from the alkane hydrocarbons are designated by the stem name of the hydrocarbon with the ending *yl* (methyl —CH_3, ethyl —C_2H_5, etc.). They are often referred to, inclusively, as *alkyl* radicals. These radical names are commonly used for halogen derivatives, for example, methyl bromide and ethyl chloride.

Another method of naming, which is applicable to halogen derivatives of hydrocarbons, is the I.U.C. (International Union of Chemistry) system whereby the parent hydrocarbon is mentioned by name, the carbon atoms are numbered consecutively, and the number and positions of the substituents are included in the name. This method is exemplified in the names of compounds included in the accompanying table (p. 288).

QUESTIONS

1. What is a hydrocarbon? What is the chief natural source of hydrocarbons? Name at least five compounds that are hydrocarbons. Name at least five hydrocarbon mixtures of common commercial importance.
2. What is the essential difference in chemical behavior between saturated and unsaturated hydrocarbons? How is this difference explained in terms of molecule structure? How is it represented in the formula?
3. Name three solvents that would be effective in removing a petroleum jelly stain from linen? What is the basis for your selection?
4. What is the chief component of rubber? Account for the softening which occurs on frequent lubrication of rubber with mineral oil or petroleum jelly.
5. What substances are commonly used for removal of adhesive from the skin? How do they function? What safeguards should be observed, habitually in their use? Reasons?
6. What three hazards accompany the use of gasoline or other volatile hydrocarbon mixtures as cleaning agents in closed rooms? When using such cleaning agents, what precautions should be observed to decrease these hazards?
7. Illuminating gas contains hydrocarbon components such as methane, ethylene, and acetylene.
   a. Assemble word and formula equations for the matter and energy transformations which take place when these hydrocarbons burn with adequate oxygen supply.
   b. What condition accounts for their occasional burning with a smoky flame? How would you proceed to remedy this condition? Assemble equations (as in *a*) for the reactions involved under this condition.

[3] Hughes, James P.: "Hazardous Exposure to Some So-called Safe Solvents," *J.A.M.A.*, 154:234–37, 1954.

c. If same quantities of the same hydrocarbons are burned under conditions specified in *a* and *b*, which provides the greater heat product? Give reason.

8. What is a polymer? How does the chemist account for the building up of polymers? What change in physical state accompanies this process? Name two polymers derived from hydrocarbons; describe each and cite its common uses.

9. What is meant by a halogen derivative of a hydrocarbon? Name several.

10. Why is a carbon tetrachloride fire extinguisher preferred for use in automobiles and garages to the type which provides carbon dioxide and water?

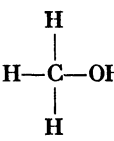
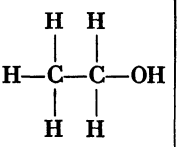
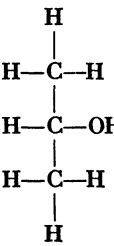
11. What hazard is associated with the use of carbon tetrachloride as a cleaning agent? What precautions should be observed when it is so used in the home? Explain.

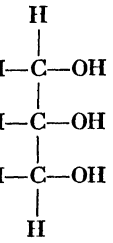
12. Assemble structural and semistructural formulas for the compounds ethylene, formula C_2H_4, and 1,1,2-trichloroethene, formula C_2HCl_3. What common physiological effect is characteristic of these related compounds? In what respect would they differ in physiological effects?

CHAPTER 22

ALCOHOLS

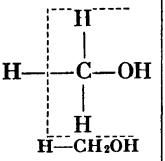
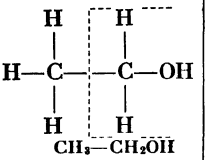
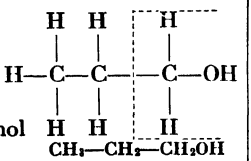
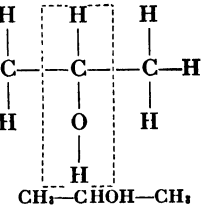
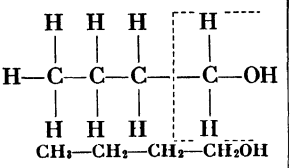
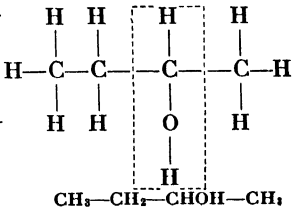
What is an alcohol? People commonly associate the word *alcohol* with the two substances methyl or wood alcohol, and ethyl or grain alcohol. Actually, there are many alcohols. They can be regarded as compounds in which one or more hydroxyl radicals have been substituted for part of the hydrogen in hydrocarbons. Examples of a few representative alcohols, together with various names and formulas, are presented in the accompanying table.

COMMON NAME	CHEMIST'S NAMES	FORMULA FOR MOLECULAR WEIGHT	STRUCTURAL FORMULA FOR MOLECULE	SEMI-STRUCTURAL FORMULA
Wood alcohol	Methyl hydroxide Methyl alcohol Methanol	CH_3OH		$H—CH_2OH$
Grain alcohol	Ethyl hydroxide Ethyl alcohol Ethanol	C_2H_5OH		$CH_3—CH_2OH$
	Isopropyl hydroxide Isopropyl alcohol Isopropanol 2-Propanol	C_3H_7OH		$CH_3—CHOH$ $\quad\quad\quad

COMMON NAME	CHEMIST'S NAMES	FORMULA FOR MOLECULAR WEIGHT	STRUCTURAL FORMULA FOR MOLECULE	SEMI-STRUCTURAL FORMULA
Glycerin	Glyceryl hydroxide Glyceryl alcohol Glycerol	$C_3H_5(OH)_3$		CH_2OH $\vert$ $CHOH$ $\vert$ CH_2OH

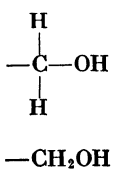
A study of structural formulas for alcohols shows that only 1 hydroxyl group is represented as attached to any 1 carbon atom; if more than 1 hydroxyl is present in the molecule, each is attached to a different carbon atom. This represents the chemist's experience with organic compounds, and his belief that 2 hydroxyl groups substituted on the same carbon atom are rarely found in a stable compound.

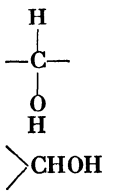
Primary and secondary alcohols. All alcohols exhibit certain common chemical behaviors, but, because of characteristic differences evidenced in their reactions with oxidizing agents, alcohols fall into three classes: *primary*, *secondary*, and *tertiary alcohols*. We shall confine our study to the first two classes and, for the present, consider only the way in which molecules of these alcohols differ in structure. Reference to the formulas in the accompanying table will show that in the molecule of a *primary alcohol* the hydroxyl group is substituted on an end carbon atom in the hydrocarbon chain. Such alcohols are therefore distinguished by a characteristic atom group ($-CH_2OH$) with 1 valence bond of the carbon atom reaching out to attach to the next carbon atom in the hydrocarbon chain. In a *secondary alcohol* the hydroxyl group is believed to be substituted on a carbon atom other than an end one. As a result, the secondary-alcohol atom group likewise has its own distinctive composition ($>CHOH$) with 2 of its valence bonds reaching out to be satisfied by 1 of the bonds on each of 2 adjacent carbon atoms in the hydrocarbon chain. The contrasting compositions of these two alcohol

PRIMARY ALCOHOLS	SECONDARY ALCOHOLS
Methyl alcohol Methanol 	None on methane (why?)
Ethyl alcohol Ethanol 	None on ethane (why?)
Primary propyl alcohol Primary propanol 	Secondary propyl alcohol Secondary propanol 
Primary butyl alcohol Primary butanol 	Secondary butyl alcohol Secondary butanol 

groups, as represented in their respective structural and semistructural formulas, are as follows.

Primary-alcohol atom group ***Secondary-alcohol atom group***





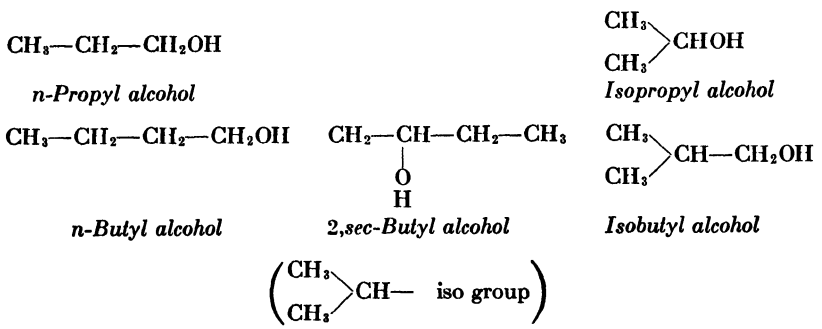
Familiarity with these characteristic structures provides a simple and conspicuous means for recognizing whether a compound of given

structural or semistructural formula contains a primary- or secondary-alcohol constituent, or both.

Wherever the primary-alcohol group is present, regardless of the composition of the rest of the molecule, the substance can be expected to behave at that point as a primary alcohol. Similarly, the presence of a secondary-alcohol group indicates that behavior characteristic of secondary alcohols can be anticipated wherever it occurs in the molecule. (See table, pp. 291 to 292.) Both methyl and ethyl alcohols can be expected to react as primary alcohols; isopropyl alcohol will behave as do secondary alcohols; but glycerol can be expected to exhibit the behavior of both a primary and a secondary alcohol. Presently we shall consider some of these chemical behaviors.

Nomenclature. The names methyl alcohol and ethyl alcohol are already familiar. They illustrate one method for naming alcohols, namely, to designate the particular alcohol by use of the name of the hydrocarbon radical to which the hydroxyl group is attached. A newer system of nomenclature uses the stem of the name of the parent hydrocarbon with the ending *ol* to indicate that the compound is an alcohol. Thus, methyl alcohol is also called methan*ol* and ethyl alcohol is ethan*ol*.

Beginning with propyl alcohol, *isomeric alcohols* are encountered. The primary alcohol on the straight carbon chain is designated as the *normal* alcohol. For a secondary alcohol the prefix *secondary* (*sec-*) is used and the position of the hydroxyl group on the carbon chain is indicated by number, as in 2,sec-butyl alcohol.



The prefix *iso* refers to the presence, at the end of the chain, of an atom grouping as represented in the above structural formula. In the foregoing formulas for the alcohols involved, it will be noted that, whereas isopropyl alcohol is a secondary alcohol, isobutyl alcohol is a primary alcohol.

Physical properties. There are no gaseous alcohols. Methyl, ethyl, and propyl alcohol are volatile liquids. With increasing molecular weight an oily character becomes evident, and alcohols of

high molecular weights are solids. Volatile alcohols have odors. Alcohols that have more than 1 hydroxyl group are more or less sweet to taste, as may be noted in glycerol (p. 299) and the sugars (pp. 373–75). Liquid alcohols are solvents for many substances, some of which do not dissolve in water. This property is used to advantage in many industrial processes, in the pharmacy, and in the household.

React with acids. Alcohols react with acids to make water and an organic compound known as an *ester*. The following are examples of such reactions.

$$\text{Alcohol} + \text{Acid} \rightarrow \text{Water} + \text{Ester}$$

$$\text{Ethyl alcohol} + \text{Sulfuric acid} \rightarrow \text{Water} + \text{Ethyl sulfate}$$

$$2\,C_2H_5OH + H_2SO_4 \xrightarrow{\text{(dilute)}} 2\,H_2O + (C_2H_5)_2SO_4$$

$$\text{Methyl alcohol} + \text{Acetic acid} \rightarrow \text{Water} + \text{Methyl acetate}$$

$$CH_3OH + HC_2H_3O_2 \longrightarrow H_2O + CH_3C_2H_3O_2$$

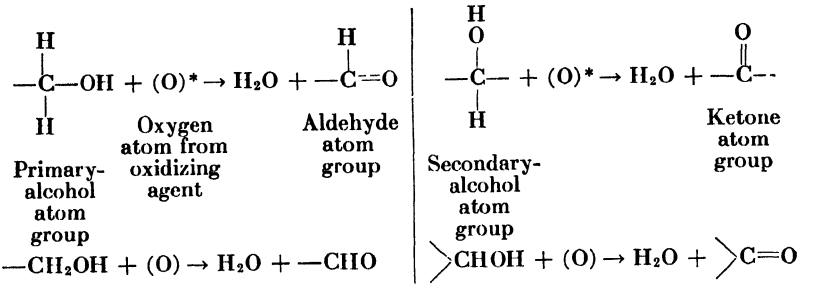
Because alcohols are nonelectrolytes, these reactions with acids are slow; hence, catalysts are frequently required to increase the speed of the reactions. Moreover, the ester reacts with water to remake the alcohol and acid, thus bringing the reaction to equilibrium unless the products are separated from each other. This is sometimes accomplished by introducing a dehydrating agent, such as concentrated sulfuric acid, to combine with and remove the water. If the ester is volatile this separation may also be accomplished by distillation.

Alcohols with oxidizing agents. Primary and secondary alcohols respond somewhat differently to attack by oxidizing agents. A *primary alcohol reacts with an oxidizing agent to make the corresponding aldehyde* and water. If conditions are favorable, the aldehyde, in turn, may be oxidized to make an acid (p. 304). *A secondary alcohol reacts with an oxidizing agent to make a ketone.*

$$\text{Primary alcohol} + \text{Oxidizing agent} \longrightarrow \text{Water} + \text{Aldehyde}$$

$$\text{Secondary alcohol} + \text{Oxidizing agent} \longrightarrow \text{Water} + \text{Ketone}$$

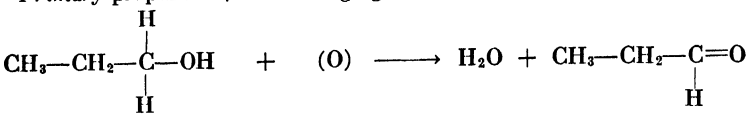
It is believed that, during these reactions, the alcohol group gives up 2 atoms of hydrogen to combine with an oxygen atom from the oxidizing agent and to form a molecule of water. The primary alcohol group is thereby replaced by an aldehyde group and the secondary alcohol group by a ketone group. These reactions may be represented as follows.



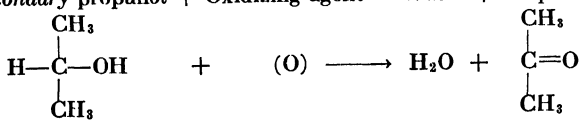
* This expression (O) represents only the oxygen atom provided by the compound that serves as the oxidizing agent, since frequently it is not necessary to complicate the issue by stressing what happens to the rest of the oxidizing agent. But this expression (O) should not be confused with the formula O_2 which is always shorthand for the simple substance oxygen.

Hence in specific application:

Primary propan*ol* + Oxidizing agent → Water + Propan*al*



Secondary propan*ol* + Oxidizing agent → Water + Propan*one*



SOME IMPORTANT ALCOHOLS

Methanol or methyl alcohol. Methanol, or methyl alcohol, is also commonly called wood alcohol because it has long been made by the "destructive distillation" of wood.[1] Today most of the methanol for commercial use is made from carbon monoxide and hydrogen in the presence of a favoring catalyst, such as zinc and chromium oxides.

$$CO + 2\,H_2 \xrightarrow{\text{catalyst}} CH_3OH$$

[1] Destructive distillation is the process whereby materials of plant or animal origin—wood, coal, fuel oils, bones, skin, etc.—are shut up in closed containers out of contact with oxygen and heated to very high temperatures. Numerous substances are made during each of these processes, but by what reactions is not known.

Uses. Methanol has numerous uses. It is used on a small scale as fuel for alcohol burners, and this is a reminder that it must be stored and used with recognition that it is a flammable substance.

$$\begin{array}{lcl} \text{Methanol} + \text{Oxygen} & \longrightarrow & \text{Carbon dioxide} + \text{Water} \\ 2\ CH_3OH + 3\ O_2 & \longrightarrow & 2\ CO_2 + 4\ H_2O \end{array}$$

It is used industrially as a solvent for lacquers, shellacs, and varnishes; also in the synthesis of certain dyes, drugs, and disinfectants. One of the greatest demands for methyl alcohol is for oxidation to make formaldehyde. Because of its low freezing point (−98.7°C) it is found in antifreeze mixtures used in automobiles.

Physiological effects. In common with other volatile alcohols, methanol is a central-nervous-system depressant. It appears to make a special attack upon the optic nerve and, when taken internally, may cause permanent blindness. The same result may follow from continuous exposure to the vapor, which upon absorption is believed to be oxidized in body cells to make formaldehyde and formic acid (see p. 305); this accounts for the acidosis which accompanies poisoning by methanol. Methanol is used extensively in industry, and the consequent exposure of workmen to this substance constitutes one of the so-called industrial hazards.

Ethanol or ethyl alcohol. These are the two names that are preferred by chemists for this alcohol; but by many people it is called grain alcohol. It is the alcohol in most common use and the one present in tinctures and alcoholic beverages.

Ethyl alcohol has been known since ancient times and it is made today, as for centuries in the past, by the fermentation of monosaccharides, chiefly glucose, obtained from the hydrolysis either of starches or disaccharides. If starch from barley or any other grain is the initial carbohydrate employed, the series of reactions involved is as represented below.

$$\begin{array}{lcl} \text{Starch} + \text{Water} & \xrightarrow{\text{diastase}} & \text{Maltose} \\ (C_6H_{10}O_5 \cdot C_6H_{10}O_5)_n + n\ H_2O & \longrightarrow & n\ C_{12}H_{22}O_{11} \end{array}$$

$$\begin{array}{lcl} \text{Maltose} + \text{Water} & \xrightarrow{\text{maltase}} & \text{Glucose} \\ C_{12}H_{22}O_{11} + H_2O & \longrightarrow & 2\ C_6H_{12}O_6 \end{array}$$

$$\begin{array}{lcl} \text{Glucose} & \xrightarrow{\text{zymase}} & \text{Carbon dioxide}^2 + \text{Ethyl alcohol} \\ C_6H_{12}O_6 & \longrightarrow & 2\ CO_2 + 2\ C_2H_5OH \end{array}$$

[2] Carbon dioxide made after this manner is collected under pressure in metal tanks to be used in various ways, including therapeutic uses for inhalations, and the making of solid carbon dioxide, commonly called "dry ice."

The alcohol obtained by fermentation must be separated from water and various other components of the fermentation mixture. This is accomplished by repeated distillations, taking advantage of the fact that ethyl alcohol has a lower boiling point (78.5° C) than water, and hence is more volatile. However, complete separation of alcohol from water cannot be effected by distillation; the resulting solution is a mixture of 95 per cent alcohol and 5 per cent water. This is the usual concentration for commercial use. If "absolute alcohol" (nearly 100 per cent) is required, a more complete removal of water can be brought about by treating the solution with a dehydrating agent such as calcium oxide.

Uses. Ethyl alcohol has a much more extensive use as a *fuel*, employed in alcohol burners, than has methyl alcohol, and it is a better fuel since, gram for gram, more heat product is made from its burning with oxygen than from the burning of methyl alcohol. This is due to the fact that more oxygen, hence more transformable chemical energy, is brought into the reaction with grain alcohol than with the same quantity of wood alcohol.

1 gm 1.5 gm Methanol + Oxygen → Carbon dioxide + Water	5.33 Cal
1 gm 2.08 gm Ethanol + Oxygen → Carbon dioxide + Water	7.11 Cal

Due to the volatility of grain alcohol, and this applies also to wood alcohol, the kindling temperature of alcohol and oxygen mixture is low and constitutes a fire hazard.

In *hospital* practice the commonest uses for ethyl alcohol are for alcohol rubs and as an antiseptic. In the *laboratory* it is used as a preservative for biological specimens and as a solvent for materials that are not soluble in water. Its function both as an antiseptic and as a preservative depends upon the fact that this alcohol denatures the proteins of bacterial cells.

Commercially, ethanol has numerous uses. It is the solvent which is employed in various medicinal preparations called tinctures, elixirs, essences, and spirits as well as in flavor and perfume preparations. Like methanol, it is a solvent for varnishes and shellacs and finds extensive commercial uses in this capacity. Ethyl alcohol is essential to the manufacture of a great many drugs and antiseptics, including ether, chloroform, and tribromoethanol (in Avertin). Except for certain specific purposes, ethyl alcohol for commercial use is required by

law to be denatured; that is, it must have a small quantity of some other substance mixed with it to render it unfit for beverage purposes.

Physiological effect. Ethyl alcohol functions as a depressant of the central nervous system to lessen self-control, to produce lack of muscular coordination, and to dull nerve functioning. Following absorption it is oxidized in the cells, and the end products are water and carbon dioxide. It is noteworthy that the halogen derivative of ethyl alcohol, tribromoethanol (CBr_3-CH_2OH), is likewise a central-nervous-system depressant. It is used as an anesthetic which is administered rectally.

Ethyl ether, an important derivative. Ethyl ether (also known as diethyl ether, sulfuric ether, or simply as ether) is an important ethanol derivative. It is made by mixing concentrated sulfuric acid with ethyl alcohol, then slowly but continuously adding more alcohol under carefully controlled temperature conditions (130°–140° C). The reaction, which takes place in stages, is essentially a dehydration of ethyl alcohol, as represented in the following equation.

Ethyl alcohol ⟶ Diethyl ether + Water

$$C_2H_5O\overset{\cdot\cdot}{\underset{\cdot\cdot}{H}} + \overset{\cdot\cdot}{\underset{\cdot\cdot}{HO}}C_2H_5 \xrightarrow[\text{conc. sulfuric acid}]{} C_2H_5{-}O{-}C_2H_5 + H_2O$$

By using other alcohols, other ethers can be prepared by the same method, but diethyl ether is the most important of the ethers. It is best known because of its use as a general anesthetic. This use marks it, also, as a depressant of the central nervous system. It is an excellent solvent for many organic substances and is used for this purpose in the laboratory and in industry. It reacts readily with oxygen and, because of its great volatility, at relatively low kindling temperatures. Consequently, safeguards against fire should be observed whenever ethyl ether is in use.

Isopropyl alcohol or isopropanol. This alcohol is sometimes substituted for ethyl alcohol in rubbing lotions and astringent solutions. It is made by the reduction of acetone (see p. 312) and is relatively inexpensive. It is claimed to compare favorably with ethyl alcohol as a disinfectant and can be used in this connection for disinfecting thermometers or cleansing the skin. It is more toxic than ethyl alcohol but is less palatable.

Glycerol. The preferred name for this alcohol is glycer*ol*, although it is also called by its common name, glycer*in*. It is a syrupy liquid with a sweet taste. It has a great attraction for water and can func-

tion either as a dehydrating agent or to attract water. It is obtained commercially as a by-product of the soap industry from the reaction of sodium hydroxide with fat. The equation for this reaction, with glyceryl stearate as the specific fat, is as follows:

Glyceryl stearate + Sodium hydroxide → Glycerol + Sodium stearate

$$C_3H_5(C_{17}H_{35}CO_2)_3 + 3\ NaOH \longrightarrow C_3H_5(OH)_3 + 3\ NaC_{17}H_{35}CO_2$$

Uses. Glycerol is used as a sweetening agent, notably in pharmaceutical preparations. It is an ingredient of lotions used for chapped hands, and for this purpose it is always used in water solution because undiluted glycerol would dehydrate the tissue. Glycerol is used, in reaction with nitric acid, to make the explosive compound glyceryl nitrate, more commonly called nitroglycerin.[3]

Glycerol + Nitric acid → Water + Glyceryl nitrate (Nitroglycerin)

$$C_3H_5(OH)_3 + 3\ HNO_3 \rightarrow 3\ H_2O + C_3H_5(NO_3)_3$$

Nitroglycerin is used medicinally to dilate the blood vessels and thus lessens blood pressure, notably in angina pectoris.

Physiological occurrence. Glycerol is a product of the digestion (hydrolysis) of fats and, on absorption from the intestine, plays an important part in glucose and fat metabolism in the cells.

Glyceryl stearate (a typical fat) + Water $\xrightarrow{\text{steapsin}^4}$ Glycerol + Stearic acid

$$C_3H_5(C_{17}H_{35}CO_2)_3 + 3\ HOH \longrightarrow C_3H_5(OH)_3 + 3\ HC_{17}H_{35}CO_2$$

QUESTIONS

1. What is an alcohol? What similarities and what points of difference are there between alcohols and inorganic bases?
2. What is the functioning atom group that is characteristic of primary alcohols? of secondary alcohols? Represent each of these characteristic groups both structurally and semistructurally, indicating their valences.
3. For each of the well-known alcohols—methanol, ethanol, and glycerol:
   a. Give both structural and semistructural formulas
   b. Give three other names for the compound
   c. Tell how it is obtained commercially
4. Assemble the structural formula for two different propyl alcohols, then give distinguishing names for each of these alcohols.

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[3] From a chemical viewpoint, nitroglycerin is an incorrect name for this compound. It contains the nitr*ate* radical (—NO_3), not the nitro radical (—NO_2).

[4] Pancreatic lipase.

5. State reaction expectation for each of the following contacts; illustrate with word and formula equations using glycerol as the alcohol:

a. An alcohol with an acid

b. A primary alcohol with an oxidizing agent

c. A secondary alcohol with an oxidizing agent

6. In what industries is methyl alcohol employed? What hazards are associated with its industrial use?

7. How is ethyl alcohol made from sucrose (provided, for instance, in molasses or in fruit juices)? Assemble equations for the reactions involved in the process, indicating the functioning catalysts.

8. List the various purposes for which ethyl alcohol is used in home or hospital practice. In each instance state the property of this substance which makes it suitable for the use mentioned.

9. Why is it inadvisable to stand a bottle of alcohol or a bottle containing an alcoholic solution, such as a perfume, on a varnished or lacquered surface? Should you accidentally spill the contents of such a bottle on a varnished surface, what would be the best procedure to minimize the damage?

10. Assemble word and formula equations for (a) the burning of isopropyl alcohol, (b) the reaction of isopropyl alcohol with an oxidizing agent.

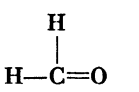
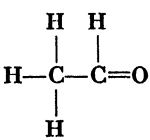
CHAPTER 23

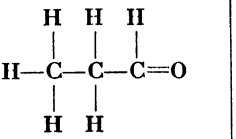
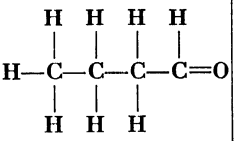
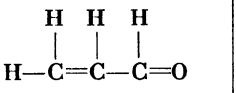
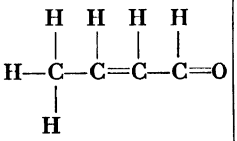
ALDEHYDES AND KETONES

Aldehydes and ketones are peculiarly organic compounds in that they have no counterparts among the types of inorganic compounds. They are considered together because of their significant similarities and differences in chemical behavior. Among the many aldehydes and ketones there are a few that have special interest because of either common industrial uses or physiological importance.

ALDEHYDES

Representative aldehydes. Several representative aldehydes are listed in the table below, together with their names and formulas.

OLDER NAMES	NAME SUGGESTING RELATED HYDROCARBON	STRUCTURAL FORMULA FOR MOLECULE	SEMISTRUCTURAL FORMULA FOR MOLECULE
Formaldehyde Formic aldehyde	Methan*al*		H—CHO
Acetaldehyde Acetic aldehyde	Ethan*al*		CH_3—CHO

OLDER NAMES	NAME SUGGESTING RELATED HYDROCARBON	STRUCTURAL FORMULA FOR MOLECULE	SEMISTRUCTURAL FORMULA FOR MOLECULE
Propionic aldehyde	Propan*al*		C_2H_5—CHO
Butyric aldehyde	Butan*al*		C_3H_7—CHO
Acrylic aldehyde	2-Propen*al*		CH_2=CH—CHO
Croton aldehyde	2-Buten*al*		CH_3—CH=CH—CHO

The aldehyde atom group. The typical atom group which identifies the compound as an aldehyde is represented below. It has a *valence of 1*, hence can appear only on the *end* of the carbon chain.

***Aldehyde atom group,** structural and semistructural formulas*



Nomenclature. Two methods for naming aldehydes are in use. The older method suggests the relation of the aldehydes to the corresponding acids; thus *form*aldehyde is related to formic acid, whereas *acet*aldehyde is related to acetic acid. The system of naming adopted by the Committee of the International Union of Chemistry indicates the relation of the aldehyde to the corresponding hydrocarbon from which it is derived. Hence

Formaldehyde is methanal (related to methane)
Acetaldehyde is ethanal (related to ethane)
Butyric aldehyde is butanal (related to butane)

The ending *al*, then, suggests an *aldehyde* just as *ol* suggests an *alcohol*. For the first two aldehydes we shall use the older and more familiar names.

Oxidation-reduction reactions. *Oxidation.* An aldehyde has a decided tendency to combine with oxygen taken from another compound to make the corresponding acid.

Aldehyde + Oxygen (from oxidizing agent) ⟶ Acid (corresponding to aldehyde)

Acetaldehyde (Ethanal) + Oxidizing agent ⟶ Acetic acid (Ethanoic acid)

$$CH_3{-}C(=O){-}H + (O) \longrightarrow CH_3{-}C(=O){-}OH$$

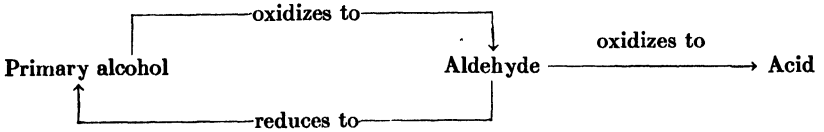
Reduction. An aldehyde can be reduced by the addition of hydrogen, taken from another substance, to make the corresponding primary alcohol. Therefore, the aldehyde atom group, by the addition of hydrogen atoms, becomes reduced to the primary-alcohol atom group.

Aldehyde + Hydrogen (from reducing agent) ⟶ Primary alcohol (corresponding to aldehyde)

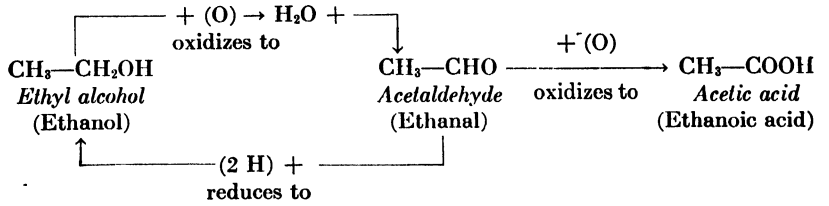
Acetaldehyde (Ethanal) + Hydrogen (from reducing agent) ⟶ Ethyl alcohol (Ethanol)

$$CH_3{-}C(H)(=O) + (2\,H) \longrightarrow CH_3{-}C(H)(H){-}OH$$

A significant observation. Although it is well to have the two foregoing aldehyde reactions stand out as individuals, it is of equal importance to fit them into the general scheme of reaction sequences among organic compounds. When this is done it appears that *an aldehyde is a transitional compound* between the corresponding primary alcohol and acid in an oxidation series of reactions. Thus, briefly summarized:



For example, when acetaldehyde is fitted into this reaction sequence it follows that:



Similarly, formaldehyde or methanal is the transitional compound between methyl alcohol and formic acid, and propanal is transitional in the reaction series from propyl alcohol to propionic acid.

These fundamental reaction sequences do occur in test tubes and beakers, and there is evidence of similar oxidation-reduction sequences in the vitally important reactions within living cells.

Aldehydes as reducing agents. Aldehydes are good reducing agents. They react with even very mild oxidizing agents, such as cupric hydroxide and silver hydroxide, to reduce these compounds. So marked is this property that it has come to be used as a means for testing for the probable presence of an aldehyde group in a compound. Ketones, by comparison, require stronger oxidizing agents.

Cupric hydroxide as an oxidizing agent. One of the oxidizing agents frequently employed in laboratory tests for the possible presence of an aldehyde is *cupric hydroxide* [$Cu(OH)_2$]. The reason for this selection is that if reduction occurs it is rendered conspicuous to the eye by the making of vividly *red cuprous oxide* (Cu_2O). It is cupric hydroxide that functions as the oxidizing agent in Fehling's reaction: Fehling's solution I contains cupric sulfate and solution II contains sodium hydroxide. Consequently, when these solutions are mixed, cupric hydroxide, the desired oxidizing agent, is made.

$$CuSO_4 + 2\ NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

Then if a good reducing agent, such as an *aldehyde*, is present, the cupric hydroxide is reduced to make red cuprous oxide. (See also p. 383.) With formaldehyde as the specific reducing agent, the reaction is as follows.

Cupric hydroxide + Formaldehyde → Formic acid + Cuprous oxide + Water

$$2\ Cu(OH)_2 + H—CHO \longrightarrow H—COOH + Cu_2O + 2\ H_2O$$

Silver hydroxide as an oxidizing agent. In Tollen's reagent silver hydroxide is made in a solution of ammonium hydroxide.[1] Aldehydes react with this metal hydroxide to make silver substance, water, and the corresponding acid.

$$2\ AgOH + H—CHO \longrightarrow 2\ Ag + H—COOH + H_2O$$

[1] In this solution the silver ion is held in solution as the complex silver ammonia ion, $Ag(NH_3)_2^+$.

The silver, thus made, will deposit on the wall of a very clean test tube to form a silver mirror. In fact, mirrors are silvered by a similar process.

Certain of the sugars will reduce both cupric hydroxide and silver hydroxide, indicating that there are aldehyde groups in their molecules. These include glucose, galactose, lactose, and maltose. Because of this behavior they are known as *reducing sugars.*

Polymerization. Aldehydes tend to form polymers (p. 285). It is believed that this reaction represents the combination of several, sometimes many, aldehyde molecules to form the large and heavier polymer molecule. For example:

$$\underset{n \text{ molecules of formaldehyde}}{n\ \text{H—CHO}} \xrightarrow{\text{combine to make}} \underset{\text{1 molecule of paraformaldehyde (or paraform)}}{(\text{H—CHO})_n}$$

Such compounds no longer behave like aldehydes, indicating that the aldehyde group becomes bound in forming the polymer.

Paraform, one of the polymers of formaldehyde, is a white solid which, on heating, decomposes to remake formaldehyde, thereby providing a convenient method for obtaining this gaseous substance.

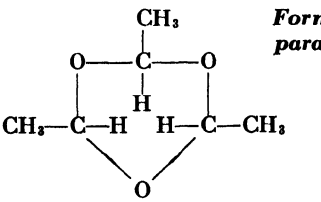
$$\underset{\textit{Paraform}}{(\text{HCHO})_n} \longrightarrow \underset{\textit{Formaldehyde}}{n\ \text{H—CHO}}$$

Paraform is used in this way to obtain formaldehyde for disinfection of certain types of instruments and other objects that are likely to be injured by dry or moist heat.

Paraldehyde is a polymer made from acetaldehyde, as suggested by the following equation.

$$\underset{\textit{Acetaldehyde}}{3\ \text{CH}_3\text{—CHO}} \rightleftarrows \underset{\textit{Paraldehyde}}{(\text{CH}_3\text{—CHO})_3}$$

Formula for paraldehyde



Paraldehyde is a liquid with an unpleasant taste and odor. It is used medicinally as an hypnotic.

Formaldehyde, or methanal. Formaldehyde is a gaseous substance with a penetrating odor. When inhaled it is very irritating to the mucous membranes of the nasal passages. It is prepared commercially by passing methanol vapor and air over hot copper (p. 295). The metal is claimed to function as a catalyst for the oxidation of the alcohol. Formaldehyde is very soluble in water; therefore, it is col-

lected in water as a convenient means for sale distribution. A 40 per cent solution of formaldehyde in water is sold under the name Formalin. Commercially, formaldehyde (or methanal) is the most important of all aldehydes. It has limited uses in hospitals and laboratories but numerous uses in industries.

In *hospital practice* formaldehyde is used as a disinfectant. For general purposes, such as soaking of clothing or cleaning of surfaces, a 2 to 4 per cent solution is used. Mixtures of Formalin and alcohol are sometimes used for disinfecting instruments. The manner of its reaction as a disinfectant is not certain, but because it is an aldehyde, hence a reducing agent, one attack may be through the reduction of compounds within the cells of microorganisms, thus interfering with their life activities. Such a reaction might be represented in a general way in the following manner.

$$\underset{\text{H—CHO}}{\text{Formaldehyde}} + \underset{\text{(Oxygen compounds)}}{\text{Bacterial compounds}} \longrightarrow \underset{\text{H—COOH}}{\text{Formic acid}} + \underset{\text{bacterial remains}}{\text{Compounds of}}$$

Or, the germicidal action may be due to the reaction of formaldehyde with the proteins within the microbial cell to produce insoluble compounds, thus accomplishing the death of the microorganism. The usefulness of this disinfectant is limited by the fact that solutions of formaldehyde are irritating to the skin, an effect that may be attributed to reaction with the proteins of the skin tissue cells. For this reason, in using formaldehyde, the skin should not be exposed to contact with it unnecessarily, nor should more concentrated solutions be used when a dilute solution would be effective.

Formaldehyde is used, sometimes, as a *urinary antiseptic*, that is, to inhibit the growth of any bacteria that may have invaded the urinary tract. It is made from the drug hexamethylenamine, or methenamine. This drug is inactive in alkaline environment but *active in acid environment.* Hence, when absorbed into the blood it remains unchanged in the alkaline blood, but when excreted in acid urine in the urinary tract it reacts with water to make the desired *formaldehyde.* Presumably it attacks bacterial compounds in the same manner here as elsewhere.

$$\underset{(CH_2)_6\text{—}N_4}{\text{Hexamethylenamine}} + \underset{6\ H_2O}{\text{Water}} \rightarrow \underset{6\ \text{H—CHO}}{\text{Formaldehyde}} + \underset{4\ NH_3}{\text{Ammonia}}$$

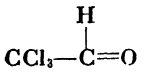
In the *laboratory*, formaldehyde is employed as a preservative for biological and pathological specimens, and as a "fixative" for mate-

rial on bacterial slides. In both of these uses, aside from the attack on bacteria, the aldehyde reacts with the proteins present to make insoluble compounds, which results in the "stiffening" of specimens and the "fixing" of material on microscopic slides.

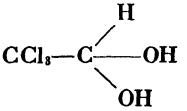
Formaldehyde has many *industrial uses*, one of the most important of which is for making plastics. For example, formaldehyde condenses with phenol (carbolic acid) and the formaldehyde-phenol combination subsequently yields a polymer sold under the name of *Bakelite*. Formaldehyde condenses with urea and also with a number of other organic compounds to make still other plastics in common use.[2] Another important industrial use is in the manufacture of certain dyes.

Chloral and chloral hydrate. Chloral, or trichloroacetaldehyde, is a derivative of acetaldehyde. It is an oily liquid which reacts with water to make a crystalline substance known as chloral hydrate.[3]

Chloral



Chloral hydrate



Both of these compounds are central-nervous-system depressants; chloral hydrate is used medicinally as a hypnotic and anticonvulsant. It is believed to be reduced in the body to form trichloroethanol, a substance closely related to tribromoethanol which is used as an anesthetic (p. 299).

KETONES

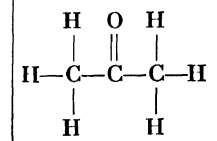
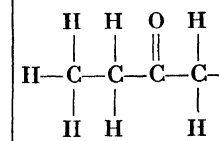
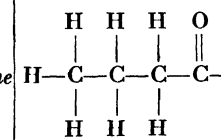
Representative ketones. Acetone or propanone is the ketone most frequently encountered. It is the first ketone derivative that is possible from hydrocarbons of the methane series; no ketone is possible on either methane or ethane. Acetone is derived from propane.

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[2] See Lowy, Alexander; Harrow, Benjamin; and Apfelbaum, Percy M., *Introduction to Organic Chemistry*, John Wiley & Sons, Inc., New York, 1951, Chapter 29, for a table of common synthetic plastics.

[3] Chloral hydrate is an unusual compound because it is exceptional to find a stable compound in which 2 hydroxyl groups are attached to the same carbon atom, but such appears to be the case with this substance. Jenkins, G. L., and Hartung, W. H.: *Chemistry of Organic Medicinal Products*, John Wiley & Sons, Inc., New York, 1949, p. 166.

Next in sequence are butanone, pentanone, etc. These three ketones are listed with their formula representations in the accompanying table.

COMMON NAME	NAME SUGGESTING RELATED HYDROCARBON	STRUCTURAL FORMULA FOR MOLECULE	SEMISTRUCTURAL FORMULA
Acetone	Propan*one*		$CH_3—CO—CH_3$
	Butan*one*		$CH_3—CH_2—CO—CH_3$
	2-Pentan*one*		$CH_3—CH_2—CH_2—CO—CH_3$

Characteristic atom group and valence. The atom group which is believed to be present within molecules of all ketones is similar to that which characterizes the aldehyde molecule. It is represented below in comparison with the aldehyde group.

Aldehyde  —CHO

Ketone  =CO

The ketone group is 2-valent, both valence bonds reaching out to be satisfied through attachment to adjoining carbon atoms in the hydrocarbon chain. This group, therefore, always involves a carbon atom other than those at the two ends of the chain.

Naming of ketones. The ending *one* is significant of a ketone. The customary method for naming these compounds is to use the stem name of the related

hydrocarbon with the ending *one*, as in propan*one*, butan*one*, and pentan*one*. When it becomes necessary to distinguish isomeric ketones, or to indicate the presence of a ketone group in the molecule of a more complex compound, the position of the carbon atom carrying the characteristic double-bonded oxygen atom ($-\overset{|}{\underset{|}{C}}=O$) is indicated by number. For example:

$$\overset{1}{CH_3}-\overset{2}{CO}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

2-pentanone

$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CO}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

3-pentanone

In reaction with oxidizing agents. Ketones, like aldehydes, are transitional compounds between alcohols and acids in an oxidation series of reactions. But there are these important differences.

1. Ketones arise from the oxidation of the corresponding secondary alcohols. (How is it with aldehydes?)

2. A ketone oxidizes to make an acid (or acids) containing less carbon than the ketone concerned. (Again, how is it with aldehydes?)

A secondary alcohol $\xrightarrow{\text{oxidizes to}}$ a ketone (corresponding) $\xrightarrow{\text{oxidizes to}}$ an acid containing less carbon

3. Oxidations of ketones do not take place as readily as do those involving aldehydes; hence, only excellent oxidizing agents, for example, potassium permanganate, can be used with appreciable results.

To account for the appearance of an acid product with less carbon content, it is claimed that when a ketone molecule is oxidized, its chain of carbon atoms is broken at the point where the ketone atom group is located instead of remaining intact as when the aldehyde molecule is oxidized. In the oxidation sequence involving acetone or propanone the following are represented happenings.

Factually

Secondary propanol $\xrightarrow{\text{oxidizes to}}$ Acetone or propanone $\xrightarrow{\text{oxidizes to}}$ Acetic acid + Carbon dioxide + Water

Theoretically

1 molecule of secondary propanol

$$H-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow{+ (O)} H_2O +$$

1 molecule of acetone or propanone

$$\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}=O \xrightarrow{+ (4\,O)}$$

1 molecule of acetic acid

$$\overset{\overset{CH_3}{|}}{\underset{\underset{COOH}{|}}{}} + CO_2 + H_2O$$

When a *ketone is reduced by the addition of hydrogen* the product is the secondary alcohol. But, although the reduction of ketones is important among organic reactions, in this study, the chief interest in the chemical behavior of ketones is with the oxidation sequence.

Acetone, or propanone. This is the ketone of outstanding industrial importance. It is also of interest because of its significance in relation to metabolic disturbances. As a derivative of propane, it should be called propanone, but the older name, acetone, has a fixed hold industrially and will probably continue in common use. Acetone is a volatile liquid with a sweet odor. It is very flammable, as might be inferred from its chemical composition and its volatility. It is made for commercial use by various methods including the oxidation of isopropyl alcohol (secondary propanol), the reaction being favored by the presence of an appropriate catalyst.

Acetone is an excellent solvent for many organic materials including fats, lacquers, and varnishes. This property accounts for the use of this ketone in the cleansing of garments, in paint removers, as a solvent for nail polishes, and in many similar ways. In its capacity as solvent, as is true also of methyl and ethyl alcohols and of formaldehyde, acetone has contributed very largely to the progress made in the manufacture of rayons, artificial leathers, plastics, and many other materials of modern usage. Because of its chemical activity acetone is used in the manufacture of many compounds, including some drugs.

Ketones of physiological importance. A number of ketones appear as intermediate compounds in the metabolism of glucose, fats, and proteins. *Pyruvic acid*, both a ketone and an acid, is an important intermediate in glucose metabolism; it also appears among the intermediates of protein metabolism. *Acetoacetic acid* is made from fatty acids and can be oxidized in muscle cells, and perhaps in other tissues, for the production of energy. *Acetone* is made from acetoacetic acid, notably when this acid is being produced in excess of immediate cell needs.

Pyruvic acid	*Acetoacetic acid* (*Diacetic acid*)	*Acetone*
CH_3	CH_3	CH_3
$\vert$	$\vert$	$\vert$
CO	CO	CO
$\vert$	$\vert$	$\vert$
$COOH$	CH_2	CH_3
	$\vert$	
	$COOH$	

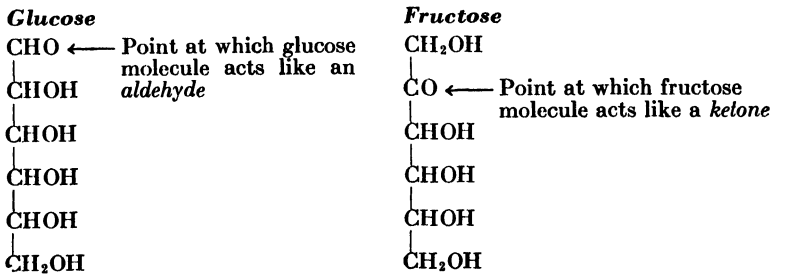
Pathologically, in acute starvation and in severe diabetes, the two ketones *aceloacetic acid* (also known as diacetic acid) and *acelone* are excreted frequently in appreciable quantities in urine, in smaller quantities in perspiration, and sometimes the sweetish odor of acetone can be detected on the breath. The appreciable excretion of these ketones is indicative of a serious metabolic disturbance involving both carbohydrate and fat metabolism. (For further discussion see pp. 474 and 507.)

SUGARS ARE ALDEHYDES OR KETONES

Notable among common sugars which are either aldehydes or ketones are the following (pp. 373 to 375).

Aldehydes	*Ketone*	*Neither*
Glucose	Fructose	Sucrose
Galactose		
Maltose		
Lactose		

Semistructural formulas for molecules of glucose and fructose which indicate the presence of their respective aldehyde or ketone atom groups are as follows.



QUESTIONS

1. Represent the composition of the aldehyde group showing the conventional structural and semistructural forms.

2. Assemble the structural formula for: (a) formaldehyde and (b) acetaldehyde, showing electron distribution. How does this help to account for the chemical activity of aldehydes?

3. Aldehydes are referred to as transitional compounds between primary alcohols and acids. Illustrate this with reference to methanal.

4. What is the principle underlying Fehling's reaction? Account for the fact that glucose responds to this test. Name at least three other compounds which will react with this reagent.

5. Account for the disinfectant action of formaldehyde, indicating two possible attacks on the microorganism. Why does formaldehyde have an irritating effect on the skin?

6. Paraform when heated yields formaldehyde gas. What is the relation of paraform to formaldehyde? In what situations is paraform used when disinfection is required?

7. The following compounds are all used as central-nervous-system depressants: ethanol, tribromoethanol, chloral hydrate, and paraldehyde. Assemble their structural formulas and point out their chemical similarities.

8. What atom group is characteristic of ketones? Assemble structural formulas for two ketones and identify this group.

9. Compare aldehydes and ketones as to their responses to (a) oxidizing agents, (b) reducing agents. How can they be distinguished from one another by laboratory test?

10. Acetone is sometimes used to remove plastic nail polish. How does it function? Why do nails subjected to this treatment, repeatedly, become dry and brittle?

CHAPTER 24

ORGANIC ACIDS. ORGANIC SALTS. ESTERS

ORGANIC ACIDS

The study of organic acids should be at least partially familiar. The acid components of foods are organic acids; conspicuous among these are tartaric acid in grapes and citric acid in lemons, acetic acid —a component of vinegar, and lactic acid of sour milk. From a chemical viewpoint organic acids are, indeed, acids; consequently certain of their chemical characteristics can be anticipated.

Carboxyl atom group. It is noteworthy that the formulas for organic acids as used by the organic chemist differ in appearance from those used by the inorganic chemist. The latter stresses the radical parts—the hydrogen radical and the acid radical; the organic chemist stresses the atom group which contains the replaceable hydrogen atoms. This characteristic atom group is called the carboxyl; its composition and structure are as represented below.

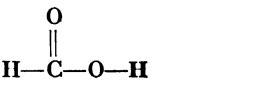
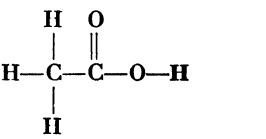
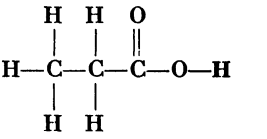
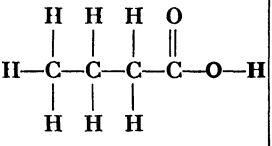
The carboxyl group



The presence of the carboxyl in specific acids is indicated in their formulas as given in the following table. **H**, in heavier type, indicates the replaceable hydrogen atom—the hydrogen that is responsible for the acid nature of the compound.

In general, the number of carboxyl atom groups in the molecule of an organic acid is determined by the number of replaceable hydrogen atoms present therein, and vice versa. Thus, the formic acid

molecule has *1* carboxyl group, since it has *1* replaceable hydrogen atom, whereas the tartaric acid molecule has 2 carboxyl groups because it has 2 replaceable hydrogen atoms (p. 317).

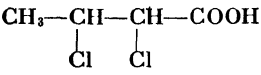
OLDER NAME AND NEW NAME	FORMULA AFTER INORGANIC METHOD	STRUCTURAL FORMULA	SEMISTRUCTURAL FORMULA
Formic acid Methan*oic* acid	$HCHO_2$		H—COOH
Acetic acid Ethan*oic* acid	$HC_2H_3O_2$		CH_3—COOH
Propionic acid Propan*oic* acid	$HC_3H_5O_2$		CH_3—CH_2—COOH
Butyric acid Butan*oic* acid	$HC_4H_7O_2$		CH_3—CH_2—CH_2—COOH

Nomenclature. There is less conformity to a definite system in the naming of acids than with the preceding classes of organic compounds. Many of the well-known acids have well-established, handed-down names such as formic acid, oxalic acid, and tartaric acid. Even so, for the saturated monocarboxylic acids—as for the alcohols, aldehydes, and ketones—a system of naming has been developed which indicates the hydrocarbons from which the acids are derived. According to this system, the stem name of the hydrocarbon is used with the ending *oic* to designate the acid. Thus, formic acid is also called methan*oic* acid, acetic acid is ethan*oic* acid, etc.

For indicating the placement of substituent atoms or atom groups in the molecule of an acid, the system differs from that used for classes of compounds studied previously: (1) Letters of the Greek alphabet[1] are used instead of numerals to indicate where substitutions occur on the hydrocarbon chain. (2) The *alpha* (α) position is on the carbon atom *next to the carboxyl group*, with

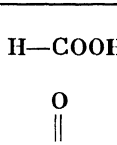
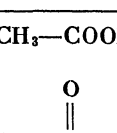
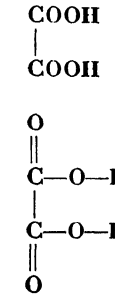
[1] See pp. 281–82.

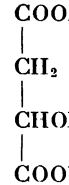
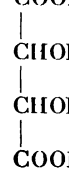
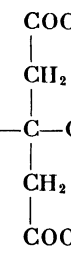
beta (β) position on the second carbon atom from the carboxyl, gamma (γ) position on the third carbon atom from the carboxyl, and so on. Thus:



α, β—dichlorobutanoic acid

Familiar and important organic acids. The accompanying table (pp. 316 to 318) lists some of the more common organic acids and also a few which, although less familiar, are important physiologically. It also cites facts of interest concerning them.

NAME	FORMULAS	REMARKS
The two simplest acids		
Formic acid or Methanoic acid		This acid was known to the ancients and was obtained from red ants. (Latin, *formica*, or ant.) It occurs in ants, bees, and nettles. The irritation caused by the sting of ants, and perhaps of bees and other insects, is due in part to the injection of this acid under the skin.
Acetic acid or Ethanoic acid		This is the chief acid in vinegar. It is a product of the fermentation of sugar to make alcohol which, in time, oxidizes to acetaldehyde; then, as should be expected, to acetic acid.
In fruits and plants		
Oxalic acid		Oxalic acid, together with its salts, is widely distributed in leaves and fruits of plants. The sour taste of some leaves, such as the sorrel, is due to its presence. It is one of the strongest of the organic acids. Taken internally, it is not oxidized, and hence disturbs the acid-base balance in the blood. It also reacts with calcium salts and makes insoluble compounds. It is a good reducing agent; its use as a bleach and stain remover is due to this property.

NAME	FORMULAS	REMARKS
In fruits and plants *(cont.)*		
Malic acid		Malic acid is widely distributed in fruits—apples, pears, grapes, strawberries, and other fruits. This acid is also made in animal cells.
Tartaric acid		It is interesting to note the chemical relationship between tartaric and malic acids. Both are dicarboxylic, and both are derivatives from butane. Both are also secondary alcohols, malic acid with one such group, tartaric acid with two. Tartaric acid occurs in fruits and is especially abundant in grapes.
Citric acid		This acid derives its name from its occurrence in citrus fruits, notably in lemons, its chief commercial source. It is widely distributed in fruits, including lemons, limes, gooseberries, and currants. Citric acid is also made in animal cells (p. 468).
Fatty Acid		
Butyric acid	$C_3H_7—COOH$	These acids are made from the hydrolysis of the fats butyrin, palmitin, stearin, and olein, respectively (p. 392). They are made as digestive products of fats in the intestine and as hydrolysis products in the cells. Butyric acid is present in rancid butter, in cheese, and in perspiration. It has an unpleasant odor.
Palmitic acid	$C_{15}H_{31}—COOH$	
Stearic acid	$C_{17}H_{35}—COOH$	
Oleic acid	$C_{17}H_{33}—COOH$	

NAME	FORMULAS	REMARKS
Other acids of physiological importance		
Lactic acid or α-hydroxypropionic acid	CH_3 | $CHOH$ | $COOH$	Lactic acid, derived from lactose, is a component of sour milk. All three of these acids appear in the cells as intermediate compounds in the metabolic series of reactions. *Lactic acid* is made during the metabolism of glucose (p. 463). *β-hydroxybutyric acid* and *acetoacetic acid* are made in the fatty-acid oxidation series of reactions, and under some conditions they are excreted in the urine (p. 475).
β-hydroxybutyric acid	CH_3 | $CHOH$ | CH_2 | $COOH$	
Acetoacetic acid or Diacetic acid or β-oxybutyric acid	CH_3 | CO | CH_2 | $COOH$	

Physical properties. In general, the first members of the monocarboxylic acid series are liquids with strong odors and are soluble in water. With increasing molecular weight, the hydrocarbon character becomes more evident, and the acids of high molecular weight are waxy solids and relatively insoluble in water. As a rule, acids with more than one carboxyl group are more soluble in water than are the related monocarboxylic acids.

Chemical behavior of acids. As is true of all acids, the following reactions can be expected of organic acids.

As electrolytes. In water solution organic acids yield hydronium ions (hydrated hydrogen ions) and acid-radical ions.

For example[2]

$$\underset{\text{Acetic acid}}{HC_2H_3O_2} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Hydronium ions}}{H_3O^+} + \underset{\text{Acetate ions}}{C_2H_3O_2^-}$$

$$\underset{\text{Tartaric acid}}{H_2C_4H_4O_6} + 2\,\underset{\text{Water}}{H_2O} \longrightarrow 2\,\underset{\text{Hydronium ions}}{H_3O^+} + \underset{\text{Tartrate ions}}{C_4H_4O_6^{--}}$$

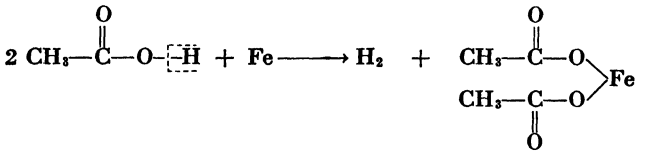
[2] As previously stated in this text, the functioning of water in the ionization of acids is recognized and, at times, represented in the equation. But in the subsequent discussion the term "hydrogen ion" is used instead of "hydronium ion."

Almost all organic acids are *weak electrolytes;* that is, when in water solution less than 50 per cent of the molecules of the acids are ionized. However, oxalic acid is capable of yielding a sufficiently high concentration of hydrogen ions (p. 219) to render it a dangerous substance to have around where a careless person might possibly mistake it for a prescribed medicine. Such tragic mistakes have happened. Other organic acids of common occurrence—including lactic acid and the acids of fruits—are weak enough to be relatively harmless.

As acids with metals above hydrogen. Organic acids react with metals above hydrogen to make hydrogen and salts.

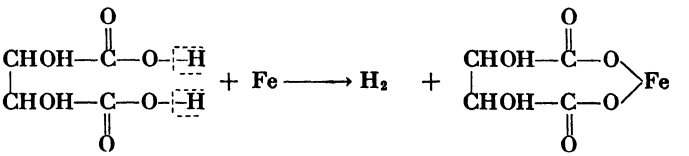
Acetic acid + Iron → Hydrogen + Ferrous acetate

$$2\,HC_2H_3O_2 + Fe \longrightarrow H_2 + Fe(C_2H_3O_2)_2$$



Tartaric acid + Iron → Hydrogen + Ferrous tartrate

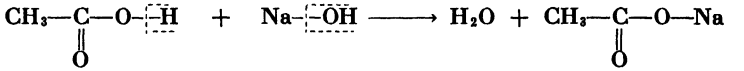
$$H_2C_4H_4O_6 + Fe \longrightarrow H_2 + FeC_4H_4O_6$$



As acids with bases. Organic acids react with bases to make water and salts. Thus, in specific application:

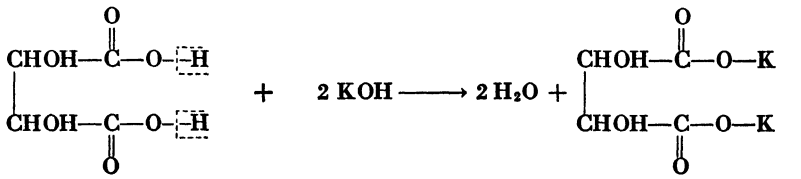
Acetic acid + Sodium hydroxide → Water + Sodium acetate

$$HC_2H_3O_2 + NaOH \longrightarrow H_2O + NaC_2H_3O_2$$



Tartaric acid + Potassium hydroxide → Water + Potassium tartrate

$$H_2C_4H_4O_6 + 2\,KOH \longrightarrow 2\,H_2O + K_2C_4H_4O_6$$



As acids with alcohols. Organic acids react with alcohols to make water and *esters* (p. 325). Reactions of the foregoing acids with ethyl alcohol are represented below.

Acetic acid + Ethyl alcohol → Water + Ethyl acetate

$$CH_3—COOH + C_2H_5OH \rightarrow H_2O + CH_3COOC_2H_5$$

Tartaric acid + Ethyl alcohol → Water + Ethyl tartrate

$$\begin{array}{l} COOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ COOH \end{array} + 2\ C_2H_5OH \rightarrow 2\ H_2O + \begin{array}{l} COOC_2H_5 \\ | \\ CHOH \\ | \\ CHOH \\ | \\ COOC_2H_5 \end{array}$$

As acids with metal oxides. Organic acids can also be expected to react with metal oxides to make water and salts.

Acetic acid + Ferric oxide → Water + Ferric acetate

$$6\ HC_2H_3O_2 + Fe_2O_3 \longrightarrow 3\ H_2O + 2\ Fe(C_2H_3O_2)_3$$

Tartaric acid + Ferric oxide → Water + Ferric tartrate

$$3\ H_2C_4H_4O_6 + Fe_2O_3 \longrightarrow 3\ H_2O + Fe_2(C_4H_4O_6)_3$$

Reactions of organic acids in the foregoing types of contacts are of practical importance. They are frequently involved in the manufacture of organic compounds; they are sometimes encountered in the home, notably in preparation of food. Contacts of the aluminum or iron pan or kettle with the acid components of foods result in slow reactions. Although the reactions are slow, salts of such metals do collect in detectable quantities in the food. It is also well known that foods that contain acids will "clean" iron rust (ferric oxide) or aluminum rust (aluminum oxide) from utensils. (For a more detailed discussion see Chapter 14.)

FATTY ACIDS

Representative fatty acids. Fatty acids result from the hydrolysis of fats. Those most frequently mentioned are butyric, palmitic, stearic, and oleic acids; but there are others, including valeric, caproic, linoleic, and linolenic acids. The last two mentioned are made from the hydrolysis of fat components present in linseed oil. Formula representations for these fatty acids are as follows.

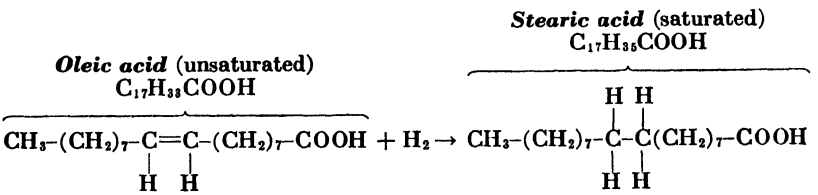
NAME	FORMULA STRESSING CARBOXYL GROUP	SEMISTRUCTURAL FORMULA FOR MOLECULE
Saturated fatty acids		
Butyric acid	C_3H_7COOH	$CH_3—CH_2—CH_2—COOH$
Valeric acid	C_4H_9COOH	$CH_3—CH_2—CH_2—CH_2—COOH$
Caproic acid	$C_5H_{11}COOH$	$CH_3—CH_2—CH_2—CH_2—CH_2—COOH$ or more briefly $CH_3—(CH_2)_4—COOH$
Palmitic acid	$C_{15}H_{31}COOH$	$CH_3—(CH_2)_{14}—COOH$
Stearic acid	$C_{17}H_{35}COOH$	$CH_3—(CH_2)_{16}—COOH$
Unsaturated fatty acids		
Oleic acid	$C_{17}H_{33}COOH$	$CH_3(CH_2)_7—CH=CH—(CH_2)_7—COOH$
Linoleic acid	$C_{17}H_{31}COOH$	Two sets of 2 carbon atoms joined with double bonds
Linolenic acid	$C_{17}H_{29}COOH$	Three sets of 2 carbon atoms joined with double bonds

The term *fatty acids* is applied not only to acids that are made by the hydrolysis of fats but also to *all acids of the open-chain saturated series* to which most of these fatty acids belong. Thus, formic acid and acetic acid, chemically related to butyric, palmitic, and stearic acids, are likewise called fatty acids, although they are not products of the hydrolysis of fats.

Chemical behavior as acids. Fatty acids are weak electrolytes. They react with bases and alcohols, as do all acids, to make salts and esters. From a commercial angle it is as the result of reactions of fatty acids with bases that soaps are made (p. 327). From a physiological viewpoint it is through reactions of such acids with glycerol, as an alcohol, that body fats are made (p. 477).

Saturated and unsaturated fatty acids. It is known that whether a fatty acid, or any other organic acid, is saturated or unsaturated depends entirely upon its hydrocarbon part. If this hydrocarbon is saturated (p. 279), the fatty acid is called a saturated fatty acid; but, if the hydrocarbon part of the acid is unsaturated, the fatty acid is regarded as being unsaturated. Accordingly, butyric acid, valeric acid, caproic acid, palmitic acid, and stearic acid are saturated because, supposedly, all carbon atoms within the molecules are joined with single bonds; hence, there are no electrons

available for sharing with other elements. Oleic acid, linoleic acid, and linolenic acid are unsaturated because, according to belief, 1 or more pairs of carbon atoms within their molecules are joined with double bonds. Therefore, at points where double bonds occur, *direct combination* with hydrogen atoms, or atoms of other elements, is possible. Of course when this happens the double bond between carbon atoms gives way to a single bond, and the hydrocarbon part of the molecule, hence the fatty-acid molecule as a whole, becomes saturated. Such a reaction between oleic acid and hydrogen is represented as follows.



The chief importance of these two varieties of fatty acids is in relation to fats, because fats are saturated or unsaturated (p. 393) depending upon whether the fatty-acid-radical constituents are saturated or unsaturated. The contrasting chemical behavior of these two varieties of fats has a significant bearing in everyday concerns (pp. 398 to 399).

AMINO ACIDS

Representative amino acids. Among the various organic acid derivatives that are of vital importance are the *amino acids*. The *amino* is a derivative of ammonia (NH_3),[3] hence, its name. It has a composition and valence as is indicated in its formula $-NH_2$, represented thus.

Amino atom group (structural and empirical formulas)

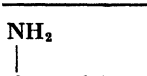
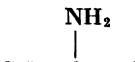
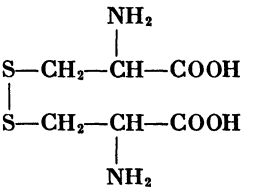
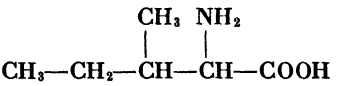


$-NH_2$

The molecule of every amino acid must contain both carboxyl and amino atom groups. This is indicated in the semistructural formulas for the amino acids listed in the table on page 324. (See also pp. 410 to 414.)

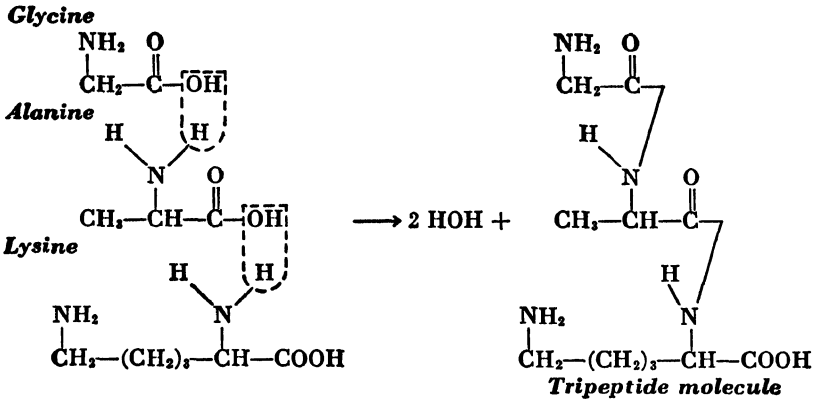
[3] Another radical derived from ammonia is called *imino*. Its formula and valence are represented thus: >NH.

In the structural names for these acids, *alpha* (α) *amino* signifies that the amino group is substituted on the carbon atom that is *next to the carboxyl*, while epsilon (ϵ) designates a substituent on a carbon atom in the fifth position beyond the carboxyl.[4]

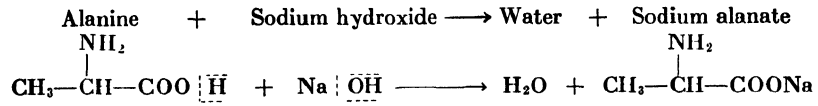
COMMON NAME	STRUCTURAL NAME	FORMULA
Glycine	Alpha(α)-amino-acetic acid	
Alanine	Alpha(α)-amino-propionic acid	
Cystine	An alpha(α)-amino derivative of 2 molecules of propionic acid. It is also an important sulfur derivative.	
Lysine	Alpha(α), epsilon(ϵ)-diamino-caproic acid	
Isoleucine	Alpha(α)-amino, beta(β)-methyl-valeric acid	

Amino acids dehydrolyze to make proteins. It is *believed* that the various animal cells select specific amino acids from among those brought to them by the blood stream and subject them to the process of dehydrolysis to make cell proteins of their own peculiar character. Presumably, during such reactions, hydroxyl atom groups are taken from the carboxyl and hydrogen atoms from the amino groups of amino acids to make molecules of water. The amino acids, thus rendered incomplete, combine with each other to make protein molecules. A combination between three amino acid molecules is represented below. In making a protein molecule, hundreds of amino acids are believed to be thus linked together.

[4] Alpha (α), beta (β), gamma (γ), delta (δ), epsilon (ϵ).



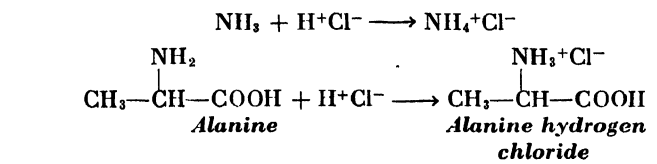
Amino acids with bases. Amino acid molecules, at the replaceable hydrogen atoms in their carboxyl groups, react in the usual manner with bases to make *water* and *salts*. Thus with molecules of alanine and sodium hydroxide:



As nitrogen bases with acids. The amino group in any compound provides a point at which acids can react, in direct combination, to form salts. For this reason compounds containing amino groups are frequently referred to as *nitrogen bases*.[5] For example:

Alanine + Hydrochloric acid ⟶ Alanine hydrogen chloride
Glycine + Sulfuric acid ⟶ Glycine hydrogen sulfate

The reaction at the amino group may be compared to that which takes place between ammonia and an acid.



[5] Either the amino (—NH_2) or imino (>NH) atom group is a constituent of every alkaloid molecule and accounts for its behavior as a nitrogen base in reaction with acids. It is this behavior that gives rise to the class term, *alkaloids*.

Amino acids are amphoteric. This means that amino acids have a double nature: (1) Through their carboxyl groups they are acids; hence, they react with bases. (2) Through their amino groups they react with other acids. Because of this dual capacity for reaction, amino acids of body cells, intercellular fluids, and blood function as one means by which hydrogen-ion concentrations are controlled within the range vital to the healthy, living animal.

ORGANIC SALTS AND ESTERS

Organic salts. Compounds composed of metal or ammonium radicals in combination with organic acid radicals are classed as *organic salts*. This is in contrast with *esters*, which are composed of hydrocarbon radicals in combination with acid radicals. The following are typical examples of each group.

ORGANIC SALTS			ESTERS		
Sodium acetate	$NaC_2H_3O_2$	$\begin{matrix}CH_3\\\vert\\COONa\end{matrix}$	Methyl chloride	CH_3Cl	$CH_3—Cl$
Ammonium oxalate	$(NH_4)_2C_2O_4$	$\begin{matrix}COONH_4\\\vert\\COONH_4\end{matrix}$	Ethyl acetate	$C_2H_5C_2H_3O_2$	$\begin{matrix}CH_3\\\vert\\COO—C_2H_5\end{matrix}$
Potassium tartrate	$K_2C_4H_4O_6$	$\begin{matrix}COOK\\\vert\\CHOH\\\vert\\CHOH\\\vert\\COOK\end{matrix}$	Glyceryl stearate	$C_3H_5(C_{17}H_{35}CO_2)_3$	See p. 394
			Glyceryl nitrate	$C_3H_5(NO_3)_3$	$\begin{matrix}CH_2—NO_3\\\vert\\CH—NO_3\\\vert\\CH_2—NO_3\end{matrix}$

Organic salts, chemical behavior. Organic salts are *strong electrolytes;* hence, they are capable of providing high concentrations of their contributing ions when in water solution. As a result, they are chemically active and engage in the same types of chemical reactions as do other salts. Among such possibilities are the following.

React with acids. Organic salts react with acids as should be expected.

$$\text{Salt} + \text{Acid} \longrightarrow \text{Salt} + \text{Acid}$$

Sodium acetate + Sulfuric acid → Sodium sulfate + Acetic acid

$$2\ CH_3COONa + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ CH_3COOH$$

React with water in hydrolysis. Since most organic salts are salts of weak acids (p. 189), they are subject to hydrolysis. Thus:

$$\text{Organic salt} + \text{Water (in hydrolysis)} \longrightarrow \text{Base} + \text{Organic acid}$$

Ammonium oxalate + Water ⟶ Ammonium hydroxide + Oxalic acid

$$\begin{matrix}\text{COONH}_4\\ |\\ \text{COONH}_4\end{matrix} + 2\ \text{HOH} \longrightarrow 2\ \text{NH}_4\text{OH} + \begin{matrix}\text{COOH}\\ |\\ \text{COOH}\end{matrix}$$

Potassium tartrate + Water ⟶ Potassium hydroxide + Tartaric acid

$$\begin{matrix}\text{COOK}\\ |\\ \text{CHOH}\\ |\\ \text{CHOH}\\ |\\ \text{COOK}\end{matrix} + 2\ \text{HOH} \longrightarrow 2\ \text{KOH} + \begin{matrix}\text{COOH}\\ |\\ \text{CHOH}\\ |\\ \text{CHOH}\\ |\\ \text{COOH}\end{matrix}$$

Soaps. ***Composition.*** Soaps, which are among the most important of the *organic salts*, have for constituents a metal or an ammonium radical in combination with fatty-acid radicals obtained from fats. The following are examples.

Cleansing soaps		*Noncleansing soaps*	
Sodium stearate	$NaC_{17}H_{35}CO_2$	Calcium stearate	$Ca(C_{17}H_{35}CO_2)_2$
Potassium palmitate	$KC_{15}H_{31}CO_2$	Magnesium palmitate	$Mg(C_{15}H_{31}CO_2)_2$
Sodium oleate	$NaC_{17}H_{33}CO_2$	Zinc stearate	$Zn(C_{17}H_{35}CO_2)_2$

Cleansing soaps. Sodium soaps are those most commonly used for cleansing purposes. They appear in the familiar cakes, flakes, and powders. Potassium soaps are encountered less frequently; they are used for special purposes, chiefly shaving creams and liquid preparations.

All cleansing soaps give colloidal dispersion in water, as evidenced by the familiar translucent effect obtained when a soap and water system are shaken and suds appear (p. 195). They also form gels on standing, another characteristic of colloidal dispersions (p. 212). Soaps will dissolve in alcohol, for example, in the preparation known as "green soap."

Soapmaking. For making soaps, fats are mixed with either sodium or potassium hydroxide and the reaction is usually, though

not always, favored by prolonged heating. Without going into details of the process involved in the manufacture of soap, the reactions are believed to include the following steps. (1) The fats hydrolyze to make glycerol and fatty acids, the base acting as a *catalyst* for the reactions; (2) the fatty acids then react with the base to make water and the soap. With glyceryl stearate as the fat and sodium hydroxide as the base, reactions occur as follows.

$$\begin{array}{lcl} \text{Glyceryl stearate} + \text{Water} & \xrightarrow{\text{Sodium hydroxide}} & \text{Stearic acid} + \text{Glycerol} \\ C_3H_5(C_{17}H_{35}CO_2)_3 + 3\ HOH & \longrightarrow & 3\ C_{17}H_{35}COOH + C_3H_5(OH)_3 \end{array}$$

$$\begin{array}{lcl} \text{Stearic acid} + \text{Sodium hydroxide} & \longrightarrow & \text{Water} + \text{Sodium stearate (the soap)} \\ C_{17}H_{35}COOH + NaOH & \longrightarrow & HOH + C_{17}H_{35}COONa \end{array}$$

Frequently, these reactions are represented as occurring in only one step between the fat and the base, thus:

$$\begin{array}{lcl} \text{Glyceryl stearate} + \text{Sodium hydroxide} & \longrightarrow & \text{Glycerol} + \text{Sodium stearate (the } \textit{soap}\text{)} \\ C_3H_5(C_{17}H_{35}CO_2)_3 + 3\ NaOH & \longrightarrow & C_3H_5(OH)_3 + 3\ C_{17}H_{35}COONa \end{array}$$

In making soap the naturally occurring fats that are used are *fat mixtures;* hence, the resulting soap products are soap mixtures.

In pioneer days soapmaking was one of the regular home tasks. Scrap fats were saved up during the year for the spring soapmaking. The year's yield of wood ashes was accumulated and "leached" to obtain "potash." Actually, as is now known, potash is largely potassium carbonate, which reacts with water to yield potassium hydroxide for making soap. In those days to obtain "good soap" was an art, in that favoring proportions of potash and fat could be arrived at only by numerous trial-and-error procedures. Today soapmaking is on a scientific basis. One difference between the "then" and "now" lies in the fact that today chemists understand the reactions that occur and can compute the exact quantities of fat and base to be used and the exact quantities of soap product which will result.[6]

The functioning of soaps. Cleansing soaps function by acting as emulsifying agents. Thin films of soap collect around oil droplets, hindering their coalescence and holding them in dispersion with the water. The long hydrocarbon chain of the fatty-acid ion is believed to be attracted to the fat and oil while the positively charged sodium or potassium ion is attracted to the water. In this way the emulsi-

[6] For details as to commercial soaps and their manufacture, the student is referred to Fieser, L. F., and Fieser, M.: *Organic Chemistry*, 2nd. ed. D. C. Heath and Company, Boston, 1950, pp. 418–21.

fying agent encircles the oily droplets, separating them from the surface of the skin, fabric, or utensil, and holding them in suspension in water as is suggested by the diagram in Figure 86. Particles of dirt are attracted to the surface of the soap film between the two liquids. Thus, oily material and adherent dirt, both insoluble in water, can be removed in emulsion. (Also see Emulsions and emulsifying agents, pp. 214 to 217.)

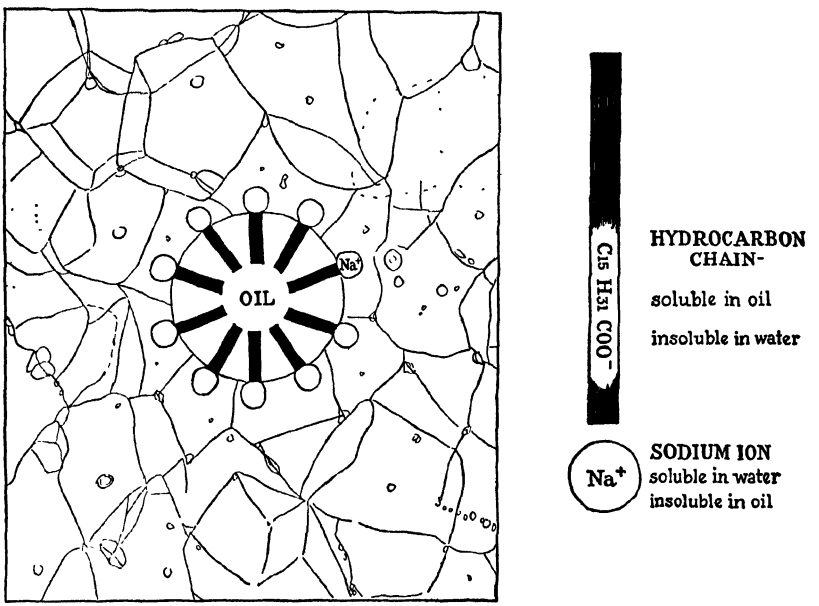
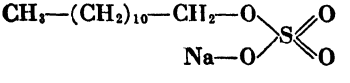


Fig. 86. A diagrammatic representation of soap functioning as an emulsifying agent. The hydrocarbon chain of the acid radical ion is attracted to the oil droplet while the sodium ion is attracted to the water. Thus, a film of soap surrounds the oil droplet and prevents droplets from coalescing.

New detergents. Although soaps are still the most widely used detergents, a number of new compounds have been developed which are proving to be equally serviceable as cleaning agents and, in some instances, have advantages over soaps.

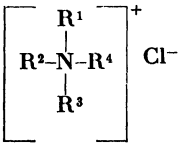
The term "*sulfonated*" *detergent* is used to designate one variety of compound. These are really sulfates, part salt and part ester, as is suggested by the following formula for one such compound. Oils which provide hydrocarbon radicals

Sodium lauryl sulfate

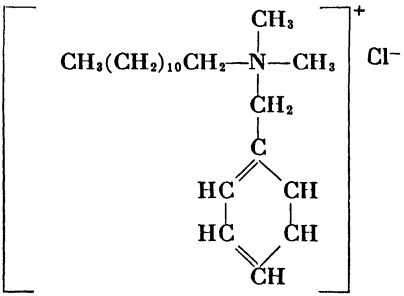


of from 12 to 18 carbon atoms are used in the manufacture of these compounds. The lauryl radical with a 12-carbon-atom chain is present in many of these detergents. As sulfate salts these detergents can be used without difficulty with hard water because they do not form insoluble compounds with calcium and magnesium ions. Neither acids nor bases interfere with their action. Detergents of this type are sold under various trade names.

Another type of detergent which is proving to be of value is related chemically to ammonium salts; in fact, these detergents may be thought of as ammonium compounds in which the hydrogen atoms are replaced by hydrocarbon radicals. At least one of the radicals must be a long-chain hydrocarbon—the lauryl radical, for instance. The accompanying formulas are suggestive of the type of compounds involved.



General formula
R^1, R^2, R^3, R^4
represent different
hydrocarbon radicals



Formula representation for a
specific ammonium (cationic) detergent

These compounds are often referred to as "*cationic detergents*" because, in contrast to soaps from the standpoint of their composition, the hydrocarbon portion of the compound is in the positively charged radical (cation) rather than in the negatively charged acid radical. These *quaternary ammonium* detergents have some germicidal value but they are ineffective for spore-forming microorganisms.[7] In hospital practice they are used for cleansing the skin and for preserving previously sterilized instruments. They react with soaps; even a low concentration of soap interferes with their germicidal action. The salts of hard water do not interfere with their use.

Yet another type is the nonionic detergent, a compound that is composed of a long hydrocarbon radical and a "water-loving" group such as an ether or alcohol. For example:

$$CH_3—(CH_2)_{10}—CH_2—O—(CH_2)_2—O(CH_2)_2—O—(CH_2)_2—O—CH_2—CH_2OH$$

These detergents are viscous fluids and find their chief use in cleaning dishes and equipment.

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[7] A number of these detergents are described by the Council on Pharmacy and Chemistry of the American Medical Association: *New and Nonofficial Remedies*—1954, J. B. Lippincott Company, Philadelphia, pp. 79–85.

Esters. Esters are compounds composed of a hydrocarbon radical combined with an acid radical. They can be made in the laboratory from the reaction of an alcohol with an acid (p. 320). Typical examples, with formulas, were introduced on page 325.

There are many naturally occurring esters. Both fats and waxes are esters of high molecular weight, hence, nonvolatile. Many esters of low molecular weight are volatile oils and contribute to the flavor and odor of fruits and flowers; for example, ethyl butyrate ($C_3H_7COOC_2H_5$) occurs in pineapples and in the oil of roses, octyl acetate ($CH_3COOC_8H_{17}$) is found in oranges. Numerous volatile esters are synthesized and used in the preparation of artificial perfumes and flavors.

As nonelectrolytes. Esters are nonelectrolytes; consequently, in contrast to organic salts, their reactions are slow unless favored by catalysts.

Hydrolysis of esters. The only type of chemical behavior characteristic of esters which we shall consider is their reaction with water in hydrolysis. Either acids or bases may serve as catalysts for these reactions. Thus:

$$\text{Ester} + \text{Water (in hydrolysis)} \xrightarrow{\text{Base or acid}} \text{Alcohol} + \text{Acid}$$

$$\text{Ethyl chloride} + \text{Water} \xrightarrow{\text{Base or acid}} \text{Ethyl alcohol} + \text{Hydrochloric acid}$$
$$C_2H_5Cl + HOH \longrightarrow C_2H_5OH + HCl$$

$$\text{Ethyl acetate} + \text{Water} \xrightarrow{\text{Base or acid}} \text{Ethyl alcohol} + \text{Acetic acid}$$
$$CH_3COOC_2H_5 + HOH \longrightarrow C_2H_5OH + CH_3COOH$$

In soapmaking, the first reaction involved is hydrolysis of the fat with the base functioning as a catalyst. The digestion of fats provides an example of hydrolysis of an ester with an enzyme, steapsin or pancreatic lipase, functioning as a catalyst (p. 449).

Some important esters. From the standpoint of composition, *fats* are esters composed of the 3-valent glyceryl radical and fatty acid radicals which vary from fat to fat. The following are widely distributed as components of natural fats.

Glyceryl palmitate	$C_3H_5(C_{15}H_{31}COO)_3$
Glyceryl stearate	$C_3H_5(C_{17}H_{35}COO)_3$
Glyceryl oleate	$C_3H_5(C_{17}H_{33}COO)_3$

The fats will be considered in greater detail in Chapter 27.

A number of esters are used *medicinally*. *Ethyl chloride* is a well known local anesthetic. Both *amyl nitrite* (isoamyl nitrite) and *glyceryl trinitrate* (nitroglycerin) are used in the treatment of angina pectoris. *Ethyl nitrite* is used as a diuretic, its alcoholic solution being known as sweet spirits of niter.

QUESTIONS

1. What atom group is typical of organic acids? Represent this group both structurally and semistructurally. Indicate the ionizable hydrogen.
2. Assemble word and formula equations for typical reactions characteristic of organic acids. Represent organic compounds by semistructural formulas.
3. What, if any, reaction is to be expected from each of the following contacts?
   a. Grapes cooked in an aluminum dish
   b. Apples cooked in an iron kettle
   c. Bicarbonate of soda used with sour milk in cookery
   d. Sodium bicarbonate or ammonium hydroxide solution in the treatment of skin irritation caused by nettles or by a bee sting
4. What are fatty acids? What is their usual source? Name at least six fatty acids. Why are they important physiologically?
5. What is an amino acid? Give examples with formula representations. What is their usual source? Why are they important physiologically?
6. Amino acids are amphoteric. What does this mean? Illustrate by reference to the amino acid lysine, giving formula equations for the reactions.
7. What is an organic salt? Give examples. How does an ester differ from other organic salts: (a) as to composition? (b) as to chemical behavior? (c) Give examples of esters that contain inorganic acid radicals; organic acid radicals.
8. What is a soap? How are soaps made commercially? Assemble word and formula equations representative of the reactions involved. With glyceryl stearate as the fat, how much fat and how much sodium hydroxide would be required to make 5 lb of soap?
9. a. Why can the cationic detergents be used in hard water without interference with the calcium and magnesium salts?
   b. Assemble a formula equation representing the reaction of a detergent of this type with sodium stearate. What would be the physical character of the resulting organic compound?
10. Fats are classed as esters. Why? Illustrate with reference to some specific fat.

CHAPTER 25

CYCLIC COMPOUNDS AND THEIR DERIVATIVES

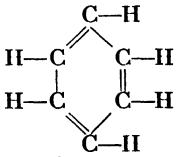
The organic compounds that have claimed our attention thus far are all aliphatic, or straight-chain, compounds. We shall now consider the ***aromatic*** or ***cyclic*** compounds. The substances in this classification are many and varied; in fact, of the numerous known organic compounds, more than half contain cyclic structures. Some of these substances are of interest because of their physiological importance; for instance, this group includes some of the amino acids, cholesterol, hemoglobin, the vitamins, some of the enzymes and hormones. Many compounds used as drugs are cyclic derivatives—some originating in the cells of plants or animals, some produced in the pharmaceutical laboratory. Practically all of the dyes in common use for coloring fabrics, for laboratory stains, for use as indicators of hydrogen-ion concentrations, and even as bactericidal agents belong in this group. Indeed, the development of the modern dye industry, which has provided fast dyes (resistant to fading) in shades and tints unknown to earlier generations, is a story of research in the field of cyclics. Many other modern developments, such as synthetic plastics, photographic supplies, and other substances too numerous to mention, lie within the field of cyclic compounds.

Class names and their significance. The class name ***aromatic*** is largely of historical interest. It was given to this group because many of the cyclic compounds have fragrant odors, as of spices and balsams. But, this property of odor is not distinctive for cyclic compounds, many of which are odorless while compounds other than cyclics frequently have odor. The other class name, ***cyclics,*** has real chemical meaning. It signifies that within molecules of all members

of this family of compounds there are carbon atoms, and frequently atoms of other elements, combined with one another in a *closed-chain* or *ring formation.*

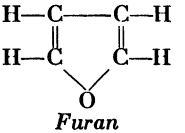
Carbocyclic and heterocyclic compounds. If there are only carbon atoms in the closed ring structure, the compound is referred to as a *carbocyclic;* if an atom or atoms of some other element are included in the ring, the compound is classed as a *heterocyclic.* The following are structural formulas for some of these two types of cyclic compounds.

A carbocyclic compound

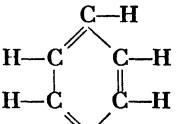


Benzene
C_6H_6

Heterocyclic compounds



Furan
C_4H_4O



Pyridine
C_5H_5N

Reasoning which leads to the belief in cyclic structures. Benzene is one of the simplest of the cyclic compounds; also, it is the aromatic compound which has more derivatives than any other cyclic. But for years after it became *known* that its molecular weight is composed of 6 atomic weights of carbon and 6 atomic weights of hydrogen, chemists were puzzled as to how 6 atoms of carbon and only 6 atoms of hydrogen could be arranged within a molecule and still provide for each carbon atom a valence of 4 and for each hydrogen atom a valence of 1.

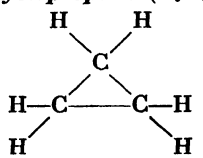
Alternate single- and double-valence bonds. It was in 1865 that the chemist Kekulé suggested that *the carbon atoms are combined in a ring formation with alternate double- and single-valence bonds,* the fourth bond on each carbon atom being satisfied by the 1 valence bond of a hydrogen atom. These conditions are represented in the foregoing structural formula for benzene.

A study of the structural formula for benzene indicates that each of the 6 carbon-hydrogen atom groups should have exactly the same relationship within the molecule and be susceptible to the same chemical attack. There are factual findings which support this belief. Simple as these suggestions made by Kekulé may seem to the student of today, they formed an epoch in the history of chemistry and led to a fairly satisfactory explanation for the composition of many organic compounds other than benzene.

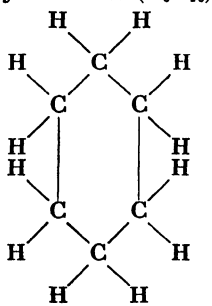
The representation of double bonds in alternate positions in the benzene ring has not been entirely satisfactory to the chemist. It suggests that this compound could readily become involved in reactions to form addition products; but this is not the case. Benzene does engage in such reactions, but not readily. Kekulé suggested that, in the ring compounds, the double bonds might be constantly shifting their positions within the molecule. This idea was not consistent with accepted theory of his period, but today it fits naturally into the concept of *resonance;* that is, the belief that electrons contributing to the double bonds can, under certain conditions, shift their positions within the molecule. Thus, in the benzene ring, the extra pairs of electrons are continually oscillating from the position suggested by the double bond to the adjacent position between the neighboring pair of carbon atoms. Such a continual shifting of electrons would help to explain the stability of the ring structure.

The cycloparaffins. There is also a small group of compounds whose composition and chemical behavior can best be explained by the assumption that, within their molecules, the carbon atoms are combined in ring formation *with single valence bonds.* One such substance is the gaseous hydrocarbon *cyclopropane* which is used as an anesthetic. The empirical formula for this compound is C_3H_6, and the structural formula for its molecule is represented below. Another such compound is *cyclohexane,* with the formula C_6H_{12}. These compounds are isomeric with the straight-chain hydrocarbons propene and hexene, respectively. But, there is this important difference: chemically, cyclopropane and cyclohexane behave as *saturated* hydrocarbons whereas propene and hexene are *unsaturated.*

Cyclopropane (C_3H_6)



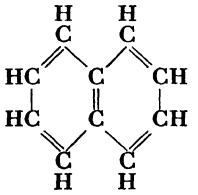
Cyclohexane (C_6H_{12})



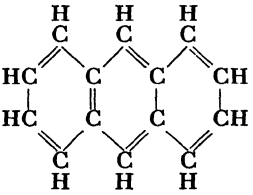
Condensed cyclics. There are still other organic compounds whose composition has led to the deduction that their molecules contain two or more cyclic structures in close combination. The

structural formulas for molecules of *naphthalene* ($C_{10}H_8$), *anthracene* ($C_{14}H_{10}$), and *phenanthrene* ($C_{14}H_{10}$) are represented below. Such compounds are known as *condensed cyclics.*

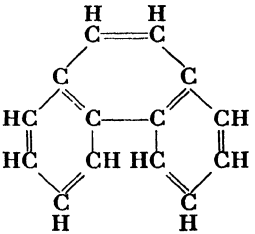
Naphthalene ($C_{10}H_8$)



Anthracene ($C_{14}H_{10}$)

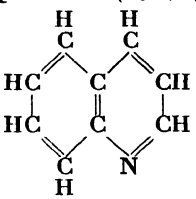


Phenanthrene ($C_{14}H_{10}$)

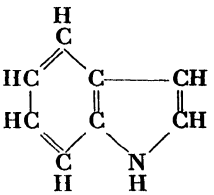


Similar cyclic condensations are encountered among the heterocyclic compounds, as is illustrated by the structural formulas for *quinoline* and *indole.*

Quinoline (C_9H_7N)

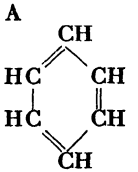


Indole (C_8H_7N)

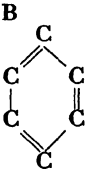


Various methods for representing cyclic structural formulas. The 6 carbon-atom ring that is characteristic of the benzene molecule, whether alone or as a nuclear part of molecules of benzene derivatives, is known as the *benzene ring.* The complete structural formula for this ring is as represented in A. However, this structure is frequently represented in an abbreviated form such as is suggested in B, C, and D below. When both carbon and hydrogen atoms are thus omitted, the reader must take their presence in the usual positions for granted. The heavy lines, in D, represent the positions of double bonds.

A



B



C

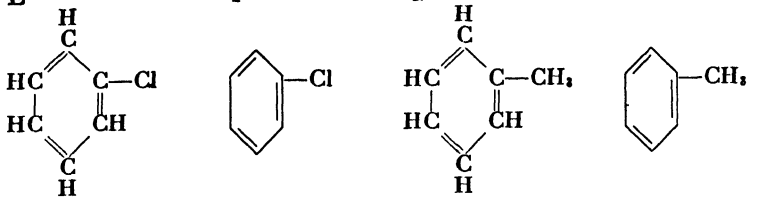


D



Substituted atoms or atom groups that are peculiar to the specific benzene derivative are always represented. Thus the complete structural formula for monochlorobenzene and methyl benzene are given in E and G (p. 336). But frequently these formulas appear in abbreviated manner as in F and H:

E F G H



Monochlorobenzene *Methyl benzene*

The same type of abbreviation is used for the structural formulas of other cyclic compounds and their derivatives.

One advantage in the use of the abbreviated formulas for cyclic compounds with complex structural features is that it is possible, by this means, to make substituent groups stand out more conspicuously than when the cyclic compound is represented in full detail.

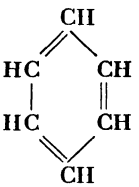
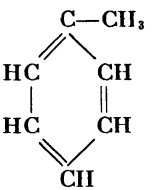
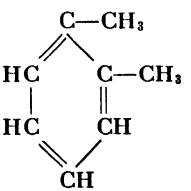
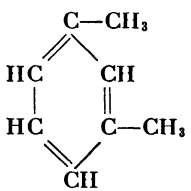
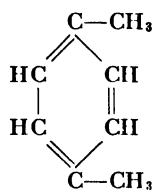
Occurrence. The aromatic or cyclic compounds occur in great numbers and varieties within the cells of plants but to a much less extent within animal cells. It would appear that whereas plants can synthesize these ring compounds from carbon dioxide and water, drawing upon nitrates and other compounds as needed, animals must obtain from the plants of their food supply the parent compounds from which to build the cyclic derivatives that they require. For centuries man has turned to plants for certain drugs, poisons, perfumes, flavors, and dyes, since these substances contain cyclic structures that only plants can make. Some of these compounds the chemist has not yet duplicated in the laboratory; other cyclic derivatives found in nature—the flavor component of wintergreen and the dye turkey red, for example—are being synthesized in large quantities. Chemists are interested not only in duplicating compounds found in nature but also in making new and different cyclic derivatives, and thousands of these have been made.

Components of coal tar. An important commercial source of parent ring structures for synthetic cyclic derivatives is soft coal, the desired compounds becoming greatly concentrated in the coal-tar mixture as coal is destructively distilled. In this way compounds once made in the cells of living plants, buried centuries ago in the crust of the earth as the result of some great earth upheaval, are again rendered available for the use of man in making numerous useful substances.

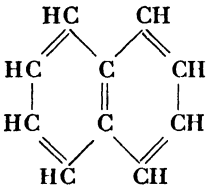
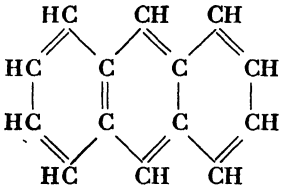
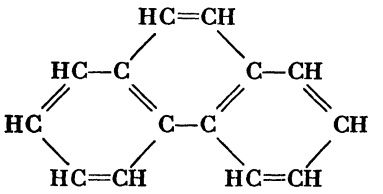
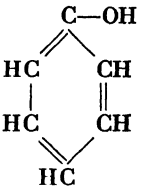
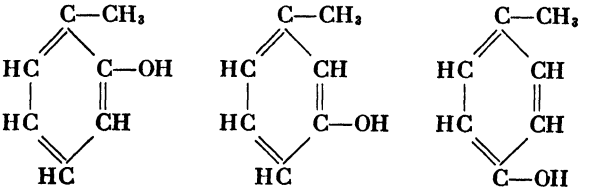
Coal is a mixture of very complex compounds which, when heated to a high temperature in a closed container, decompose to make simpler compounds.

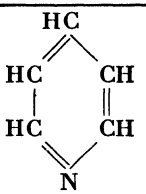
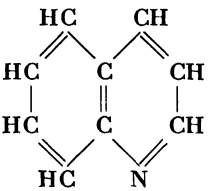
Such decomposition, through the agency of heat, and not in contact with air, is called *destructive distillation.* For many years coal was submitted to this process either for the sake of the hydrocarbons of illuminating gas or for the coke obtained. The coal-tar by-product was regarded as a necessary nuisance and utter waste, save for the relatively small quantities used for such purposes as making tar paper and surfacing roads. Even today this is the fate of much of the coal tar thus produced. It was an important day in industrial history when the chemist began to consider the possible treasure hidden away in this black, sticky mass.

A few of the important compounds present in coal-tar mixture which are separated for use as parent structures for the making of other compounds are listed in the following table.

NAME	STRUCTURAL FORMULA FOR MOLECULE	
Benzene[1]		From which are derived many drugs, disinfectants, dyes, etc.
Toluene[1] (Methyl benzene)		Parent substance for flavors, perfumes, dyes, and explosives. The famous TNT (trinitrotoluene) is a derivative.
Three xylenes[1] (Dimethyl benzene)	  	From which are derived perfumes, dyes, explosives, etc.

[1] Benzene, toluene, and xylene are sold commercially as benzol, toluol, and xylol, respectively. This is unfortunate since the ending *ol* indicates an alcohol, and none of these compounds is an alcohol. Xylene (labeled xylol) is commonly used in the laboratory as a solvent for cleaning the oil immersion lens of the microscope.

NAME	STRUCTURAL FORMULA FOR MOLECULE	
Naphthalene		Commonly met with in moth balls. An important parent substance for disinfectants, dyes, flavors, and perfumes
Anthracene		Parent substance for many dyes: for example, alizarin, commonly known as turkey red
Phenanthrene		The phenanthrene group is found in both morphine and codeine, obtained from the opium poppy (p. 359).
Phenol (Carbolic acid)		Various drugs, disinfectants, dyes, and explosives are derived from phenol
Three cresols		Antiseptics and disinfectants. Components of Lysol and tricresol

NAME	STRUCTURAL FORMULA FOR MOLECULE	
Pyridine		A heterocyclic compound from which various drugs are derived. It is a constituent of nicotine, although this drug is obtained from tobacco leaves rather than from coal tar. The vitamins nicotinic acid and pyridoxin are also pyridine derivatives
Quinoline		Pamaquine, a synthetic compound used for the treatment of malaria, is a quinoline derivative. Quinine, although obtained from the bark of the cinchona tree rather than from coal tar, is also a quinoline derivative

Chemical behavior. It is not our purpose, nor indeed would it be advisable within the limits of this text, to discuss in detail the chemical behavior of this large family of organic compounds. But it would be well to keep in mind the following characteristic behaviors. (1) The ring structure itself is very stable. It does not tend to break when the molecule becomes involved in reactions but rather appears as a unit part of the new molecule. Indeed, it is only with difficulty that reactions can be brought about which will break this ring formation. (2) Cyclic compounds show little tendency to make addition products on the ring, although such "additions" can be effected with difficulty on atoms in the ring which are joined with double bonds. When this does happen, the double bonds affected give way to single bonds. (3) Cyclic structures enter into reactions with greater or less ease to make substitution products on the ring. This makes possible the synthesis of a great variety of derivatives. (4) The chemical behavior of cyclic derivatives is determined in part by the behavior of the cyclic portion and in part by the behavior of the atom group or groups which are present as side chains attached to the ring, each participating in reactions characteristic of it.

CARBOCYCLICS

Benzene and toluene. Benzene is of special interest because of its many derivatives and its extensive industrial use. Toluene, or

methyl benzene, likewise a coal-tar derivative, perhaps ranks next to benzene in commercial importance.

Benzene is a colorless, volatile liquid and an excellent solvent for other hydrocarbons, for fats, paints, varnishes, resins, and many other compounds. It is used extensively in a great variety of industries, including dry cleaning and the manufacture of synthetic rubber, munitions, dyes, paints, and leather substitutes.

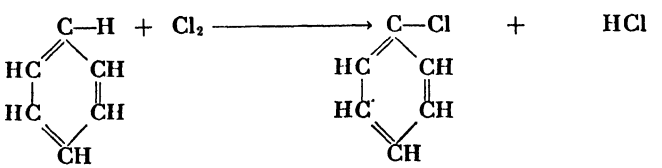
Toluene is important as the starting point for the synthesis of many compounds. The methyl group on the ring renders this compound more active chemically than is benzene. Toluene may be encountered in the hospital as a preservative for urine specimens. Because it is immiscible with and less dense than water, it can form a protective layer on the top of the specimen, thus excluding contamination from the outside.

Physiological effects. Because of their industrial use and the consequent exposure of workers to contact with these hydrocarbons and their vapors, the physiological effects of benzene and toluene have been carefully studied. Exposure to even small amounts over a long period of time results in a destructive attack on red blood cells and platelets. Exposure to concentrated vapor results in central-nervous-system depression and even death by respiratory failure.

Chemical behavior of cyclic hydrocarbons. A study of the behavior characteristic of benzene and toluene will point out types of reactions which may be expected from *carbocyclic* compounds in general.

With chlorine and bromine. *Benzene* will react with chlorine, or with bromine, under appropriate conditions to make hydrochloric acid and chlorobenzene derivatives, or hydrobromic acid and bromobenzene derivatives. The simplest of these derivatives with chlorine is monochlorobenzene, and the following equation represents the molecule involvement in the reaction.

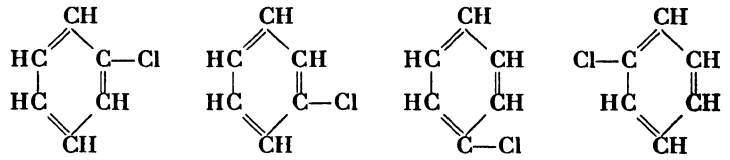
Benzene + Chlorine ⟶ Monochlorobenzene + Hydrochloric acid



Since all of the carbon-hydrogen atom groups bear the same relation to the benzene molecule as a whole, the attack of the chlorine

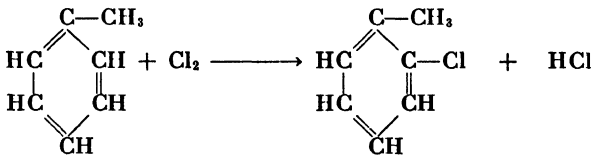
molecule can take place at any one of the six points of the benzene ring. In each case exactly the same compound, monochlorobenzene, will result although the structural formulas may look different on the page. Thus, all of the accompanying formulas are really for the same compound.

Monochlorobenzene—all four are the same formula

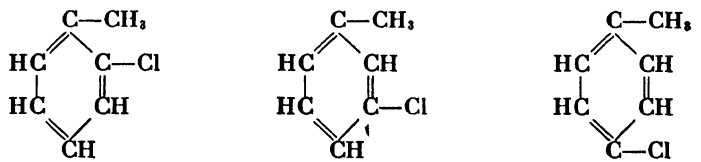


Toluene, being methyl benzene, reacts with chlorine in the benzene part of the structure in exactly the same manner.

Toluene + Chlorine ⟶ Monochlorotoluene + Hydrochloric acid



But with toluene not one but *three* monochlorotoluenes are possible, depending on whether the chlorine atom becomes substituted on the carbon atom *next* to the methyl group (*ortho position*), on the carbon atom *next but one* to the methyl group (*meta position*), or on the carbon atom *opposite* the methyl group (*para position*). Structural formulas for these three monochlorotoluenes, with their distinguishing names, are as follows.



Ortho-
monochlorotoluene

Meta-
monochlorotoluene

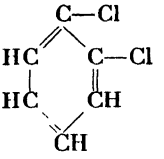
Para-
monochlorotoluene

Chlorine atom substitutions can take place until all of the hydrogen atoms on the ring structure have been replaced.

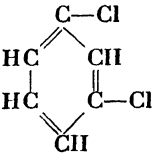
Bromine derivatives can be made in a manner similar to that used for making chlorine derivatives. Iodine derivatives must be made by more involved methods than through direct reaction with iodine.

Nomenclature. The following are structural formulas and methods of naming for some of the higher chloro derivatives on benzene and on toluene.

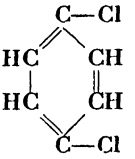
On benzene



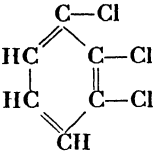
Ortho-dichlorobenzene



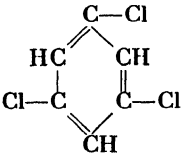
Meta-dichlorobenzene



Para-dichlorobenzene

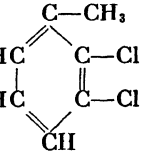


1, 2, 3-trichlorobenzene

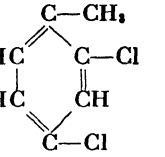


1, 3, 5-trichlorobenzene

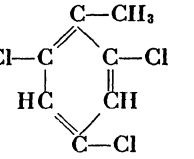
On toluene



2, 3-dichlorotoluene



2, 4-dichlorotoluene



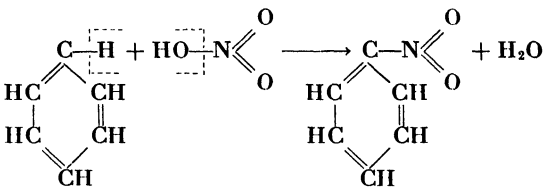
2, 4, 6-trichlorotoluene

Ortho, *meta*, and *para* are naming devices used when there are *only two substituents* on the benzene ring. If more than two substituents are present, their relative positions are indicated by numbers. *On toluene*, positions of carbon atoms in the ring structure are numbered, beginning with the carbon atom on which the methyl is substituted.

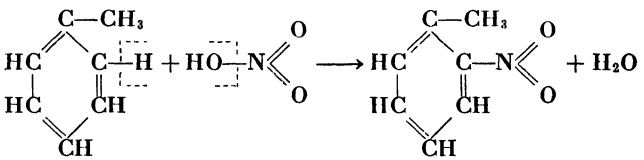
The chemist is interested in these halogen derivatives chiefly because, once a chlorine or bromine or iodine atom is substituted for a hydrogen atom on a carbon atom on any ring structure, the molecule becomes vulnerable at that point to many more attacks than with a hydrogen atom in such location.

Cyclic hydrocarbons with nitric acid to make nitro derivatives. Under favoring conditions benzene and toluene, as is true of all carbocyclics, will react with nitric acid to make *nitro* derivatives. Two such reactions are represented as follows.

Benzene + Nitric acid ⟶ Nitrobenzene + Water

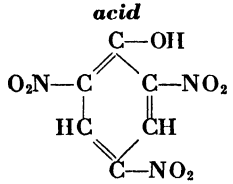


Toluene + Nitric acid ⟶ Ortho-nitrotoluene + Water

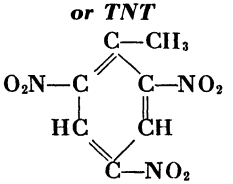


There are many important nitro derivatives of benzene, toluene, and other carbocyclic compounds. Among them is picric acid or trinitrophenol. Some of these nitro derivatives are explosives, one of the most potent of which is trinitrotoluene, commonly called by the abbreviated name of TNT. Formulas for these two nitro derivatives are given below.[2]

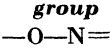
2, 4, 6-trinitrophenol or Picric acid



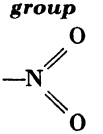
2, 4, 6-trinitrotoluene or TNT



Nitrite group



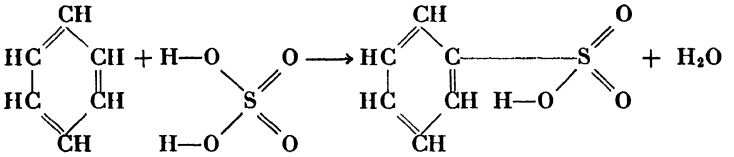
Nitro group



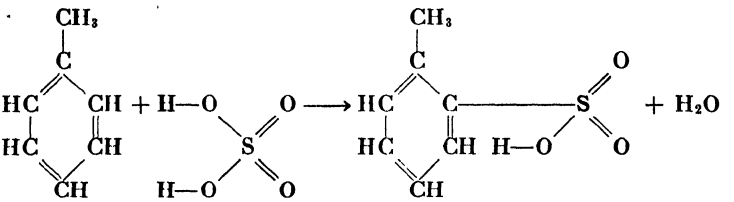
[2] The student should note the difference between the *nitro* and *nitrite* atom groups. Although both have the same composition and valence, hence are represented by the same empirical formula, namely, $-NO_2$, they are responsible for quite different behaviors on the part of the compounds containing them.

Carbocyclics with sulfuric acid to make sulfonic acid derivatives. Benzene, toluene, and other carbocyclics will also react with sulfuric acid in a manner similar to their reaction with nitric acid. Such reactions with benzene and toluene to make *sulfonic acid* derivatives are represented in the following.

Benzene + Sulfuric acid ⟶ Benzenesulfonic acid + Water

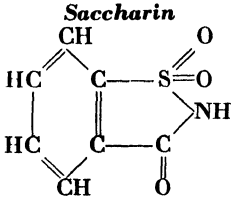


Toluene + Sulfuric acid ⟶ Orthotoluenesulfonic acid + Water



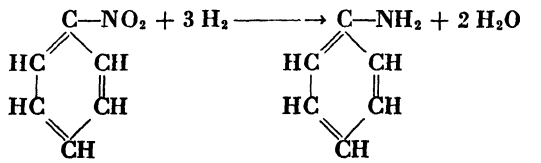
There are many other cyclic derivatives of sulfuric acid of which phenolsulfonphthalein (p. 349) and saccharin are examples. Saccharin, noted for its extremely sweet taste, is sometimes used as a sugar substitute for sweetening purposes. A comparison of the structural formulas for saccharin and sucrose (p. 375) will show that they are in no way chemically related.

Saccharin



Aniline, or aminobenzene, and derivatives. Large quantities of nitrobenzene are used with hydrogen for making aminobenzene, more commonly called aniline.

Nitrobenzene + Hydrogen → Aminobenzene (Aniline) + Water

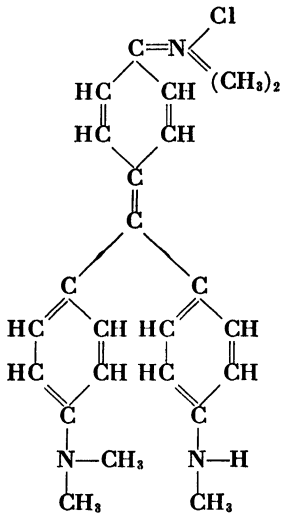


Aniline is used industrially as a solvent and as an intermediate in the synthesis of drugs and dyes. Workers exposed to aniline vapor sometimes develop symptoms of poisoning, notably disturbances of the nervous system and methemoglobin.

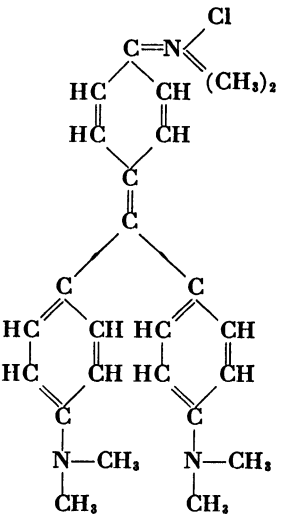
Aniline dyes. Aminobenzene is the parent compound from which aniline dyes are made. Indeed, the first dye of coal-tar origin, called mauve, which was produced on a commercial scale by its discoverer William Perkins, was made from aniline obtained from coal tar.

Methyl violet, crystal violet, and methylene or aniline blue are commonly used in the bacteriological laboratory for staining slides as a means for differentiating different strains of bacteria. The bacteriological "stain" called gentian violet is a mixture of methyl and crystal violets. Structural formulas for these three dyes reveal their aniline origin.

Methyl violet

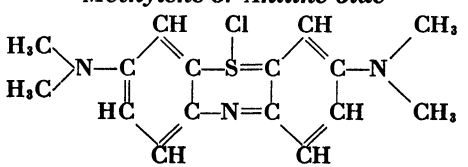


Crystal violet



***Gentian violet** is a mixture of methyl and crystal violet.*

Methylene or Aniline blue

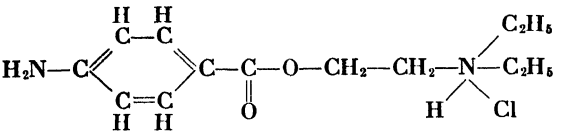


The formulas for methyl violet and crystal violet are identical save that 1 hydrogen atom in the former has been replaced by a methyl group in the latter; just this difference is responsible for the difference in shades of the two compounds.

Both *gentian violet* and *methylene blue* have a bacteriostatic effect on certain bacteria and have been used as antiseptics. Gentian violet is sometimes used in culture media because it inhibits the growth of most Gram-positive bacteria without affecting the Gram-negative organisms.

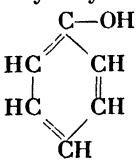
Drugs. Important drugs are also made from *aniline.* These include: acetanilid and acetophenetidin, or phenacetin, well-known analgesic antipyretics (p. 358); procaine (commercially known as Novocain), a local anesthetic produced in the laboratory as a substitute for cocaine; and the sulfanilamide drugs (pp. 364 to 365).

Procaine, a derivative of aniline

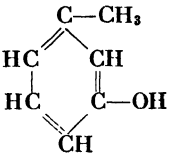


Phenols. When a hydroxide atom group is substituted for a hydrogen atom on a carbon within the ring structure a *phenol* results.

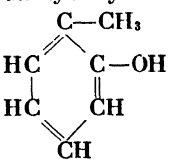
Phenol or Carbolic acid
(Monohydroxybenzene)



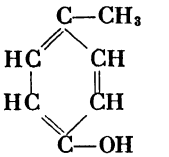
Meta-cresol
(Meta-hydroxytoluene)



Ortho-cresol
(Ortho-hydroxytoluene)



Para-cresol
(Para-hydroxytoluene)



This substitution cannot be made directly from a base in reaction with the hydrocarbon but must be made in a roundabout way through a series of reactions which we shall not consider.

The most important of all phenols and the simplest of this class of compounds is *monohydroxybenzene*, which is sometimes called simply by the class name, *phenol;* it is also called *carbolic acid.* This phenol is the parent compound for many drugs, dyes, and explosives; it is also used extensively in the manufacture of plastics of the phenol-formaldehyde type, of which Bakelite is a typical example.

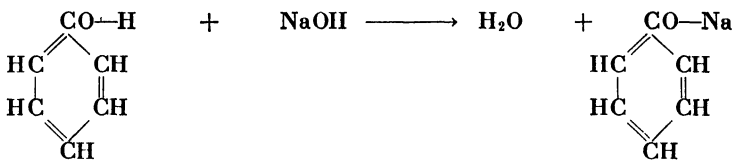
Another well-known group of phenols are the three *cresols*, which are monohydroxy substitutes on toluene. For differentiating formulas and names see page 346.

Phenols as acids. The name *carbolic acid* is not without significance because, despite the hydroxyl group and the suggestive ending *ol*, phenols are acids. The ionizable hydrogen atom is in the hydroxyl group, not one of the hydrogens on the ring. Most phenols yield hydrogen ions in very low concentration, hence are very weak acids, although the presence of a *nitro* group on the ring, as in picric acid (p. 343), makes for a relatively active organic acid. Phenols react with both bases and alcohols; the products are water and a salt or an ester.

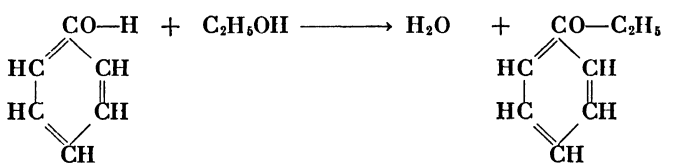
$$\text{Phenol} + \text{Base} \longrightarrow \text{Water} + \text{Salt}$$

$$\text{Phenol} + \text{Alcohol} \longrightarrow \text{Water} + \text{Ester}$$

Phenol (Carbolic acid) + Sodium hydroxide ⟶ Water + Sodium phenolate



Phenol + Ethyl alcohol ⟶ Water + Ethyl phenolate



Phenols as disinfectants. Practically all phenols have some degree of germicidal action and a number of them are used as disinfectants.

Phenol or carbolic acid (C_6H_5OH) is of historical interest as the first substance used in medicine for its disinfectant effect. It was

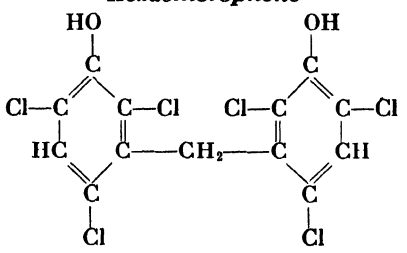
introduced in 1867 by Lister in his work in antiseptic surgery and continued to be widely used until comparatively recent years. It is a powerful disinfectant with an unusually great tendency to penetrate the tissues. Its action is due to attack on proteins; even dilute solutions are destructive to cells and, if taken internally, it is very toxic. The first-aid treatment for accidental contact of phenol with the skin is to flush with ethyl alcohol, which acts as a solvent and washes off the destructive substance. Phenol has been largely displaced by other disinfectants, some of them phenol derivatives, which are more active germicides than the parent compound and no more toxic.

The cresols (p. 346) are used as disinfectants in both homes and hospitals, usually as components of proprietary preparations such as Lysol and Creolin. Because they are only slightly soluble in water, they are frequently used in emulsion with soap functioning as the emulsifying agent. The cresols are claimed to have about three times the germicidal value of phenol; hence, they can be equally effective in more dilute solutions.

Picric acid or trinitrophenol (p. 343) is used in the treatment of superficial burns. Like the parent compound, it is a germicide with local anesthetic action. However, it must be used with caution because, if applied extensively or to the broken skin, it can be absorbed and is very toxic.

Hexachlorophene is a chlorinated phenol derivative. It is not soluble in water but will dissolve in ethyl alcohol and other organic solvents. This disinfectant is frequently incorporated in soaps and other detergent preparations which are sold under a variety of proprietary names. These preparations are widely used in surgical scrubs and for related purposes. Hexachlorophene is especially effective against Gram-positive organisms such as the streptococci and staphylococci. The substitution of chlorine in the phenol molecule is claimed to increase germicidal efficiency.

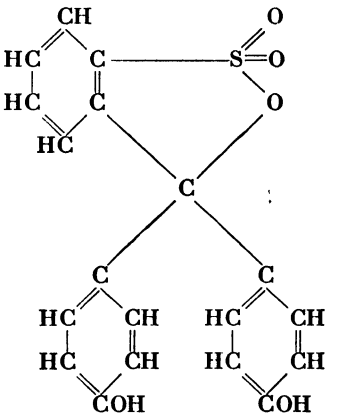
Hexachlorophene



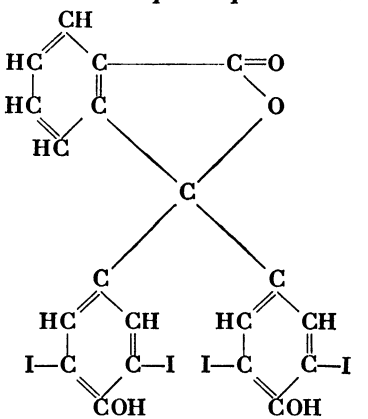
The phenolphthalein dyes. Among the phenol derivatives are the phenolphthalein dyes. These include *phenolphthalein*, used as an indicator in the laboratory because it is red in alkaline solution but

colorless in acid, also *phenolsulfonphthalein* and *sodium tetraiodophenolphthalein*, dyes used by the physician as diagnostic aids. Phenolsulfonphthalein, when injected intramuscularly, is excreted more or less promptly by the kidneys. A study of the percentage of the injected dye which is excreted with the urine within a specified time serves as a measure of the extent to which the kidneys are functioning. The sodium salt of *tetraiodophenolphthalein*, known in hospital practice as *soluble iodophthalein*, following administration, is absorbed by the gallbladder, which is thereby shown up to greater advantage on the x-ray plate.

Phenolsulfonphthalein

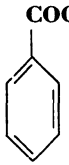
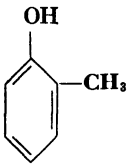
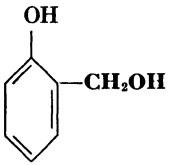
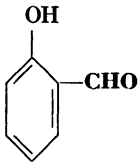
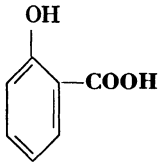


Tetraiodophenolphthalein



Aromatic alcohols, aldehydes, and acids. Our study thus far has been concerned with chemical behavior of cyclic compounds as it involves the carbocyclic structure itself. We shall now consider what can be expected from the side-chain substituents. Although each nitro and sulfonic acid substituent is subject to side-chain reactions peculiar to itself, we shall not consider these but shall limit our study to the side-chain reactions when *the substituent on the ring is a straight-chain hydrocarbon*, or *an alcohol, aldehyde*, or *organic acid* derived from such a hydrocarbon.

The student should anticipate possibilities for such reactions, because the straight-chain part of the cyclic hydrocarbon reacts like any such hydrocarbon; likewise the primary alcohol, the aldehyde, or the organic acid substituent of these aromatic compounds reacts like any primary alcohol, or any aldehyde, or any organic acid. For example:

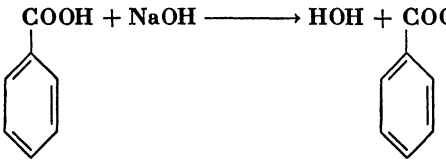
THE **methyl** PART OF THESE COMPOUNDS BEHAVES LIKE THE METHYL GROUP ANYWHERE	THE **primary alcohol** PART OF THESE COMPOUNDS BEHAVES LIKE ANY PRIMARY ALCOHOL (P. 291)	THE **aldehyde** PART OF THESE COMPOUNDS BEHAVES LIKE ANY ALDEHYDE (P. 302)	THE **carboxyl** PART OF THESE COMPOUNDS BEHAVES LIKE ANY CARBOXYL (P. 314)
 *Toluene*	 *Benzyl alcohol*	 *Benzaldehyde* (Bitter almond)	 *Benzoic acid*
 *o-Cresol*	 *Salicyl alcohol*	 *Salicylaldehyde*	 *Salicylic acid*

Note. In the above formulas the convention is introduced of showing the benzene ring without the carbon and hydrogen atoms. However, their presence in the compound should be understood. This representation brings the substituent groups, which are represented, into greater prominence.

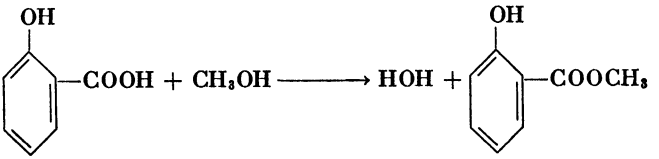
Alcohol, aldehyde, and acid derivatives in which these groups are substituted on cyclic structures, are called, respectively, ***aromatic alcohols***, ***aromatic aldehydes***, and ***aromatic acids***.

Aromatic salts and esters. As should be expected, aromatic acids will react with bases to make aromatic salts, and with alcohols to make aromatic esters of such acids. For example, sodium benzoate can be made from the reaction of benzoic acid with sodium hydroxide; methyl salicylate can be made from the reaction of salicylic acid with methyl alcohol.

Benzoic acid + Sodium hydroxide ⟶ Water + Sodium benzoate

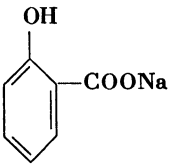
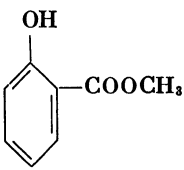
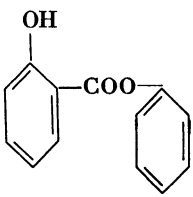
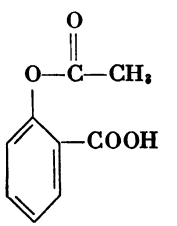


Salicylic acid + Methyl alcohol ⟶ Water + Methyl salicylate



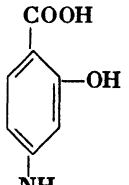
Sodium benzoate made after this manner is used as a preservative for foods; methyl salicylate made thus is synthetic wintergreen.

The salicylates. The salicylates form a group of related compounds some of which are familiar because of their medicinal uses.

NAME OF SALICYLATE	FORMULA REPRESENTATION	USE
Sodium salicylate		Used in the treatment of rheumatism and arthritis
Methyl salicylate		The active principle of oil of wintergreen, obtained both from this source and from synthetic preparation. Used externally as a counterirritant
Phenyl salicylate (Salol)		Used as a coating to protect drugs for passage through the stomach. The coating hydrolyzes in the intestine, thereby releasing the desired drug
Acetylsalicylic acid (Aspirin)		A well-known analgesic. Placement of the acetyl group is claimed to increase the antipyretic and analgesic action

Several members of this group are represented in the accompanying table (p. 351). Most salicylates have some properties in common. They are bacteriostatic in effect; they are antipyretics, meaning that they reduce the temperature in fever; they are analgesic. Salicylic acid, itself, is irritating to tissues and is used locally in certain corn remedies. The behavior common to all members of this group appears to be related, at least in part, to the release of salicylate ions in the tissues.

p-Aminosalicylic acid



Para-aminosalicylic acid (PAS) has recently come into prominence as effective in the control of tuberculosis. Its bacteriostatic action appears to be specific for certain strains of *M. tuberculosis*. It is neither an antipyretic nor an analgesic.[3]

Some cyclic compounds are complex. Some compounds of cyclic derivation are very complex, depending on the number and varieties of ring structures present in the molecule and the number and variety of side-chain substituents. Each ring structure and each side-chain substituent exhibits its own characteristic behavior.

For example, in the formula for the compound acetylsalicylic acid,

1. The carboxyl group indicates that this compound is an acid.
2. The acetyl group is attached at an ester linkage, and hydrolysis at this point will yield acetic acid and a phenol.
3. The presence of the benzene ring indicates that this compound exhibits the behavior of a carbocyclic hydrocarbon.

HETEROCYCLICS

Mention has been made of the heterocyclic compounds as substances with molecules which contain atoms of elements other than carbon in the cyclic structure. The elements most frequently included with carbon in the ring are nitrogen, oxygen, and sulfur.

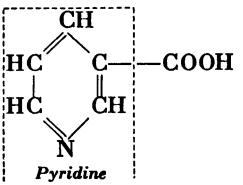
Heterocyclic compounds are abundant in plant and animal cells and many of them are of special physiological interest. Heterocyclic structures are found in coal tar; parent structures for laboratory synthesis are frequently obtained from this source.

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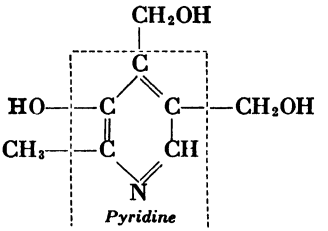
[3] Goodman, L., and Gilman, A.: *The Pharmacological Basis of Therapeutics*, 2nd ed., The Macmillan Company, New York, 1955, p. 1259.

Of physiological interest. Several members of the vitamin B complex contain heterocyclic nuclei. Both ***nicotinic acid***, or *niacin*, and ***pyridoxine***, or *vitamin* B_6, are derivatives of pyridine (p. 333).

Nicotinic acid

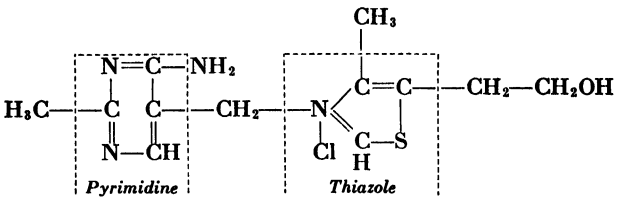


Pyridoxine



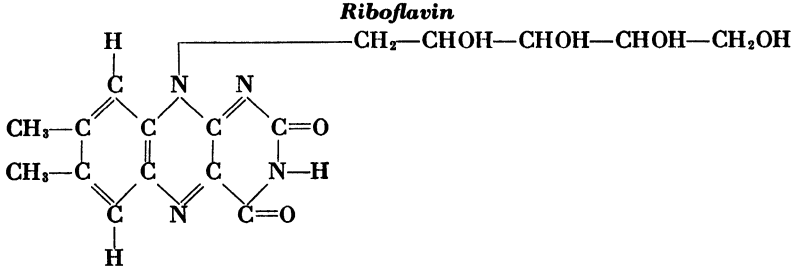
Thiamine chloride, *vitamin* B_1, is a derivative of the nitrogen-containing pyrimidine cycle and of thiazole, a heterocyclic containing both nitrogen and sulfur, as is indicated in its structural formula.

Thiamine or vitamin B_1



Riboflavin, *vitamin* B_2, likewise contains a complex heterocyclic structure attached to a carbohydrate group (p. 370)

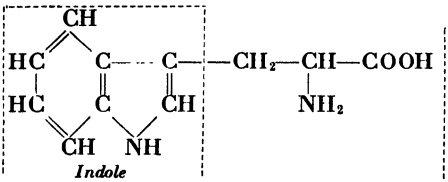
Riboflavin



All of these vitamins have now been identified as contributing to enzymes of established importance in the metabolism of glucose, fats, or protein in animal cells (p. 434).

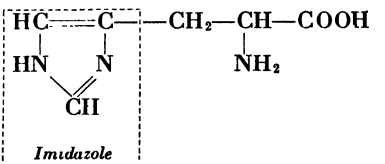
The amino acids ***tryptophane*** and ***histidine*** are derivatives of the heterocyclics *indole* and *imidazole*, respectively. Animals obtain these amino acids from foods of plant origin.

Tryptophane



Indole

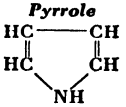
Histidine



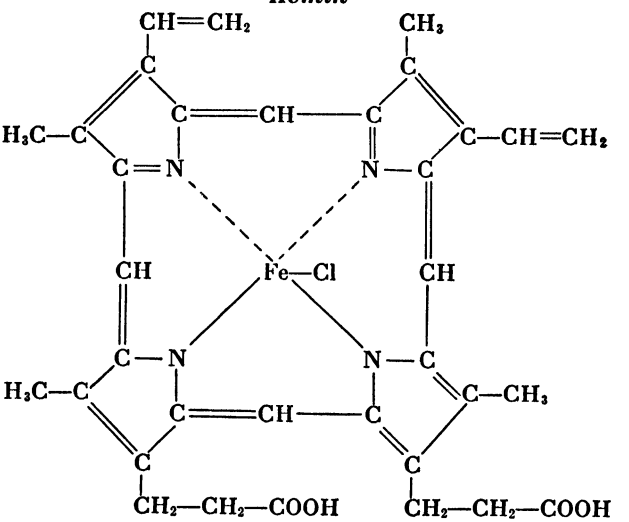
Imidazole

Finally, ***hemin,*** derived from hemoglobin, is a tetra derivative of the heterocyclic *pyrrole*. Plant *chlorophyll*, which is closely related to hemoglobin, also contains pyrrole as a constituent, but the element in the nucleus is magnesium rather than iron.

Pyrrole



Hemin

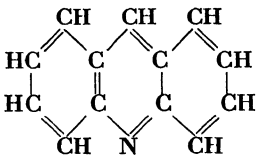


When the hemoglobin from the red blood cells is released and destroyed in the body, the pyrrole group is found in the bile pigments, bilirubin and biliverdin. The heme nucleus is also a constituent of the iron-containing enzymes known as the cytochromes.

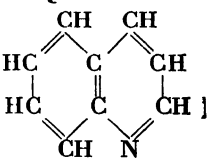
Commercial synthesis of heterocyclic derivatives. Coal-tar mixture (p. 336) also provides heterocyclic compounds from which

new compounds can be synthesized. Two such are *acridine* and *quinoline*.

Acridine

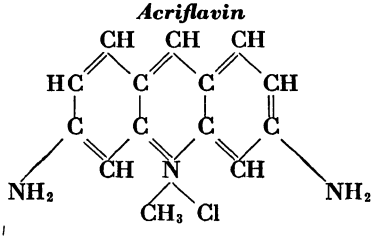


Quinoline

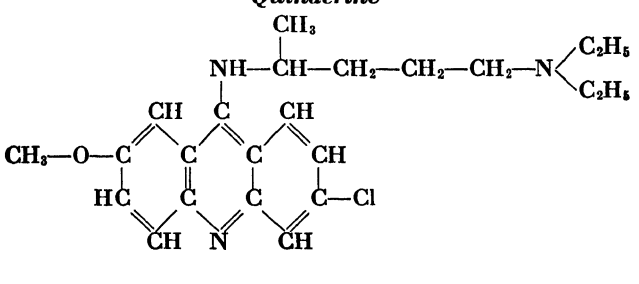


Acridine derivatives. Acridine serves as the parent structure for both dyes and drugs. One of the acridine dyes is *acriflavin*, so named because of its yellow color. This compound was first used by Ehrlich in his search for substances that would destroy protozoa. It proved, however, to be more effective as a bactericidal agent and is used for dressing wounds. *Quinacrine* is also an acridine derivative, and, like acriflavin, it is a yellow dye. It was introduced in 1930 under the name *Atabrine* for use in the treatment of malaria. During World War II, it played an important part in the control of certain types of malaria in the topics.

Acriflavin



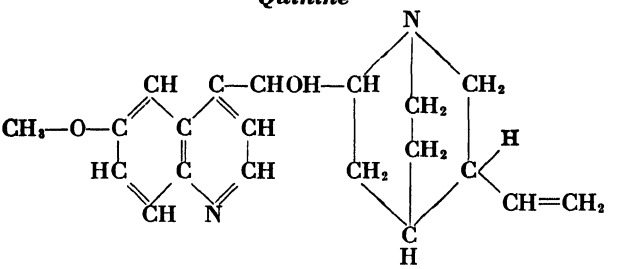
Quinacrine



Quinoline derivatives. *Quinine*, long used for the treatment of malaria, is a quinoline derivative. For centuries it has been obtained

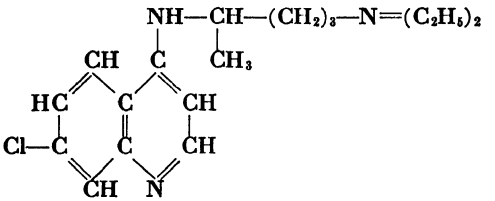
from the bark of the cinchona tree; it was first synthesized in the laboratory in 1944. But even before this synthesis was accomplished,

Quinine



chemists had succeeded in making some less complex quinoline derivatives which had antimalarial effect. But, these proved to be of limited usefulness because of their toxic effects. When, during World War II, the quinine imported from the Dutch East Indies was suddenly cut off, efforts to make synthetic quinine substitutes were greatly stimulated. A number of quinoline derivatives with antimalarial action were made, one of which is *chloroquine.*

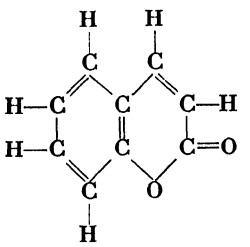
Chloroquine



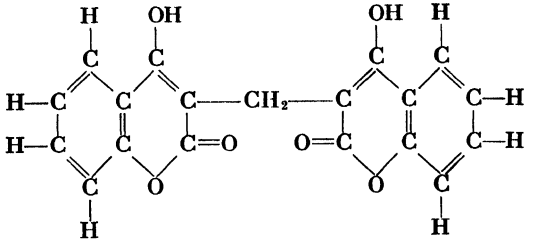
The quinoline derivatives have an advantage over the acridine derivatives in that they do not discolor the skin.

Coumarin and dicoumarol. Coumarin is an example of the heterocyclic compounds that contain oxygen in the ring structure. This compound has the odor of new-mown hay and is found in appreciable quantities in sweet clover. Bishydroxycoumarin, known as *dicoumarol,* was discovered to be in improperly cured clover-containing hay which was hemorrhagic for cattle. The chemical relation between these two compounds is evident in their formulas.

Coumarin



Bishydroxycoumarin[4]
Dicoumarol



The compound known as *dicoumarol* is now prepared synthetically and used medicinally as an anticoagulant. It delays clotting, an effect that can be counteracted by administration of vitamin K (p. 497).

The alkaloids. For many of the heterocyclic compounds which produce from mild to violent physical effects man still turns to living plants, just as the herb gatherers have since earliest times. The important group of drugs known as *alkaloids* are, for the most part, of natural occurrence. Thus, *atropine* is derived from the belladonna plant; *caffeine* from the coffee bean or tea leaves; *morphine* from the milk of the opium poppy—although its synthesis in the laboratory has recently been reported.

Chemically, alkaloids are nitrogen-containing heterocyclics. They are called alkaloids because, like alkalies, they react with acids to make salts. When used medicinally, usually the salts are prescribed, since alkaloids themselves are not soluble in water, whereas the salts made through reaction with certain acids, such as sulfuric and hydrochloric acids, dissolve readily. On the other hand, alkaloids form insoluble salts with some acids, tannic acids among them, hence the use of tannin as an antidote for poisoning by alkaloids.

SOME IMPORTANT DRUG GROUPS

Physiological effect in relation to chemical structure. In general, the physiological effect to be expected from many of the commonly used drugs has been known from ancient times. But it has remained for chemists of recent years to begin the task of finding

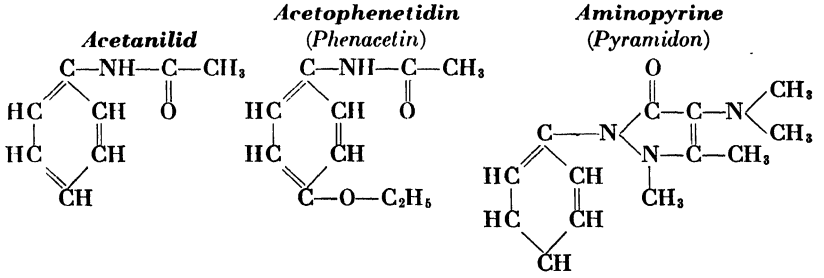
[4] *Bis*, appearing in the name of this compound, is an abbreviation for the word bisymmetrical. It refers to the 2 hydroxycoumarin groups attached in symmetrical manner to the methylene (—CH_2—) group.

what these compounds are which produce such effects, to analyze them, to determine the composition and molecular weights of these compounds, and then to reason their way as to the probable placement of atoms and atom groups within molecules of the same.

This detailed study of chemical composition and structure of molecules of compounds, together with a study of the physiological effects of various compounds, has led to the belief that certain atom groups within molecules are responsible for certain characteristic effects, whereas the behavior of the compound as a whole is mainly a summation of these various group actions. One of the researches of the pharmaceutical chemist is that of modifying a given drug in order to increase some desired physiological effect, or do away with some undesired side effect, by removing an atom or atom group and substituting some other atom or atom group.

Drugs with similar effects. The following are a few of the well-known drug groups whose chemical structure and pharmaceutical action have come to be fairly well understood. Hence this study is designed to suggest that all drugs within any group should be studied as related compounds—where such relation exists—rather than regarded, each one, as a new and different medication.

Acetanilid, *acetophenetidin* (or phenacetin), and *aminopyrine* (or Pyramidon) are analgesic antipyretics, meaning that they relieve pain and reduce fever. A study of the structure of their molecules suggests certain significant similarities and differences in composition.

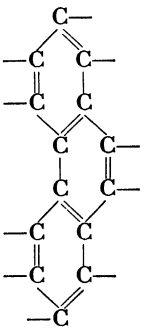


The common antipyretic effect exhibited by all three of these substances is attributed to the benzene nucleus. A similar effect is also seen in the salicylates (p. 351), whose molecules also contain the benzene ring. In their toxic effects both acetanilid and phenacetin resemble the parent compound, aniline, in that they form compounds with hemoglobin, thus interfering with the transportation of

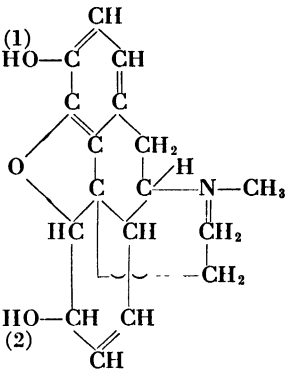
oxygen and producing cyanosis. Aminopyrine is not an aniline derivative as are the other two compounds. And, although very much like them in physiological effect, it does not engage in reaction with hemoglobin. However, this drug has been held responsible for an allergic type of reaction known as agranulocytosis which is characterized by a destructive attack on white blood cells.

The morphine family. These drugs depress the central nervous system, especially the cerebrum, and both relieve pain and induce sleep. They are all habit forming. The most important member of the group is *morphine*, which is used primarily to relieve pain.

Phenanthrene nucleus

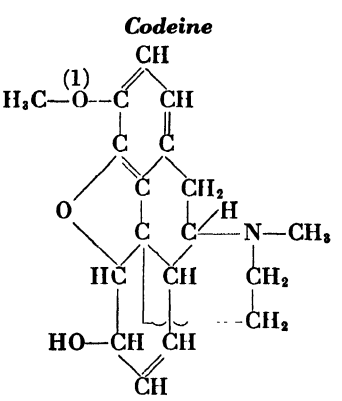


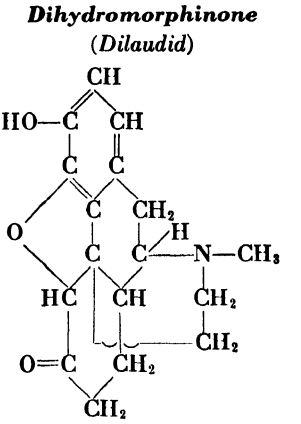
Morphine



Because of the complexity of these compounds the details of their structural formulas have been difficult to discover. The cyclic structure common to morphine and related drugs (p. 360) is the phenanthrene nucleus combined with a side chain containing nitrogen. The alkaloidal properties of these compounds are attributed to the nitrogen-containing side chain. The two hydroxyl groups in morphine as designated by (1) and (2) in the above formula are also significant. Replacement of the phenolic group (1) by a methoxy group (CH_3—O—), as in *codeine*, reduces the analgesic effect, and the depression of respiration as observed with morphine. Replacement of the hydroxyl (2) exaggerates the narcotic effect, also the respiratory depression. Such a modification has been made in *dihydromorphinone* (*Dilaudid*). If either of these hydroxyls is replaced, the vomiting which frequently accompanies the use of morphine is decreased.[5]

[5] Goodman, L., and Gilman, A.: *The Pharmacological Basis of Therapeutics*, 2nd ed., p. 218.

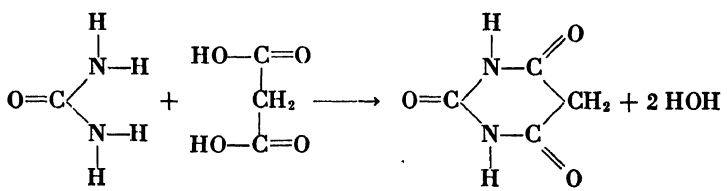




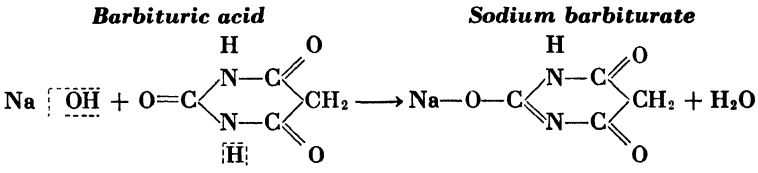
The alkaloids morphine and codeine are both of natural occurrence, being obtained from the juice of the opium poppy. Dihydromorphinone is a synthetic alkaloid. *Methyldihydromorphinone*, also known as *Metapon*, is another synthetic alkaloid. It is similar to dihydroxymorphinone but has a methyl group replacing one of the hydrogen atoms on the carbon adjacent to the ketone group. This new compound is of interest because it is a product of a systematic search on the part of the pharmaceutical chemist to find a modification which will give an effective but nonhabit-forming narcotic. Metapon has proved to be disappointing in this respect; like other members of this group, it is habit forming.

The barbiturates. These important compounds are not regarded as cyclic derivatives although their structural formulas are suggestive of such origin. Instead, they are derivatives of urea and malonic acid.

Urea + Malonic acid ⟶ Barbituric acid + Water



It will be noted that barbituric acid has no carboxyl group, but it is capable of reacting with bases to make water and salts; hence, it is regarded as being an acid. The salts thus made are more soluble than the barbituric acid itself.



The pharmaceutical chemist has been particularly successful in providing modifications within this drug group with the result that a great many barbituric acid derivatives are known and encountered in general use. In many instances both the barbituric acid derivative and its more soluble sodium salt are in use. Let us consider first the common behavior to be expected from any member of this group, then significant differences among various members.[6]

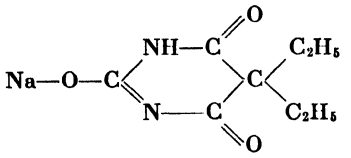
All barbiturates are sedatives and hypnotics. Some are mildly depressant and function over a long period of time; others are more powerful drugs but with a shorter functioning period; a few are depressant but quite rapidly destroyed in the body. Any one of them, in large doses, is a respiratory depressant. The varied effects are related to chemical structure. In general, as the length of the hydrocarbon substituent increases, up to side chains of 5 or 6 carbon atoms, there is an increase in the hypnotic effect of the drugs, but the period of depression is shorter. This type of modification has been achieved in *Amytal*, *pentobarbital*, and *Seconal*, as is evidenced in their formulas (p. 362). Seconal also contains an unsaturated radical, a substituent which increases the depressant effect of the drug. *Phenobarbital* or *Luminal* contains a phenyl radical, a modification which renders this drug useful in epilepsy because of its anticonvulsant effect.

Barbiturates which contain the straight-chain hydrocarbon and phenyl radicals are quite stable within the body, whereas those whose molecules contain more complex cyclic structures are rapidly destroyed, with the result that their action is of relatively shorter duration. The following compounds are selected as typical members of the group, and their formulas should be studied in reference to the foregoing discussion.

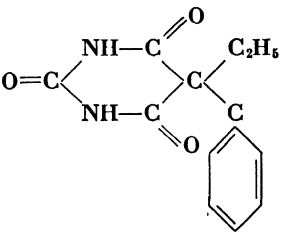
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[6] Goodman, L., and Gilman, A.: *The Pharmacological Basis of Therapeutics*, 2nd ed., pp. 123–26, 138.

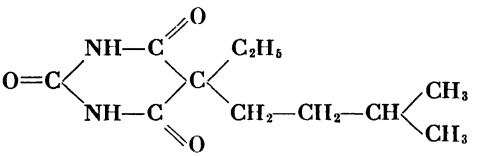
Barbital sodium or Veronal takes effect about a half hour after administration. Its effect wears off gradually, a feeling of lassitude often persisting for from 24 to 48 hours after administration.



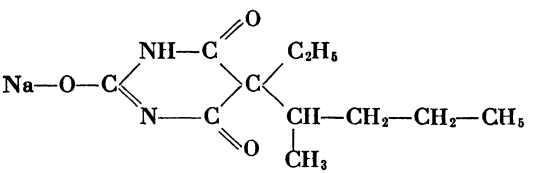
Phenobarbital or Luminal also belongs to the group of long-acting barbiturates. The anticonvulsant and prolonged sedative effects make it especially useful in epilepsy.



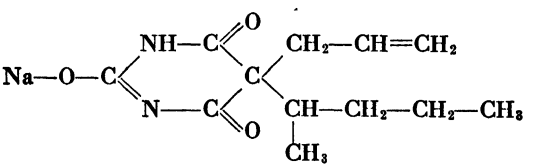
Amytal or iso-amyl-ethyl barbituric acid becomes effective in from 15 to 30 minutes after administration. Duration of action varies from 3 to 6 hours.



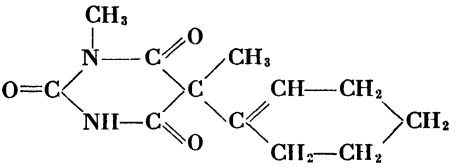
Sodium pentobarbital or Nembutal belongs to the group of barbiturates whose action is fairly rapid and the duration of the hypnotic effect is about 3 hours.



Seconal also belongs to the group whose action follows promptly upon administration but is of relatively short duration.



Hexobarbital or Evipal is used intravenously as an anesthetic. Its action is very rapid but of short duration.



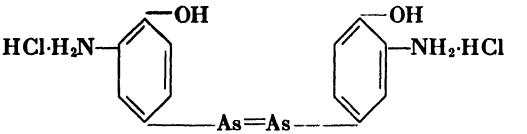
Chemical structure and materia medica. Students who are interested in the study of the many drugs in common medicinal use will meet with many instances where compounds show similarities and differences in chemical composition related to similar and dissimilar physiological effects. Recognition of the existence of such relations can be used to simplify the study of materia medica in that it enables the related drugs to be studied as a group. Thus, when a new compound comes into use, if it is a modification of compounds already familiar, its general behavior can be anticipated and attention can be directed to any particular differences which this compound exhibits in relation to other members of the group.

CHEMOTHERAPY

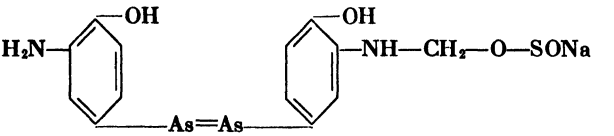
Introduction. One of the most dramatic developments in modern medical science has come in the field of chemotherapy. This term was introduced by Paul Ehrlich in 1909 in connection with his famous studies of the effect of arsenic compounds on spirochetes. Underlying this research was the concept that there should be significant differences in chemical composition and metabolism between the host and the invading organism. The ideal chemotherapeutic agent should be so selective as to attack and kill the invader without injury to the host. But there are great similarities in composition and metabolic processes in all living cells—whether of microorganisms or humans; hence the search for suitable chemotherapeutic agents proved to be tedious and often unrewarding.

The first great achievement along this line was that of Ehrlich in the synthesis of *arsphenamine*, an arsenic compound, for the treatment of syphilis. The successful compound was number 606 in the series of substances studied for this purpose. Later, *neoarsphenamine*, number 914 in the series, came into use. The modification made was that of producing a sodium sulfonate salt (p. 364).

Arsphenamine or Salvarsan



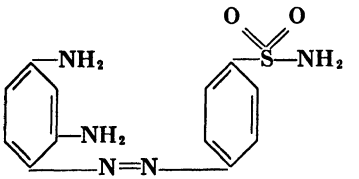
Neoarsphenamine or Neosalvarsan



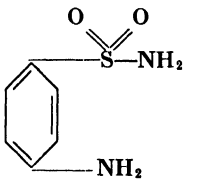
This compound is soluble in water, and the reaction of the resulting solution made it more suitable for intravenous injection than was the parent compound.

The sulfanilamides. About 1935 the attention of the medical world was called to the compound *Prontosil*, a red dye which was destructive to streptococci. Shortly after this it was discovered that the portion of the Prontosil molecule which was responsible for the effectiveness of the drug is the sulfanilamide group; so the simpler compound came into use.

Prontosil

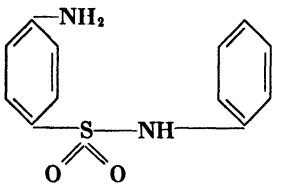


Sulfanilamide

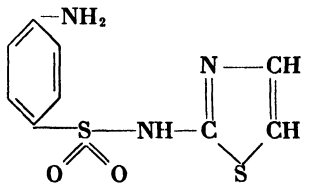


Because of the relative ease with which substituents can be made at the amino group, many derivatives of sulfanilamide have been made. Typical examples are *sulfadiazine* and *sulfathiazole*.

Sulfadiazine



Sulfathiazole



Certain of the sulfanilamide derivatives have proved to be very

poorly absorbed from the intestinal tract and can be administered by mouth for local action against intestinal bacteria. One example of this group is succinylsulfathiazole in which the succinyl radical, $COOH—CH_2—CH_2—CO—$, is substituted for one of the hydrogen atoms at the free amino group of the sulfathiazole molecule.

The "sulfa drugs" proved to be very effective not only against certain of the streptococci but against many other organisms, including pneumococci, gonococci, and meningococci, also certain of the pathogenic viruses.

The startling success which followed the introduction of the sulfanilamide drugs not only gave new impetus to this line of research, but introduced a different concept concerning the functioning of chemotherapeutic agents. Although the mechanism of action of these compounds is still uncertain, there is experimental evidence to suggest that they may act by interfering with the functioning of enzyme systems which favor reactions of vital importance to the microorganisms. In this way the infection is held in check until the host's own defensive mechanism can dispose of the invader. One theory in regard to the behavior of the sulfanilamides is that they compete with the compound para-aminobenzoic acid—a vitamin required by some bacteria, and which has a structure somewhat similar to sulfanilamide—for a position within an essential enzyme system. If the sulfanilamide molecule is accepted into the enzyme structure (instead of para-aminobenzoic acid) the resulting compound cannot function as an enzyme.

Para-aminobenzoic acid



All of the sulfanilamide drugs are capable of provoking toxic reactions. It should not be surprising to discover that some of these disturbances are similar to those shown by other aniline derivatives (p. 358). Certain of these compounds, notably sulfapyridine and sulfadiazine, are not very soluble in acid environment and, if the urine is acid, these drugs may precipitate in the kidney as crystals which cause pain and mechanical damage in that organ. Salts such as sodium bicarbonate, sodium lactate, or sodium citrate are frequently administered as an accompanying medication to ensure an alkaline urine in which these compounds stay in solution.

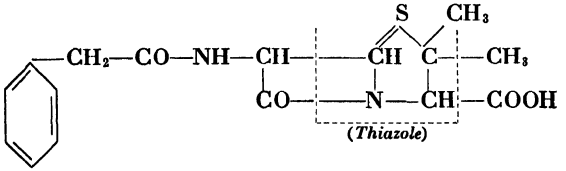
Antibiotics. Shortly after the introduction of the sulfanilamides as therapeutic agents came the discovery of penicillin, the first of

the *antibiotics.*[7] These substances are produced in the cells of molds, bacteria, and other microorganisms and have proved effective in the control of a variety of infections. They are believed to interfere with the life activities of the invading microorganisms, thus holding the invader in check. Many substances have been tested for antibiotic action and a number of substances of this nature are now in use.

Following the identification of material with antibiotic action one of the first problems confronting the pharmaceutical chemist is to separate the effective substance from impurities with which it is invariably associated. Then he must determine its chemical composition and structure. The chemical nature of a number of antibiotics has been determined, in whole or in part, and structural formulas for the molecules have been proposed. Practically all members of this group appear to be complex and quite dissimilar compounds. Up to the present only two, *penicillin* and *chloramphenicol,* have been prepared synthetically—and chloramphenicol is the only antibiotic as yet available, commercially, in synthetic form.

Penicillin was isolated by Fleming from the mold known as *Penicillium notatum.* It proved to be effective against a wide range of microorganisms, including staphylococci, streptococci, meningococci, and the spirochete of syphilis. The first penicillin preparations introduced in medicine were crude drugs, accompanied by various impurities. But by 1945, crystalline penicillin had been obtained from this material, and its composition had been determined. A number of different but closely related compounds have been discovered in the mixture and designated as penicillins F, G, K, and X, respectively. They are all acids of similar structure, built around a thiazole nucleus. One of these compounds, *penicillin G* or *benzylpenicilloic acid,* has been synthesized. Its structural formula is as follows.[8]

Penicillin G or Benzylpenicilloic acid



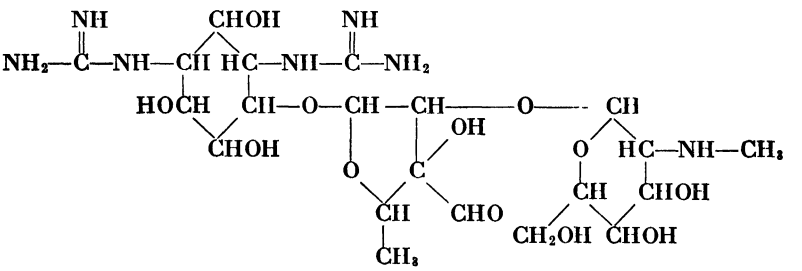
[7] Antibiotic, coming from the Greek, *anti* (against) and *bios* (life), refers to a substance produced by one organism which is detrimental to the life of another organism.

[8] Editorial Board of the Monograph in the Chemistry of Penicillin: "The Chemical Structure of Penicillin: A Brief History," *Science,* 105:653–59, 1947.

Pure crystalline sodium penicillin G is relatively stable in dry form. In a neutral buffered solution, even at room temperature, it has a half-life period of 10 days, but in a moist acid environment it is rapidly destroyed.[9] The sodium and potassium salts of penicillin G are the chief components of the penicillin mixtures now in use.

Streptomycin, produced by a fungi known as *Streptomyces griseus*, is of special interest because it is the one antibiotic which, to date, has proved effective in the treatment of tuberculosis. Its structural formula is as follows.

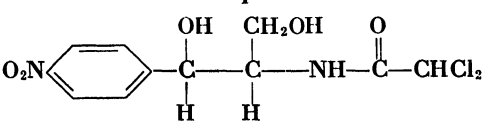
Streptomycin



This substance is relatively stable at room temperature in both dry form and in solution. One of its limitations as a therapeutic agent is the marked tendency of microorganisms against which it first proved to be effective to develop resistant strains. It also exhibits toxic effects, notably through an attack on the auditory nerve. Some individuals become sensitive to this substance and develop skin irritations on coming in contact with it.

Chloramphenicol or Chloromycetin was first isolated from one of the streptomyces organisms which inhabit the soil. It can also be produced synthetically. Of all the presently known antibiotics this substance has the simplest composition. Its structural formula is as follows.

Chloramphenicol



This antibiotic is effective against many Gram-negative organisms,

[9] Goodman, L., and Gilman, A.: *The Pharmacological Basis of Therapeutics*, 2nd ed., p. 1328.

including the typhoid fever organism. As a nitrobenzene derivative it is not surprising to find that it frequently gives toxic effects, notably disturbances of the bone marrow, the site of production of blood cells. This seriously limits its usefulness.

There are a number of other important antibiotics, but these three will serve to indicate that they are not a chemically related group but a variety of quite different compounds. Moreover, the mechanisms whereby antibiotics control the activities of microorganisms are still obscure. The possibility that they interfere with the functioning of enzymes has been suggested and, in some instances, tested in the laboratory. However, no specific answer to this question is as yet forthcoming.

QUESTIONS

1. What is meant by each of the following? Give an example of each by means of its structural formula and name: (a) cyclic compound, (b) cyclic derivative, (c) carbocyclic, (d) heterocyclic, (e) condensed cyclic.
2. What is a nitro derivative; a sulfonic acid derivative; a chloro derivative? In each case select a suitable cyclic derivative for illustration, assemble its structural formula, and indicate the significant atom group. If possible cite other examples of compounds whose names indicate that they belong to any of the above classifications.
3. What is a phenol? Name several disinfectants that are phenols.
4. In regard to the compounds carbolic acid and picric acid:
   a. Give another name for each.
   b. Why are these compounds called acids?
   c. What are their respective uses?
   d. Cite other items of interest in respect to each?
5. Benzene and aniline are both widely used in industry. Name some of the industries in which each of these compounds is used. If workers in these industries are not afforded adequate protection from contact with these compounds, to what health hazards will they be subjected?
6. In respect to sodium salicylate, methyl salicylate, salol, and aspirin:
   a. Of what cyclic compound are these drugs derivatives?
   b. What, if any, physiological effects are common to all members of this group?
   c. How are similarities in chemical behavior accounted for? What may be responsible for differences in behavior?
   d. What recently developed chemotherapeutic compound is chemically related to salicylic acid? For what is it used?
7. What significant difference in the structure of the codeine molecule is believed to be responsible for the less powerful narcotic action of this drug in comparison with the effect produced by morphine? What modification in dihydromorphinone is believed to make it a more powerful analgesic than morphine?

8. What advantage is gained in the use of sodium salts of barbituric acid derivatives over the use of the derivatives themselves?

9. What is meant by the term "chemotherapy"? What principle underlies the use of drugs for such purpose and why has the search for suitable drugs been so difficult? Name two drugs used successfully in chemotherapy, and specify for what function.

10. What theory has been advanced to account for the functioning of the sulfanilamide drugs?

11. What advantage, from the standpoint of possible therapeutic use, has come through the synthesis of a penicillin compound?

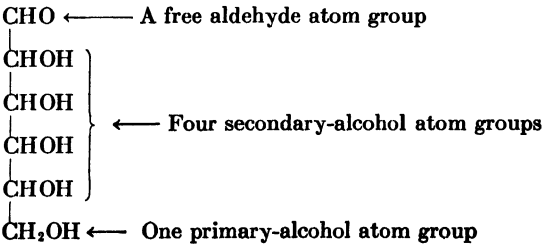
12. Which of the currently used antibiotics has been synthesized and prepared commercially? Of what cyclic compound is it a derivative? What serious limitation has been encountered in the use of this compound?

CHAPTER 26

CARBOHYDRATES

The carbohydrates include sugars, starches, and celluloses; they are widely distributed in nature—abundantly in plants and to a limited extent in animals. *Sugars* are found circulating in all plant fluids. *Starches* are stored in the roots of some vegetables and in the ripened seeds of many plants. The woody structure of trees, as well as the supporting fibers of all stems and leaves of plants, is largely *cellulose*, and cotton fiber is relatively pure cellulose. The importance of these carbohydrates of plant origin is recognized when one considers the large part that sugars and starches play in providing the food supply of man and of other animals and the usefulness of celluloses as fuels, in construction, and in the production of paper, fabrics, and an ever-increasing group of useful synthetic materials. Carbohydrates also occur in animals. Thus, *glucose* is found in blood and lymph, *lactose* is produced in the mammary glands, and *glycogen*, which is related to the starches, is stored in tissue cells, particularly those of the liver and muscles.

Composition. Carbohydrates, as their name implies, are composed of the elements carbon, hydrogen, and oxygen. This is illustrated in the formulas for glucose ($C_6H_{12}O_6$) and sucrose ($C_{12}H_{22}O_{11}$). The chemical behavior of carbohydrates indicates that their mole-



cules contain both primary and secondary alcohol groups together with either an aldehyde or a ketone group—which may be free or bound within the molecule. These characteristic atom groups are illustrated in the preceding structural formula for the glucose molecule.

Photosynthesis. Carbohydrates are made in the chlorophyll-containing cells of the green plants from carbon dioxide obtained from the air and water entering through the roots. The other product of this reaction is oxygen, which escapes into the air. This synthesis is possible only as radiant energy from sunlight is captured within the plant cells and transformed into chemical energy, hence, the name *photosynthesis*. The intermediate steps in the building of carbohydrate are as yet uncertain, in spite of much able research. It is generally accepted that oxygen is released from water and that the hydrogen is thus made available for the reduction of carbon dioxide. The carbohydrate is made through a series of intermediate reactions. Chlorophyll functions to absorb light radiations, which are transformed into chemical energy. Approximately 690 kg-calories[1] of radiant energy must be transformed for the synthesis of 1 mole of glucose and the accompanying 6 moles of oxygen. The following equation summarizes the reaction, assuming glucose to be the carbohydrate made.

$$\begin{array}{ccccccccccc} 6\,CO_2 & + & 12\,H_2O & \xrightarrow{\text{chlorophyll}} & C_6H_{12}O_6 & + & 6\,O_2 & + & 6\,H_2O \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ \text{Chemical energy} & + & \text{Chemical energy} & + \text{ Sunlight} \rightarrow & \text{Chemical energy} & + & \text{Chemical energy} & + & \text{Chemical energy} \end{array}$$

No reaction known to man is of greater importance than this synthesis. Plant carbohydrates are important foods as well as having other useful functions. Fats and proteins are also believed to originate from products of photosynthesis. The oxygen made continuously by this process replenishes the supply of this essential substance in earth's atmosphere. And through this reaction sunlight is captured by plants and transformed into chemical energy which is stored in plant carbohydrate and oxygen. This energy, in turn, becomes available for subsequent transformations within living cells, to produce the various energies essential for living, and in the environment for the production of heat and other forms of energy.

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[1] Since a mole of glucose weighs 180.156 gm, the amount of radiant energy required for the synthesis of 1 gm of glucose is approximately 3.82 kg-calories.

Basis for classification. Carbohydrates are classed as monosaccharides, disaccharides, and polysaccharides on the basis of their hydrolysis possibilities.

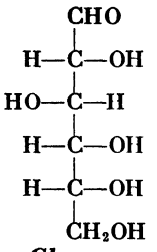
1. *Monosaccharides* are not subject to hydrolysis.
2. A *disaccharide* is a carbohydrate, 1 molecular weight of which reacts with water in hydrolysis to make 2 molecular weights of monosaccharide.
3. A *polysaccharide* is a carbohydrate, 1 molecular weight of which reacts with water in hydrolysis to make *several*, sometimes *many*, molecular weights of monosaccharide.

Monosaccharides. Among the monosaccharides which occur in plant and animal cells, the most important are the *hexose* sugars. A *hexose* is a carbohydrate 1 molecular weight of which contains 6 atomic weights of carbon, hence whose molecule, supposedly, contains a chain of 6 carbon atoms. The three monosaccharides of greatest interest to us, namely, *glucose*, *fructose*, and *galactose*, belong in this group.

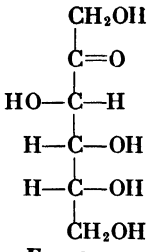
There are monosaccharides other than hexoses, likewise classed according to the number of atomic weights of carbon within their molecular weights, hence, according to the number of carbon atoms chained together in their molecules. Thus, there are bioses, trioses, pentoses, etc. Pentoses occur commonly in plant cells; one pentose, known as ribose, contributes to cell nuclei in both plant and animal tissues; it also forms part of an important enzyme system.

Both glucose and fructose occur, associated with sucrose, in the juices of fruits and vegetables. Glucose is of special importance because it is the carbohydrate found in circulation in blood and lymph on its way to the cells, where it functions with oxygen in the production of energy. Galactose is obtained from the hydrolysis of milk sugar, or lactose, and also from the seaweed known as agar. It contributes to components of nerve tissue.

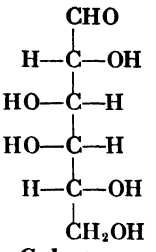
All three of these monosaccharides have the same molecular weight and the same element composition as is represented by the same empirical formula, $C_6H_{12}O_6$. Similarities and differences in their chemical behavior are explained as presumably being due to similarities and differences in the arrangement of the atoms within their molecules, as represented in the following structural formulas. These formulas should be studied closely and note made of points within the three molecules wherein they are alike and wherein they are different.



Glucose



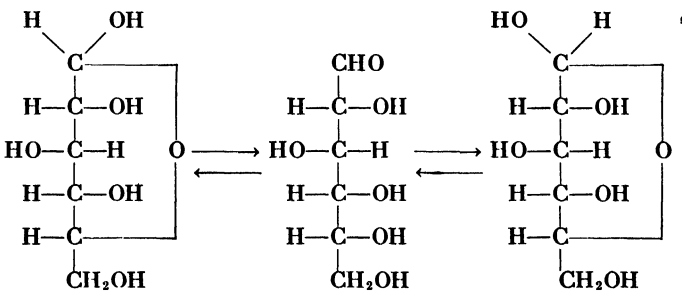
Fructose



Galactose

Aside from being both primary and secondary alcohols (p. 293), each of these monosaccharides functions at one point in its molecule either as an aldehyde or as a ketone. For this reason glucose and galactose are sometimes called *aldoses*, meaning sugars which are, in part, aldehydes; whereas fructose for a similar reason is called a *ketose*.

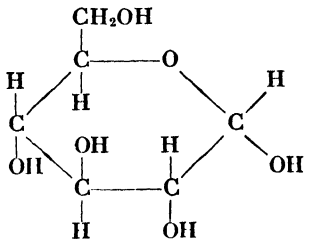
Although glucose and galactose are regarded as aldehydes, and fructose as a ketone, there is evidence that when these sugars are in water solution they exist,



for the most part, in less active forms. The active form, presumably, disappears as the oxygen atom from either the aldehyde or ketone group becomes a link between 2 carbon atoms in the molecule. In the inactive glucose molecule an "oxygen bridge" is believed to occur between the first and the fifth carbon atoms, as represented below. Two such inactive forms, designated as alpha (α)- and beta (β)-glucose, are believed to exist in glucose solutions in equilibrium with the more active aldehyde form.

When glucose reacts as an aldehyde the equilibrium between these three forms is disturbed in favor of making more of the aldehyde form from the less active molecules with oxygen bridges. Fructose and galactose, likewise, are believed to exist in solution, with both active and inactive forms at equilibrium with each other.

The formulas for these sugars that indicate the presence of oxygen bridges are frequently represented as ring structures as suggested below for α-glucose. A study of this formula will show that the same general structural relationships between the atom groups are represented both in ring and straight-chain formulas.



α-Glucose

Disaccharides from hexoses. ***Occurrence.*** The three important disaccharides are sucrose, maltose, and lactose. *Sucrose* is found in fruit and other plant juices, usually in association with the two monosaccharides glucose and fructose. It is especially abundant in the sap of sugar cane and the sugar beet, and it is from these plants that most of the world's commercial supply of sucrose is obtained. The sugar in the sap of the sugar maple is also largely sucrose. *Maltose* occurs in sprouted grain, and it is one of the first products of the hydrolysis of starches (p. 380). *Lactose*, commonly called milk sugar, is present in the milk of all mammals.

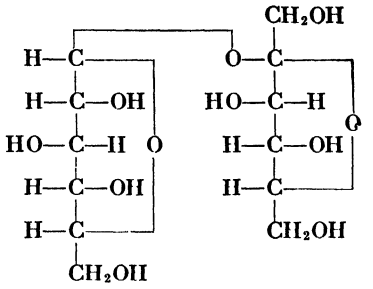
Composition. These three disaccharides have molecular weights of identical composition, all represented by the same empirical formula, $C_{12}H_{22}O_{11}$. They are, nonetheless, different compounds. Some of these significant similarities and differences are represented in the structural formulas for their molecules. Because it is known that 1 molecular weight of sucrose hydrolyzes to make 1 molecular weight of glucose and 1 molecular weight of fructose, the sucrose molecule is represented as composed of 1 incomplete molecule of glucose combined with 1 incomplete fructose molecule. Similar reasoning leads to the conclusion that the molecule of maltose is composed of 2 incomplete glucose molecules. And, because lactose hydrolyzes to make glucose and galactose, it is reasoned that the molecule of lactose consists of an incomplete glucose molecule combined with an incomplete galactose molecule. Structural formulas for molecules of these disaccharides are as follows:

EMPIRICAL REPRESENTATION STRUCTURAL REPRESENTATION

A. ***Sucrose molecule***

Incomplete glucose molecule $(C_6H_{11}O_6)$ · Incomplete fructose molecule $(C_6H_{11}O_5)$

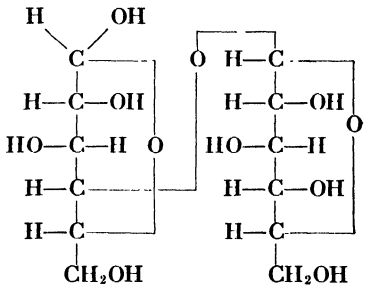
$C_{12}H_{22}O_{11}$



B. ***Maltose molecule***

Incomplete glucose molecule $(C_6H_{11}O_6)$ · Incomplete glucose molecule $(C_6H_{11}O_5)$

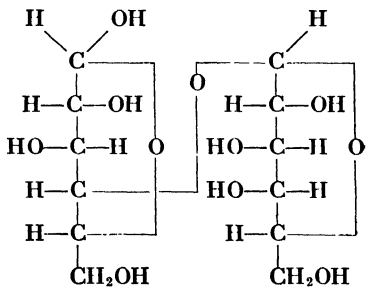
$C_{12}H_{22}O_{11}$



C. ***Lactose molecule***

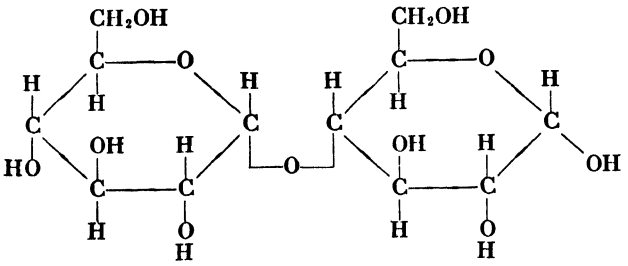
Incomplete glucose molecule $(C_6H_{11}O_6)$ · Incomplete galactose molecule $(C_6H_{11}O_5)$

$C_{12}H_{22}O_{11}$



Careful study of these structural formulas should show that they represent both the disaccharide nature of the three carbohydrates and the specific monosaccharide constituents which are combined in each of these molecules. It is less evident, at first glance, that a potential aldehyde group is present in the molecules of lactose and maltose. But reference to the formula for α-glucose (p. 373) reveals that at the first carbon atom of both lactose and maltose there is a structural configuration similar to that of the inactive glucose molecule. At this point the disaccharide molecules can yield the active aldehyde form. In the sucrose molecule structure, the potential aldehyde group of glucose and the potential ketone group of fructose are bound in the link which joins the two molecule fragments; this, seemingly, should render sucrose inactive at these points and, actually, sucrose is not a reducing sugar.

As with the monosaccharides, the disaccharides are also frequently represented by cyclic formulas. The following is the cyclic formula for maltose.



Formula for *maltose molecule*

Polysaccharides. The polysaccharides of greatest importance are the *starches*, *dextrins*, *celluloses*, and *glycogen*. The first three are of plant origin; glycogen, as far as is known, is the only polysaccharide present in animal cells. Polysaccharides also contribute to the structure of microorganisms, being found in the protective capsules of the pneumococci, streptococci, and certain other encapsulated bacteria.

Starches are the storage carbohydrates for plants. They are the chief components of grains; they occur in roots and tubers, in ripe corn and legumes, and in unripe fruits. They serve as a reserve of nutrient for the growing plant. They also make up a portion of man's food supply. *Dextrins* are intermediate products of the hydrolysis of starches.

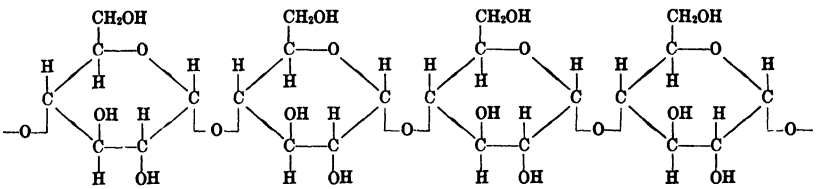
Celluloses form the supporting fibers of the roots, trunk, stem, and leaves of plants. They have little food value for man, probably because he has not been provided with enzymes for their hydrolysis. However, they function in the food mass to provide bulk, which is needed for effective peristalsis. Aside from this physiological function, celluloses are also important in man's external concerns. They are the principal components of wood, which is valued as a fuel and for construction. As fibers of cotton and flax, celluloses contribute to fabrics. Celluloses, obtained chiefly from wood, are used in the manufacture of paper, rayons, and a variety of plastics—including photographic films, lacquers, cellophane wrappings, the protective layer of "safety glass," and many other materials in common use.[2]

Composition. The formula $(C_6H_{10}O_5)_n$ represents the composition of the molecular weight of all of the above-mentioned polysaccharides. It indicates that they are *hexosans*, that is, polysaccharides

[2] Lowy, A.; Harrow, B.; and Apfelbaum, P. M.: *Introduction to Organic Chemistry*, 7th ed. John Wiley & Sons, Inc., New York, 1951, pp. 210–13.

which on hydrolysis yield monosaccharides of the hexose variety. Starches, dextrins, celluloses, and glycogens all hydrolyze to yield glucose. The empirical formula indicates also that the hexosan molecules are composed of n hexose units—the number (n) varying for different polysaccharides. The very large molecular weights of these polysaccharides indicate that many monosaccharide units combine to form the polysaccharide molecule.

Starches, although commonly referred to as if they were single substances, are composed of two different components known as *amylose* and *amylopectin*, respectively. Both are made up of glucose units but their molecules are built according to different patterns. *Amylose* appears to have a simple structure consisting of a long single chain of incomplete glucose molecules, as is suggested by the following structural formula.



Amylopectin, also *glycogen*, seem to have more complex structures which are characterized by branched molecules also made up of glucose units, as is suggested in Figure 87.

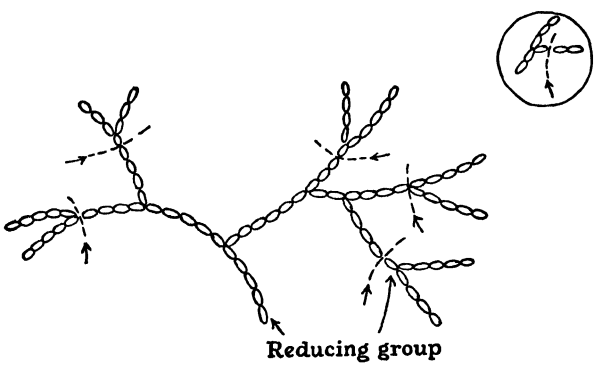


Fig. 87. Diagrammatic representation of the branched structure of the amylopectin molecule. Each small link represents a glucose unit. The arrows suggest points at which hydrolytic enzymes may attack the molecule. (Adapted from diagrams by Meyer.)

Other polysaccharides. There are also polysaccharides which hydrolyze to make substances other than glucose. The *pectins*, which are widely distributed in fruits, notably in apples, grapes, and citrous fruits, contain polysaccharides which hydrolyze to yield galactose and arabinose, a pentose. It is these pectins that are responsible for the "setting" of fruit jellies. *Hyaluronic acid* is a polysaccharide which appears to serve as cementing material for subcutaneous tissues in animals. It hydrolyzes to yield glucuronic acid and acetyl glucosamine, both of which are monosaccharide derivatives. *Hyaluronidase*, the enzyme which favors this hydrolysis, is sometimes used medicinally to favor the spreading of solutions introduced into the subcutaneous tissue layer.

PHYSICAL PROPERTIES

Solubilities and diffusion tendencies. Both *monosaccharides* and *disaccharides* form true solutions in water. Consequently, they are subject to osmotic pressure and to diffusion through suitable membranes (p. 199). The distribution of these sugars to and from actively functioning cells in either plants or animals depends on this property. However, it is noteworthy that in living membranes cells often show a selectivity not exhibited by dead membranes; for example, the living intestinal membrane facilitates, by some means, the diffusion of monosaccharides but does not appear to permit the passage of disaccharides, whereas dead membranes show no such selectivity.

None of the *polysaccharides* forms a true solution in water. Celluloses do not even form colloidal dispersions. In hot water starch granules burst and the amylose and amylopectins separate. The amylose forms an almost clear colloidal dispersion whereas the amylopectins, which make up about 80 per cent of the mixture, absorb water and, on standing, form a colloidal gel. This physical behavior can be observed when cornstarch or flour is used as a thickening agent. Dextrins and glycogens also form colloidal dispersions in water.

The inability of polysaccharides to form true solutions and their consequent inability to diffuse through membranes (p. 196) is significant in both plant and animal life. Because of these properties, plants can store starches in their seeds and roots and animals can maintain glycogen stores in the cells of liver, muscle, and other tissues.

Dextrans are polysaccharides which have recently become of interest as plasma extenders. They are used to help maintain osmotic pressure in the blood vessels following severe hemorrhage. They are made from sucrose by certain bacteria and are composed of glucose units linked together in what appears to be a branched pattern similar to that of amylopectin and glycogen. As polysaccharides they are not diffusable and remain in the blood for several days. Their ultimate fate in the body is uncertain.

Taste. Solutions of both monosaccharides and disaccharides are more or less sweet; polysaccharides are tasteless. The degree of sweetness of sugars varies with their solubility. Fructose is one of the most soluble of the sugars and it is the sweetest; the extreme sweetness of honey is due to the large proportion of fructose present therein. The ease with which sucrose dissolves in water, also its sweetness, is familiar to everyone. Lactose is much less readily soluble in water and notably less sweet than sucrose; moreover, this lower degree of sweetness of lactose makes it possible to use it in a relatively large quantity for sweetening a drink when it is desired to increase the caloric value of the beverage without making it unpalatable.

CHEMICAL BEHAVIOR

Hydrolysis of disaccharides. As has been stated previously, monosaccharides are not subject to hydrolysis as are disaccharides and polysaccharides. One molecular weight of a disaccharide will react with water to make 2 molecular weights of monosaccharide. Hydrolysis can be brought about by long boiling of the solution but is favored by an acid environment. The reaction takes place speedily, even at ordinary temperatures, if the appropriate enzyme catalyst is provided. For example, making boiled candy involves the hydrolysis of sucrose, and a little vinegar or cream of tartar (potassium hydrogen tartrate) is frequently added to provide the favoring acid environment. The digestion of the disaccharides maltose, sucrose, and lactose involves hydrolysis reactions with the specific enzymes maltase, sucrase, and lactase, which are provided in the intestinal juice, functioning as most effective catalysts.

Equations for the hydrolysis of disaccharides are given below. The second formula equation represents both the disaccharide nature of these carbohydrates and the hydrolytic nature of the reaction.

$$\text{Sucrose} + \text{Water} \xrightarrow{\text{Sucrase}} \text{Glucose} + \text{Fructose}$$

$$\text{Maltose} + \text{Water} \xrightarrow{\text{Maltase}} \text{Glucose} + \text{Glucose}$$

$$\text{Lactose} + \text{Water} \xrightarrow{\text{Lactase}} \text{Glucose} + \text{Galactose}$$

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 2\ C_6H_{12}O_6$$

$$C_6H_{11}O_6 \cdot C_6H_{11}O_5 + HOH \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Hydrolysis of polysaccharides. Polysaccharides also undergo hydrolysis. When the reaction is carried to completion, each molecular weight of polysaccharide hydrolyzes to make several, often many, molecular weights of monosaccharide. Starches, dextrins, celluloses, and glycogen all react with water to make glucose. The equation for any one of these reactions is as follows.

$$(C_6H_{10}O_5)_n + n\ HOH \longrightarrow n\ C_6H_{12}O_6$$

The hydrolysis of starch can be brought about by long boiling in an acid environment, a method that is commonly used for making glucose commercially. Starch hydrolysis can also be obtained at ordinary temperatures by the use of exceedingly effective enzyme catalysts called amylases. Ptyalin, or salivary amylase, and amylopsin, or pancreatic amylase, are two catalysts of this variety; but starch hydrolysis, which is favored by these enzymes, carries the reactions only through the dextrin stages to maltose. Hence, complete hydrolysis involves a series of reactions.

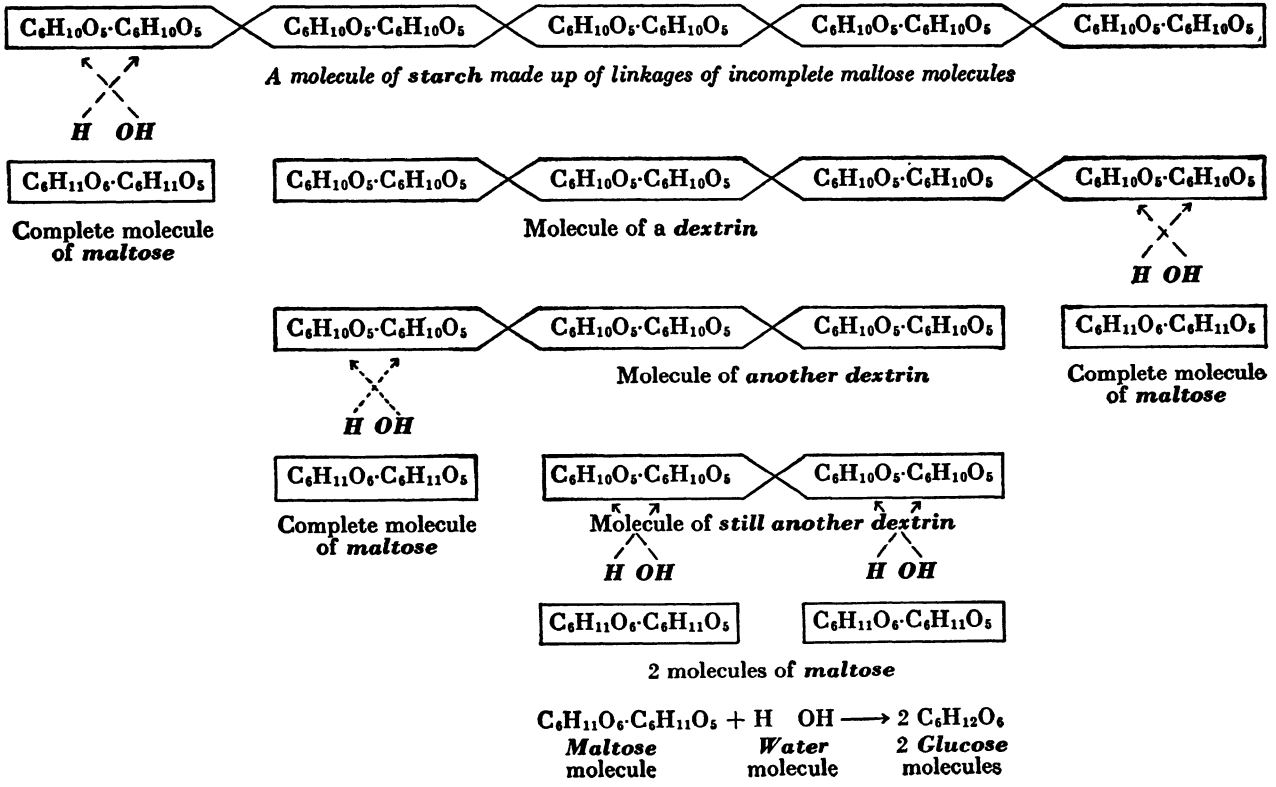
$$\text{Starch} + \text{Water} \xrightarrow{\text{Ptyalin or Amylopsin}} \text{Dextrins} + \text{Maltose}$$

$$\text{Dextrins} + \text{Water} \xrightarrow{\text{Ptyalin or Amylopsin}} \text{Maltose}$$

$$\text{Maltose} + \text{Water} \xrightarrow{\text{Maltase}} \text{Glucose}$$

Now let us follow the fate of a hypothetical starch molecule in an attempt to account for the various products. Starch molecules appear to be composed of incomplete glucose molecules which are

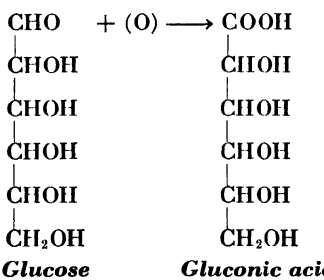
A diagrammatic representation of the hydrolysis of a starch molecule



linked in pairs as maltose units. On hydrolysis, water molecules attack the large starch molecules breaking off maltose and leaving polysaccharide molecules known as dextrins. As hydrolysis proceeds, successively smaller dextrin molecules are left until, finally, only maltose remains. If conditions are favorable, maltose molecules hydrolyze to make glucose molecules. (See diagram, page 381, and also Figure 87, page 377.)

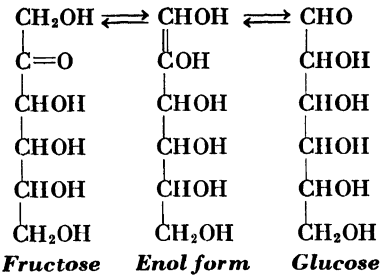
With oxidizing agents. *Glucose*, *fructose*, *galactose*, and *lactose* all react readily with oxidizing agents; hence, they are *good reducing agents*. The fact that they reduce such compounds as cupric hydroxide, bismuth hydroxide, silver hydroxide, and potassium permanganate is evidence of this. *Sucrose*, *starches*, and *glycogen* are *poor reducing agents;* they give little or no evidence of reducing these oxidizing agents.

The explanation for these differing behaviors is found in the structures of the various molecules. The good reducing agents, glucose, galactose, lactose, and maltose, have *free or potentially free aldehyde groups* in their molecules. The oxidative attack is believed to originate at these active aldehyde groups. For example, the aldehyde group of the glucose molecule is oxidized to make a carboxyl group, hence, gluconic acid. This reaction is represented as follows:



These oxidation-reduction reactions involving carbohydrates are favored by an alkaline environment.

Fructose contains a *ketone* rather than an aldehyde group. Although ketones are subject to oxidation, this reaction at the ketone group requires a strong oxidizing agent. It is surprising, therefore, that fructose readily reduces cupric hydroxide, a mild oxidizing agent. This fact is accounted for by the tendency of fructose to undergo *enolization* in an alkaline environment with the subsequent formation of glucose. The reaction is represented on page 383.



Sucrose, starches, and glycogen are *not* good reducing agents. It is believed, therefore, that within molecules of these carbohydrates the aldehyde or ketone atom groups are *bound* (pp. 375, 377). This being the case, these groups are not free for oxidative attack.

No doubt the student will have observed the possibility of oxidation at one or more of the alcohol atom groups of the carbohydrate molecules to make aldehydes or ketones. Such attacks are possible, but experimental evidence seems to indicate that the aldehyde and ketone groups of the molecule are most vulnerable in this respect, and that the attack is initiated at these points.

Laboratory use of these reactions. Oxidation-reduction reactions are used in the laboratory as aids in detecting the presence of reducing sugars. Various oxidizing agents are employed for this purpose, but the one most frequently used is *cupric hydroxide*, provided by either Fehling's or Benedict's reagent. This oxidizing agent is of special interest because it is used in urinalysis to detect the possible presence of glucose. Both Fehling's and Benedict's reagents are used in this connection. We will interrupt our main discussion at this point in order to consider similarities and differences of these two reagents.

Cupric hydroxide presents difficulties for the chemist because it is unstable and also difficult to keep in solution. These difficulties have been circumvented through somewhat different means in these two reagents.

Fehling's reagent was the one first used (p. 305). It is made up of two solutions, Fehling's I and Fehling's II, which are kept separate until immediately before use. Fehling's I contains cupric sulfate, which is blue. Fehling's II contains either sodium or potassium hydroxide and Rochelle salt (sodium potassium tartrate), both of which are colorless. Cupric hydroxide is made when the two solutions are mixed; Rochelle salt helps to keep cupric hydroxide in solution.

$$\underset{\text{sulfate}}{\text{Cupric}} + \underset{\text{hydroxide}}{\text{Sodium}} \longrightarrow \underset{\textit{hydroxide}}{\textit{Cupric}} + \underset{\text{sulfate}}{\text{Sodium}}$$

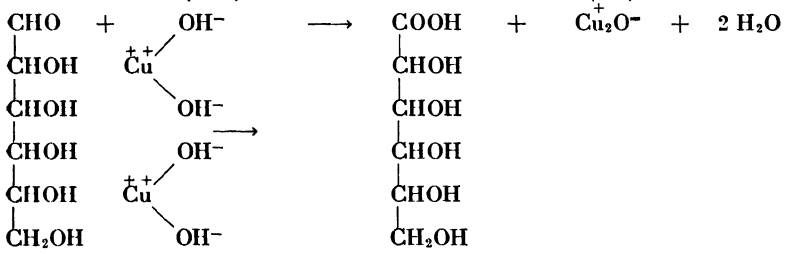
$$CuSO_4 + 2\,NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

The use of the strong base, sodium hydroxide, provides the favoring and pronounced basic environment.

Benedict's reagent is a modification of Fehling's. It has the advantages of being more stable and of having all reagents in one solution. It provides *cupric hydroxide* but in a less basic environment. Under the conditions obtained with Benedict's reagent, cupric hydroxide is considered to be more sensitive to reduction by glucose than when obtained from Fehling's reagent. In making Benedict's solution, sodium citrate, sodium carbonate, and cupric sulfate are used. Presumably sodium carbonate hydrolyzes to make a dilute solution of sodium hydroxide, which in turn reacts with the cupric sulfate to make cupric hydroxide. The sodium citrate aids in keeping the cupric hydroxide in solution.

The *cupric hydroxide* is especially useful as an oxidizing agent, not only because it is easily reduced but also because the product of the reduction is made visible owing to its characteristic red color. This product is *cuprous oxide.* Although the reaction of cupric hydroxide with the carbohydrate molecule appears to depend on the presence of the active aldehyde (or ketone) group, it does not stop with the oxidation of the aldehyde to make the corresponding acid; in alkaline environment a variety of compounds appear. The following equation represents the presumed first step in the molecule involvement when cupric hydroxide is reduced by glucose.

Glucose + Cupric hydroxide (blue) ⟶ Gluconic acid + Cuprous oxide (red) + Water



When testing for glucose in urine—in order to obtain reliable results whereby one specimen can be compared with another—it is important that conditions for the oxidative reaction be carefully controlled; these include quantity of reagent, quantity of urine, temperature of water bath, and the time the material is kept in the water bath.

Reducing agents other than glucose can produce a similar reaction; therefore, this is not a specific test for glucose. As a matter of fact, reducing agents other than glucose may be present at times in the urine; for example, during the period of lactation, lactose frequently occurs in the urine of a nursing mother, and the same visual effects will appear in the course of its reaction with cupric hydroxide as with glucose. However, in the main, glucose is the one reducing agent which is likely to be present in urine in quantities sufficient to produce conspicuous effects.

The *quantitative test for blood sugar* is another laboratory procedure which makes use of the fact that glucose is a good reducing agent. In this test provision must be made for measuring accurately the quantity of cupric hydroxide reduced, since a given weight thus reduced is an index of a given quantity of glucose present in the volume of blood tested.

With reducing agents. These monosaccharides and disaccharides, again with sucrose excepted, are subject to reduction as well as to oxidation. If aldehydes, they can be reduced to make primary alcohols, or if ketones, to make secondary alcohols. In the process of reduction there is no energy product; on the contrary, some form of energy must be provided to make such reactions possible. Physiologically, it is probable that in the cells in the course of metabolism mutual oxidation-reduction reactions are of frequent occurrence.

Fermentation of monosaccharides. The monosaccharides *glucose* and *fructose* are fermented by bread yeast to make ethyl alcohol and carbon dioxide. Some cultures ferment galactose as well. The fermentation of these monosaccharides involves a series of reactions, each of which is catalyzed by a specific enzyme. The reaction may be summarized as follows.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2\ CO_2 + 2\ C_2H_5OH$$

The activity of this zymase depends on the presence of phosphates and of a complex organic compound known as a "cozymase."[3] Carbon dioxide and ethyl alcohol are not the products of all fermentations. Similar reactions, but with different products, are produced by certain bacteria, indicating that their cells are likewise provided with enzymes capable of catalyzing fermentation reactions.

Disaccharides and polysaccharides are not in themselves subject to fermentation; but if catalysts are provided which favor their hydrolysis, the monosaccharide products of this hydrolysis can then undergo fermentation, if conditions are favorable.

Importance of monosaccharide fermentation. Commercially, fermentation reactions are important as means for obtaining *ethyl alcohol,* usually from fermentation of glucose obtained through the hydrolysis of starch. In making the *acetic acid* of cider vinegar,

[3] The cozymase which functions with the zymase of yeast has been shown to be a combination of the purine adenine, the pentose ribose, phosphate, and nicotinic acid amide, a derivative of the vitamin niacin.

the fermentation of glucose and fructose, present in apple juice, produces ethyl alcohol which, in turn, is oxidized to make acetic acid. Zymase for this fermentation is provided by yeast cells of so-called "mother," a brown jellylike mass which appears whenever vinegar stands for any length of time.

The carbon dioxide for leavening of bread dough is a product of fermentation of the monosaccharide glucose, made from hydrolysis of the starch component of flour. The bread yeast contains not only the zymase enzymes, for speeding up this fermentation of fructose and glucose, but also the enzymes maltase and sucrase. An amylase is provided in the flour.

There is no lactase in bread yeast; therefore, lactose cannot undergo hydrolysis through the agency of bread yeast to make monosaccharides; consequently, no fermentation can follow. But there are microorganisms which do produce a lactase along with a zymase. Cultures of such bacteria are useful for making ethyl alcohol (and carbon dioxide) from the lactose in milk, thereby making the "fermented liquors" of milk origin, kumiss from mare's milk being one.

The spoilage or "working" of preserved fruits is due to the fermentation of glucose and fructose components, the enzymes being made in this instance in bacterial or yeast cells which have not been destroyed by adequate sterilization.

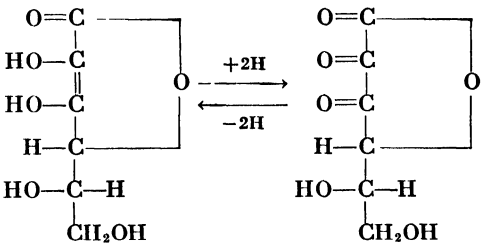
Monosaccharide fermentations are also of *physiological importance.* A certain amount of fermentation of monosaccharides is normal in the intestinal tract, the enzymes concerned being provided by bacteria normally present. Since a basic environment is favorable to these reactions, it follows that the large intestine is the location of maximum fermentation. *Bacillus acidophilus* is sometimes prescribed to check excessive intestinal fermentation. The explanation for this effect is that this bacillus secretes enzymes which favor a fermentation involving lactose, one of the products being *lactic acid.* And this acid, in turn, increases the acidity of the intestinal contents, thereby rendering the environment less favorable to such fermentation reactions as are favored by the more basic medium. The reactions that take place in muscle cells under anaerobic conditions, and result in making lactic acid from glycogen, are believed to be similar to those involved in the fermentation of glucose.

In microbiology. Many fermentation reactions catalyzed by enzymes produced by microorganisms are specific both as to the monosaccharide affected

and as to substances made. This selectiveness is frequently resorted to in the laboratory as an aid in recognition of the particular microorganism producing the enzyme. For example, organisms of the coliform group are known to favor the fermentation of lactose with the production of hydrogen and a number of organic acids. Culture media for detecting such organisms often include both lactose and the indicator litmus. Both the production of carbon dioxide and the color change from blue to red of litmus, frequently seen in such media, are characteristic of *Escherichia coli.*

VITAMINS RELATED TO CARBOHYDRATES

Ascorbic acid. Ascorbic acid, or vitamin C, is produced in the cells of many plants. Fresh vegetables and fruits, notably citrus fruits and tomatoes, are important dietary sources. This vitamin is related to the sugars, as is indicated by its structural formula. The reactions whereby it is made in plant cells are as yet unknown, but it is assumed to be made from glucose. The source of commercial ascorbic acid is glucose.

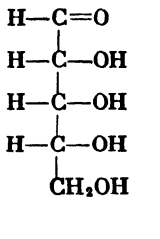


Ascorbic acid (reduced form) ***Dehydro-ascorbic acid*** (oxidized form)

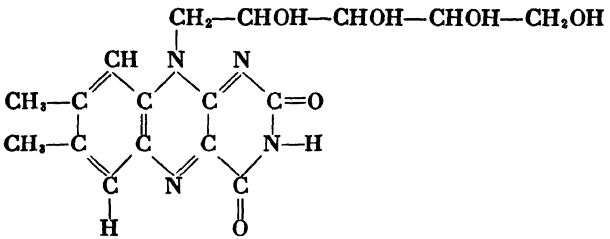
Ascorbic acid is an excellent reducing agent, hence, is readily oxidized. The first step in its oxidation (which is here represented) is reversible; oxidation beyond this point destroys the compound. This destruction is rapid when ascorbic acid is heated in contact with oxygen of air, especially in alkaline environment. Contact with copper favors the reaction. Oxidation accounts for considerable loss of vitamin C during cooking. Further loss during food preparation is the result of its solubility in water and the practice of discarding the water in which vegetables have been cooked. The physiological functioning of ascorbic acid is attributed to its ability to participate in reversible oxidation-reduction reactions. Deficiency of this vitamin in the food of man interferes with the formation of the intercellular

cement substances collagen, osteoid, and dentine.[4] The reason for this is unknown, but the results of deficiency are evident in the hemorrhages of scurvy and the retarded healing of wounds.

Riboflavin. The name riboflavin, given to the substance formerly known as vitamin G, indicates the presence of a carbohydrate group related to the pentose *ribose.* This is coupled with a complex cyclic structure known as flavin (p. 353).



Ribose



Riboflavin

Riboflavin is widely distributed in nature but is seldom found in high concentration. It is made in the green leaves of rapidly growing plants, which suggests good dietary sources. Liver muscle and eggs are also good sources of this vitamin. Riboflavin is known to contribute to a number of enzymes, including some which function in oxidation-reduction reactions within the living cells (p. 434).

CARBOHYDRATES AS FOODS

That carbohydrates make up a large part of the diet of man is evident when the sources of starches and sugars are considered. Because starchy foods such as cereals, bread, rice, and root vegetables are less expensive than fats or proteins, they tend to have a large place in the low-income diet. Carbohydrates function primarily, and importantly, in the oxidation reactions for production of energy in the animal cells. The excessive inclusion of sugars and starches is undesirable only when they displace other equally essential foods, or when the diet is thus built up until its caloric value exceeds the normal demands for energy production within the cells.

QUESTIONS

1. What varieties of compounds belong to the class of carbohydrates? What atom groups are believed to be characteristic of carbohydrate molecules?

[4] West, Edward S., and Todd, Wilbert R.: *Textbook of Biochemistry,* 2nd ed. The Macmillan Company, New York, 1955, p. 772.

2. What is the so-called "photosynthesis reaction"? Where does it take place? Why is it regarded as one of the most important reactions in all nature?

3. What is the basis for the classification of carbohydrates as monosaccharides, disaccharides, and polysaccharides? Name three carbohydrates belonging to each class. Give the empirical formulas for (a) hexose monosaccharides, (b) hexose disaccharides, and (c) hexosans.

4. Account for the fact that, whereas monosaccharides and disaccharides can diffuse through membranes, polysaccharides cannot. Of what advantage is it to the plant or animal to make a carbohydrate of the polysaccharide variety?

5. Assemble word and formula equations for the reactions involved in the hydrolysis of sucrose, lactose, and maltose. How are these reactions made appreciable (a) in cookery, (b) in the digestive tract?

6. a. Indicate by a series of word equations the steps involved in the complete hydrolysis of a starch.
   b. If iodine and Benedict's tests are used to trace the progress of such reactions, what visual evidence would you expect to obtain of these various reaction stages?

7. What is meant by *glucose* as this term is used commercially? (Consult the *Pharmacopœia of the United States* or any good encyclopedia for this information.) How does commercial glucose differ from the compound glucose? Is there any valid objection to the use of commercial glucose in the preparation of foods, candy, etc.? Give reasons for your answer.

8. What common substance is provided by both Fehling's and Benedict's reagents? In what respects do the two reagents differ? Which of the carbohydrates of our study give a positive response with these reactions? Which give no response? Account, theoretically, for these different behaviors. Assemble word and formula equations (using semistructural formulas) for the reaction involving glucose.

9. a. Is Fehling's or Benedict's test a specific test for glucose? Give reason.
   b. What conditions for reaction must be carefully controlled in order to compare urinalysis specimens which have been tested for glucose? Explain with reference to factors affecting speed of chemical reactions.
   c. What substance encountered in the urine of a nursing mother gives a positive test with either Fehling's or Benedict's reagent? What further test can be made to distinguish this substance from glucose? Explain.

10. Explain why lactose is sometimes used to build up the caloric value of a diet.

11. What is dextran? For what purpose is it used medicinally and how does it function?

12. What practices would you advocate in food preparation to minimize the loss of ascorbic acid? Explain. Explain why this compound is sometimes used medicinally to encourage wound healing.

13. What naturally occurring fibers are essentially cellulose? What modern fibers or plastics are made from cellulose?

CHAPTER 27

FATS AND RELATED SUBSTANCES

FATS

Occurrence. Fats, like carbohydrates, are widely distributed in nature in both plant and animal cells. They are found in relatively high concentration in the seeds of many plants, as is indicated by such names as olive oil, peanut oil, cottonseed oil, and corn oil; they function as a supply of stored food, available for use of the young plants as the seeds germinate. Animals store deposits of fat in their adipose tissue cells; these stored fats constitute a reserve which can be drawn upon to supply nutrients to the actively functioning cells. Fats and fat derivatives also contribute to the structure of animal cells and are regarded as essential components of the cell protoplasm.

Synthesis of fats. Fats, like carbohydrates, are composed of the elements carbon, hydrogen, and oxygen. Whether or not *plants* can build their fats directly from carbon dioxide and water is not known; there is, however, good evidence that *plants can make fats from carbohydrates*. Thus, it has been observed that, when fats are being made in ripening seeds, as the quantity of fat increases in the seeds there is a corresponding decrease in the quantity of carbohydrate present. It has also been noted that sugars are constantly carried in the sap to the cells where fats are being made, and that these sugars disappear as the fats appear.

Part of the fat in the storage cells of animals comes from the fats of the diet. Recent studies indicate that a high proportion of the dietary fat shortly appears in the adipose tissues, where it replaces previously stored fat which is being withdrawn from the storage cells for metabolic reactions in various tissues. A considerable portion of the storage fat is made from glucose. In addition to carefully con-

trolled laboratory experiments which demonstrate this origin of stored fat, there is also much evidence drawn from common experience; it has long been the practice of farmers to fatten animals by feeding them with corn and grain which are rich in carbohydrates; it is also a matter of common observation that when humans partake freely of sugars and starches, in excess of their carbohydrate needs, they store fat.

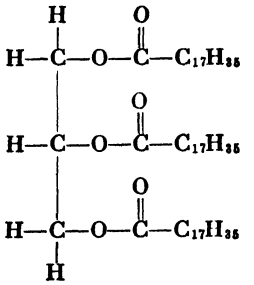
In plant and animal cells. The fats produced and stored in plant cells are liquid at ordinary temperatures, hence, are known as oils. Corn oil, cottonseed oil, and olive oil are well-known instances of such fats.

In general, the term *oil* is applied to any liquid substance or mixture of substances which has a greasy feeling. Thus mineral oil, kerosene oil, and fuel oil are not fats but are rather mixtures of hydrocarbons. The term *oil* is also applied to certain other volatile substances of plant origin which have an oily feeling, as, for example, oil of peppermint, oil of wintergreen, and oil of turpentine.

Animal fats, other than fish fats, are for the most part semi-solid or solid at ordinary temperatures; thus, butterfat and lard are soft solids, while beef suet and mutton tallow are harder in consistency. But within the *living* animal, fats must be liquid or very soft solids so that muscle mobility will not be impeded; of course the higher temperature within the living animal favors this. Moreover, each animal, given its usual selection of food, builds a fat which is peculiar to the species and adapted to the environment in which it lives and to its natural skin protection. Thus, fish which live in water at relatively low temperatures make fats which have low melting points. Sheep, with their heat-insulating coats of wool, make a hard fat with a relatively high melting point; whereas pigs, which are not provided with such a protection, make a softer fat of a somewhat lower melting point. Human fat has a melting point around 15° C.

Composition. Fats are esters each molecular weight of which is composed of 1 glyceryl radical and 3 fatty-acid radicals. The following semistructural formula which represents 1 molecule of glyceryl stearate, a typical fat, indicates the manner in which the glyceryl radical and fatty-acid radicals are believed to be combined with each other in all fat molecules (p. 392).

All three fatty acids contributing to the fat may be of the same variety, as in *butyrin* (glyceryl tributyrate), *olein* (glyceryl trioleate), or *stearin* (glyceryl tristearate). But it is also possible for more than



Note. Owing to the length of the fatty-acid-radical carbon chain it is customary to use the semi-structural formula for the fat molecule. It is suggested, however, that the student assemble the complete structural formula for the molecule.

one variety of fatty-acid radical to contribute to the make-up of a fat. For example, stearo-diolein, composed of the glyceryl radical together with 1 stearate and 2 oleate radicals, is said to be present in human fat. Palmito-distearin is present in both lard and beef fat. Such fats are known as mixed fats and are more commonly found

FATTY ACID	COMPOSITION	SOME FATS TO WHICH IT CONTRIBUTES
Saturated fatty acids		
Butyric acid	C_3H_7COOH	Butter
Caproic acid	$C_5H_{11}COOH$	Butter, human milk, cocoanut oil
Palmitic acid	$C_{15}H_{31}COOH$	Bone marrow, butter, egg, human fat, beef fat, mutton fat, lard, cottonseed oil, salmon oil, cod-liver oil, olive oil
Stearic acid	$C_{17}H_{35}COOH$	Mutton fat, beef fat, bone marrow, lard, butter, human fat, peanut oil, egg, olive oil.
Unsaturated fatty acids		
Oleic acid	$C_{17}H_{33}COOH$	Olive oil, lard, egg, human fat, peanut oil, bone marrow, corn oil, cottonseed oil, butter, mutton, salmon oil, soybean oil
Linoleic acid	$C_{17}H_{31}COOH$	Soybean oil, cottonseed oil, corn oil, linseed oil, peanut oil, egg, lard
Arachidonic acid[1]	$C_{19}H_{31}COOH$	Cod-liver oil, salmon oil, egg yolk, butter, human fat, beef fat—in each case only in traces.

[1] Arachidonic acid is included in this table, not because of frequency of occurrence, but because of its nutritional importance. The unsaturated arachidonic and linoleic acids appear to be nutritionally essential for good cell structure. (See p. 400.)

in nature than are those which contain only one variety of fatty-acid radical. The table on page 392 lists some of the commonly occurring fatty acids, and mentions some of the fats to which they contribute.

In general, the fatty-acid radicals which contribute to the make-up of fats have high radical weights; hence, the fats themselves are compounds of high molecular weight. Most *naturally occurring fats contain only fatty-acid radicals which have an even number of atomic weights of carbon in their molecular weights*,[2] the butyrate having *4*, the palmitate having *16*, while the stearate, oleate, and linoleate have, each, *18* atomic weights of carbon in their radical weights. Probably this is not without biological significance, as we shall see later when the oxidation of fats in the cells and the manner of making them are presented.

Saturated and unsaturated fats. Some fats, glyceryl stearate, glyceryl palmitate, and glyceryl butyrate among them, are saturated fats, whereas others, including glyceryl oleate and glyceryl linoleate, are unsaturated fats. An *unsaturated fat* contains 1 or more acid radicals that can react in direct combination with hydrogen, and with certain other substances, to make saturated compounds. For example, glycerol oleate, a typical unsaturated fat, reacts with hydrogen, in the presence of a suitable catalyst, to make glyceryl stearate, which is saturated.

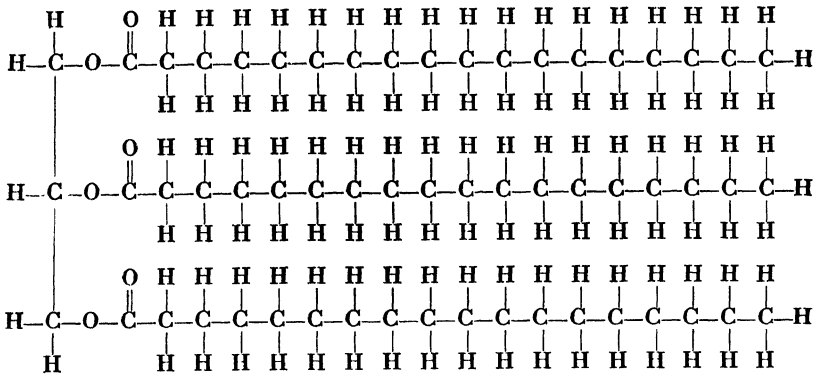
$$C_3H_5(C_{17}H_{33}COO)_3 + 3\ H_2 \longrightarrow C_3H_5(C_{17}H_{35}COO)_3$$

Saturated fats cannot react in direct combination with other substances.

Theoretically, the difference in this chemical behavior lies in the make-up of the molecule. In a *saturated fat* molecule all of the carbon atoms in the fatty-acid radicals are believed to be combined with each other by *single* bonds, a condition which is represented in the structural formula on page 394 for the molecule of glyceryl stearate. But in the molecule of an *unsaturated fat* 1 or more pairs of carbon atoms in the fatty-acid radical or radicals are supposed to be combined with *double* bonds. It is at these points in the molecule, then, that the addition of hydrogen or other atoms may take place to make

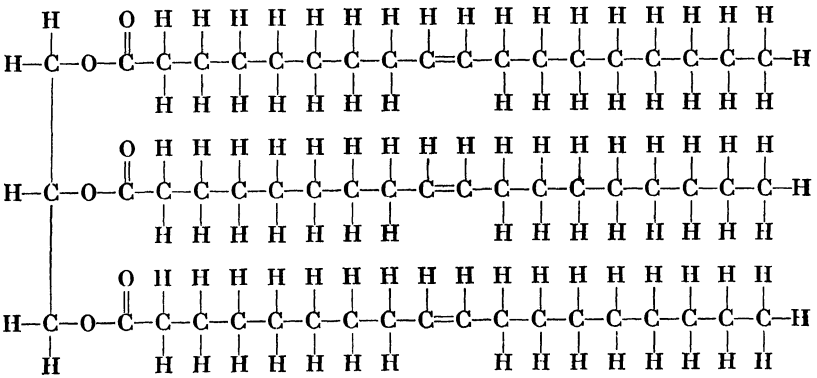
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[2] A few fatty acids with an odd number of atomic weights of carbon have been found in naturally occurring fats. Tuberculostearic acid (10-methylstearic acid), produced by tubercle bacilli, contains 19 atomic weights of carbon. Isovaleric acid (C_4H_7COOH) occurs in croton oil.



Glyceryl stearate, a saturated fat

a saturated compound. This unsaturated condition is illustrated by the following structural formula for the glyceryl oleate molecule in which a double bond is indicated between the ninth and tenth carbon atoms in the fatty-acid radicals.



Glyceryl oleate, an unsaturated fat

Glyceryl linoleate is an even more unsaturated fat than is glyceryl oleate, in that, supposedly, 2 pairs of carbon atoms are joined by double bonds in the carbon chain of the linoleate fatty-acid radicals.

Saturated fats and unsaturated fats show characteristic differences as to both physical state and chemical behavior. Unsaturated fats are liquid while most saturated fats are solid. Unsaturated fats make addition products and are generally more active chemically than are saturated fats.

Physical properties. All fats are greasy. Most fats are colorless, odorless, and tasteless; tastes and odors commonly associated with certain fats are due to the presence of other substances, some of which are made from fats themselves through certain chemical changes which they undergo.

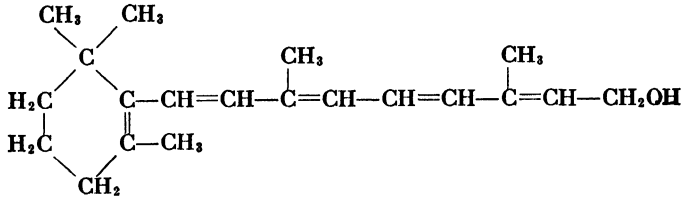
Physical state. Naturally occurring fats are mixtures, and the physical state of the mixture is determined by the physical states and proportions of the contributing fats. The saturated fats of low molecular weight, such as butyrin and caproin, are liquid. With increasing molecular weights the more solid fats appear. Thus, palmitin is a soft solid while stearin is a firm solid. Unsaturated fats, even those of high molecular weights, such as olein and linolein, are liquids. In mixed fats, the physical state of the fat is determined by its fatty-acid constituents. Vegetable oils contain a high proportion of the unsaturated oleic acid radical. Butter, with butyric, oleic, and stearic acid radicals contributing to its fats, is a soft solid at room temperature. Human fat is composed chiefly of fats containing stearic, palmitic, oleic, and butyric acid radicals in different proportions in fats in different parts of the body.

Solubilities and important consequences. Fats are not soluble in water but form true solutions with ether, acetone, chloroform, hydrocarbons, some hydrocarbon derivatives, other fats, and, to a limited extent, hot alcohol.

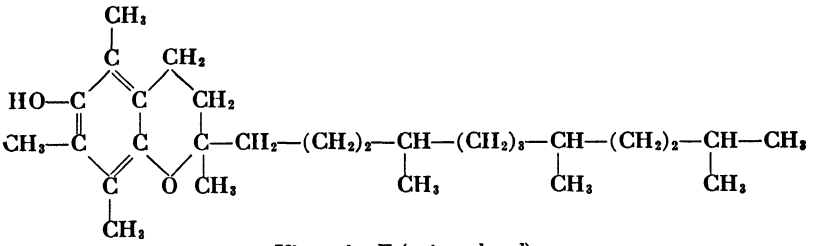
The insolubility of fats in water gives rise to various fat-removal problems, which are solved through the use of appropriate fat solvents. In the dry cleaning of clothing, various liquid hydrocarbon mixtures are in use, but the fact that these substances burn so readily with oxygen at relatively low kindling temperatures makes their use distinctly dangerous. Carbon tetrachloride, which is an excellent fat solvent, does not react with oxygen, hence, is not a fire hazard. However, its toxic effect must be considered.[3] In hospitals ether is sometimes employed in the preparation of the skin for operation, since it produces a more thorough cleansing of the area by dissolving any oils which may have accumulated in the pores. But frequent or prolonged contact of any of these fat solvents with the skin is undesirable because, by dissolving and carrying away the natural oils and waxes, they leave the skin dry and hard.

[3] Neither volatile hydrocarbons nor carbon tetrachloride should be used as cleaning agents in an unventilated room because of their physiological effect on the worker. (See p. 287.)

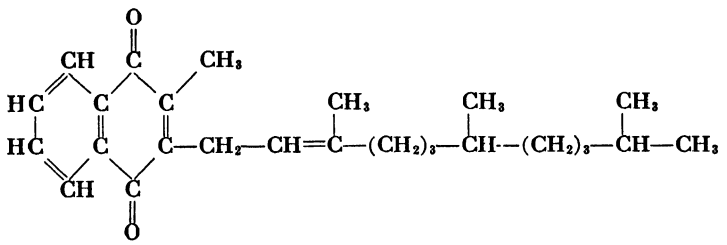
Fat-soluble vitamins. Certain of the vitamins, known to be nutritionally essential, occur in nature in solution in fats. The structural formulas for vitamin A, vitamin E, and vitamin K indicate that they are all closely related chemically to the hydrocarbons, hence their solubility in fats is a natural result. (See p. 282.)



Vitamin A_1



Vitamin E (α-tocopherol)



Vitamin K_1

Vitamin A is found in the fats of mammals, birds, and fish, whereas its precursors, the carotenes, occur in plant fats. The various vitamin-D compounds are found in animal fats, notably in butter, cream, egg yolk, and fish-liver oils (pp. 402 to 403). The *vitamin-E group* is widely distributed in nature but is especially abundant in wheat-germ oil. Liver fats and vegetable oils, such as those of cabbage, kale, spinach, and cereals, are important sources of *vitamin K*.

Form emulsions. Fats and water, when mixed and thoroughly shaken, form an emulsion, but such dispersions are only temporary, since they show a marked tendency toward separation. However, in the presence of certain substances known as stabilizers or emulsi-

fying agents these dispersions may form more or less permanent emulsions (p. 215). Sodium and potassium soaps, for example, have been found to be good emulsifying agents for keeping fats suspended in water; hence, the use of soap and water for the removal of grease from fabrics, utensils, or the skin. Other good emulsifying agents, used for specific purposes, are proteins and gum acacia. Mayonnaise, for example, is an emulsion in which egg proteins function as the emulsifying agents; milk is a natural emulsion in which the proteins present function as the stabilizers for the emulsion. From a physiological angle, the emulsification of fats in water facilitates the hydrolysis of fats in digestion by keeping them suspended in small droplets, thereby providing greater surface of contact with the water and with the enzyme pancreatic lipase. The bile salts that are always present in the intestinal contents where these reactions take place are excellent emulsifying agents for fats. In lymph and blood and in the protoplasm of actively functioning cells, fats are held in fine suspension, probably through the emulsifying agency of proteins which are always present in blood, intercellular fluids, and cells.

Chemical behavior of fats. ***Hydrolysis.*** All fats reacts with water in double decomposition to make fatty acids and glycerol, as in the reaction represented by the following equations.

Glyceryl stearate + Water ⟶ Glycerol + Stearic acid

$$C_3H_5(C_{17}H_{35}COO)_3 + 3\ HOH \longrightarrow C_3H_5(OH)_3 + 3\ C_{17}H_{35}COOH$$

$$\begin{array}{l} CH_2\text{—}\boxed{\text{—OOC—}C_{17}H_{35}} \\ CH\text{—}\boxed{\text{—OOC—}C_{17}H_{35}} \\ CH_2\text{—}\boxed{\text{—OOC—}C_{17}H_{35}} \end{array} + \begin{array}{l} \boxed{H\text{—}}\text{—OH} \\ \boxed{H\text{—}}\text{—OH} \\ \boxed{H\text{—}}\text{—OH} \end{array} \longrightarrow \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array} + 3\ C_{17}H_{35}COOH$$

Hydrolysis of fats can be speeded up to appreciable proportions by exposure to very high temperatures, as in reaction with superheated steam; or at the lower temperature of long boiling in the presence of a dilute acid or base; or at ordinary temperatures through the agency of enzyme catalysts, called *lipases*, made in plant and animal cells.

The wide distribution of lipases in both plant and animal cells indicates that fat hydrolysis reactions are of considerable biological importance. In the human body the digestion of fats involves their hydrolysis favored by catalysts of this type. Lipases are also found in the cells, and it is believed that hydrolysis of fats to fatty acids and glycerol is the first step in fat oxidation.

With bases to make soaps. Fats react with sodium and potassium hydroxides to make soaps and glycerol.

Glyceryl stearate + Sodium hydroxide ⟶ Glycerol + Sodium stearate

$$C_3H_5(C_{17}H_{35}COO)_3 + 3\ NaOH \longrightarrow C_3H_5(OH)_3 + 3\ C_{17}H_{35}COONa$$

(a soap)

Such reactions are of great commercial importance in the soap industry. Although various processes for the making of soap are in use, the principle involved is the same. The fat and sodium hydroxide solution are kept in contact for some time at a high temperature to speed up the reaction. The soap is then separated from the glycerol by "salting it out"; that is, sodium chloride is added in a sufficient quantity to result in the formation of nondispersible curds of soap which rise to the top of the mixture. When the soap has been removed the glycerol is separated from the salt solution and is a valuable by-product of the soap industry (p. 300). When potassium hydroxide is used, glycerol remains in the mixture and a soft soap results.

Hydrogenation of unsaturated fats. The fact that hydrogen can be made to combine with unsaturated fats to make saturated fats has been mentioned previously. This reaction, which would otherwise be very slow, can be hastened through the use of nickel as a catalyst (p. 51). The hydrogenation of unsaturated fats has become of considerable commercial importance as a means for obtaining solid fats, which are preferred to oils for shortening foods and for making soaps. Vegetable fats, such as cottonseed, corn, peanut, and soybean oils, contain high proportions of unsaturated fats. These fats are hydrogenated, as suggested by the reaction represented below, until enough solid fat has been made to give the desired consistency to the mixture.

$$\underset{\text{Olein, a liquid fat}}{C_3H_5(C_{17}H_{33}COO)_3} + 3\ H_2 \xrightarrow{\text{Nickel}} \underset{\text{Stearin, a solid fat}}{C_3H_5(C_{17}H_{35}COO)_3}$$

Stearin made by this process has the same composition as animal stearin, hence the same caloric value. The lard substitutes thus obtained have become valuable supplements to the world's natural supply of solid fats; they are used as shortenings and for making margarine.

Margarine is used as a substitute for butter. It is required by law to contain at least 80 per cent fat, making it comparable in this respect to butter. This fat

may be lard, the softer beef fats, or hydrogenated vegetable fats. The solid fats are dissolved in vegetable oils, and the mixture is churned with milk to give the material characteristics similar to those of butter. The product must be further enriched by the addition of vitamin A, 9000 international units per pound. Nutritional studies show that margarine can be substituted for butter without impairing growth, reproduction, or lactation.

Auto-oxidation of unsaturated fats. Unsaturated fats enter into combination with oxygen slowly to make saturated compounds even at ordinary temperature and without the presence of a favoring catalyst. Such reactions are called auto-oxidation. Reactions of this sort are in part responsible for the tendency of liquid fats to become rancid.[4]

This type of reaction is also involved in the *drying of paint.* Paint pigments are mixed with linseed oil which has as components several unsaturated fats, and these fats upon reacting with oxygen make peroxides which, in turn, polymerize and form solids.

The iodine number of a fat. Iodine reacts with unsaturated fats in direct combination to form saturated compounds. The number of grams of iodine required to saturate 100 gm of fat gives a value known as *the iodine number* of the fat. This value provides a measure of the extent of unsaturization of the fat. Typical iodine numbers are as follows:

Butter fat	26–38
Lard	50–70
Olive oil	79–90
Cottonseed oil	104–116
Linseed oil	170–200

Physiological importance of fats. Fats, as well as the carbohydrates glucose and glycogen, can be used in the active cells for production of energy through reactions with oxygen. The fat storage depots of the animal constitute a source of continuous supply of fats for this purpose, as well as a reserve upon which the animal can draw to meet demands for energy production.

Inasmuch as the animal makes much of its depot fat from glucose, the question might be raised as to whether it is necessary that fats

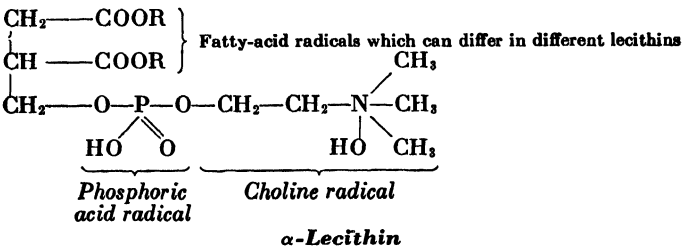
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[4] The term *rancid,* applied to fats and fatty oils, refers to certain changes which result in compounds that have either an undesirable taste or odor, or both. In general two types of chemical reactions may be involved: hydrolysis reactions (as in the case of butter in which the butyric acid produced is largely responsible for the taste and odor effects) or the oxidation of unsaturated fats. The two types of chemical change are often associated.

be provided in the diet. It is now generally agreed that certain of the unsaturated fatty acids, including either linoleic acid or arachidonic acid, are *nutritionally essential;* that is, they must be provided by the diet because the animal cannot synthesize them or they are not made rapidly enough to meet the demand. The quantity of these essential fatty acids required is not large, but if the supply is deficient certain eczematous skin conditions have been noted; these unsaturated fatty acids apparently contribute to cell structures. Fats of the food serve as carriers for the necessary fat-soluble vitamins, A, D, E, and K (p. 396); also, absorption of these vitamins accompanies absorption of fats.

SUBSTANCES RELATED TO FATS

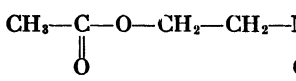
Phospholipids. The substances known as phospholipids are chemically related to fats and resemble them in feeling and solubilities. They are found in all plant and animal cells but are especially abundant in the myelinated nerve tissue and tissues of the heart, liver, kidney, bone marrow, and muscle. A typical phospholipid is composed of a glyceryl radical (usually), fatty-acid radicals (one of which is usually unsaturated), and a phosphoric acid radical which, in turn, is in combination with a nitrogen complex. The *lecithins*, which are components of egg yolk, liver, and brain tissue, constitute one type of phospholipid in which the nitrogen complex is the *choline* radical. This is illustrated in the following formula for an α-lecithin.



α-Lecithin

Choline, which contributes a radical to lecithins, is found in the liver, where it appears to have an important role in the formation of phospholipids. In the absence of choline the liver accumulates fat instead of distributing fatty acids to the active cells. The choline radical is also a constituent of *acetylcholine*, a compound which functions in the transmission of the nerve impulses to volun-

tary muscles and the parasympathetic system. Choline is regarded as a member of the vitamin-B complex.



Acetylcholine

Phospholipids are probably of even greater physiological importance than true fats; whereas fats predominate in the adipose tissue, phospholipids predominate in actively functioning cells. They are believed to contribute to the structure of cells and to provide a medium within the cells in which fat-soluble and water-soluble substances can be brought into intimate contact with each other. They appear to function in the absorption of fatty acids from the intestine and to provide transportation for fatty-acid radicals in the blood to the actively functioning cells.

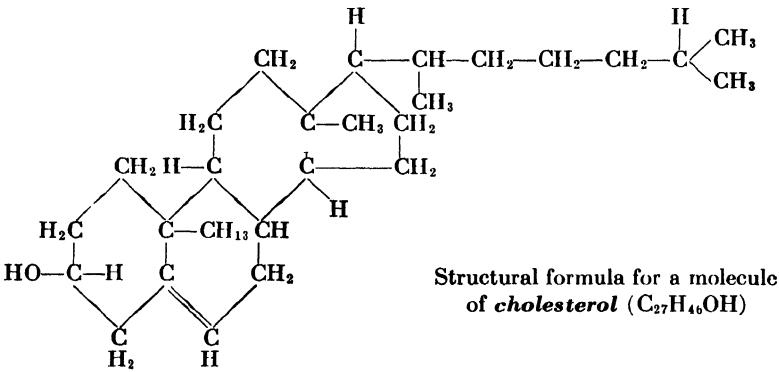
Sterols. Sterols are alcohols of high molecular weight. At ordinary temperatures they are solids, as is suggested by the name sterol, which means solid alcohol. They are greasy in character, insoluble in water, but somewhat soluble in fats and fat solvents. Sterols are widely distributed, though not in great abundance, in both plant and animal cells. Three members of this group which are of special physiological importance are *cholesterol*, *ergosterol*, and *calciferol*, or *vitamin* D_2, which is an isomer of ergosterol.

Cholesterol and its physiological importance. Cholesterol, the sterol predominating in animal cells, was first isolated from gallstones. It is now known to occur in all animal cells but it is especially abundant in nerve tissue where it contributes to the myelin sheath. It is found in high concentration in bile and apparently functions in the absorption of fatty acids from the intestinal tract. It reacts with fatty acids to make esters and aids, as do also the phospholipids, in transportation of fatty-acid radicals to the cells. In the cells, cholesterol contributes to cell structure and influences the permeability of the cell wall.

Cholesterol is both made and destroyed in the body. Normally the rate of synthesis appears to be regulated in relation to the cholesterol intake from the food in such a way as to maintain a relatively constant cholesterol level in the blood. The liver has long been recognized as a site of active cholesterol metabolism and recent studies with the carbon isotope, C^{14}, indicate that other tissues, such as the skin and adrenal cortex, participate in this function. Acetic acid and

water have been identified as probable precursors of this complex sterol.[5]

A variety of other compounds found in the animal body are chemically related to cholesterol in that they contain the same complex nucleus. These compounds include bile salts, the sex hormones, and the adrenal cortical hormones. It has long been suggested that cholesterol may contribute to the synthesis of these compounds within the animal body. Experimental evidence, obtained through the use



Structural formula for a molecule of ***cholesterol*** ($C_{27}H_{46}OH$)

of cholesterol in which deuterium (the heavy isotope of hydrogen) has been incorporated, appears to confirm this belief.[6]

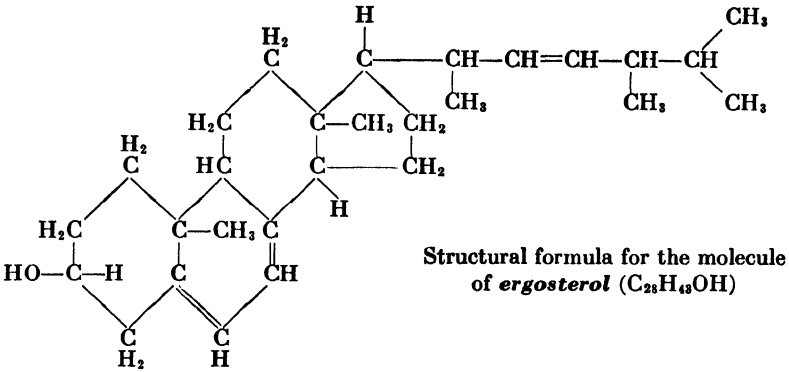
Ergosterol and calciferol or vitamin D_2. Ergosterol is a sterol which occurs in both plant and animal cells. It was first discovered in ergot and is abundant in yeast. Ergosterol is of special interest because it is the precursor of calciferol, or vitamin D_2, which has antirachitic properties.[7] When ergosterol is irradiated with ultraviolet rays, either artificial or of the sunlight, calciferol is made. Ergosterol is present in skin cells; hence, on exposure to sunlight, the body can make vitamin D_2 from this source. The following structural formulas for the molecules of ergosterol and calciferol indicate their marked chemical similarity.

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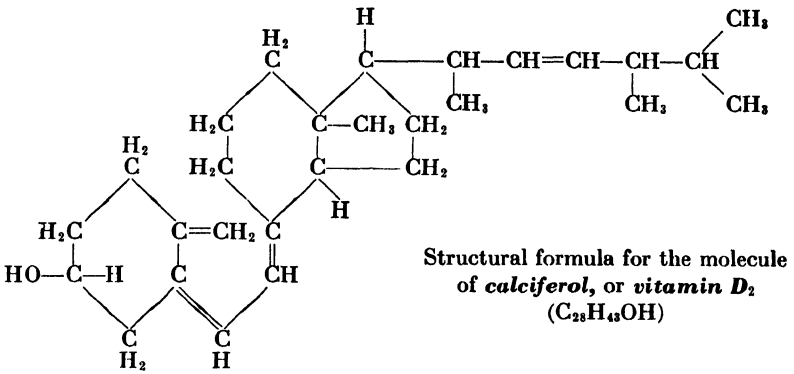
[5] Fructon, Joseph S., and Simmonds, Sofia: *General Biochemistry* John Wiley & Sons, Inc., New York, 1953, pp. 550–53.

[6] Ruigh, Wm. L.: "The Chemistry of the Steroids." *Ann. Rev. Biochem.*, 14:249, 1945; also, Fieser, Louis F.: "Steroids," *Scientific American*, 192:52-60, 1955.

[7] The term *vitamin D* is applied to a group of chemically related sterols that function to regulate the utilization of calcium and phosphate compounds in the body (p. 503). One form of this vitamin is found in fish-liver oils. Viosterol is a synthetic form of vitamin D_2 prepared by irradiating ergosterol.

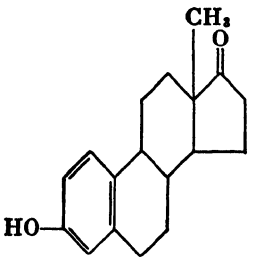


Structural formula for the molecule of ***ergosterol*** ($C_{28}H_{43}OH$)

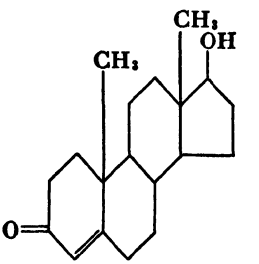


Structural formula for the molecule of ***calciferol,*** or ***vitamin D_2*** ($C_{28}H_{43}OH$)

Steroid hormones. The steroid hormones resemble the sterols in structure. This can be seen by study of their structural formulas, examples of which are presented below in skeleton form.



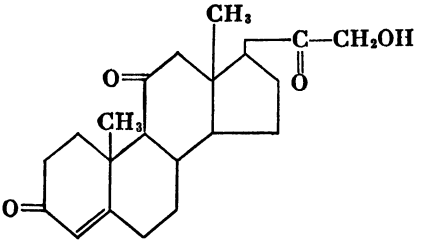
Estrone



Testosterone

Estrone, which probably originates in the ovary, and *testosterone*, made in the testes, are typical examples of the sex hormones. They function in the development of the secondary sex characteristics in female and male, respectively. Other members of this group of hormones have other functions related to reproduction.

Another group of hormones having steroid structure has been isolated from the cells of the adrenal cortex. The formula for *cortisone* is presented as representative of the group.



Cortisone

The cells of the adrenal cortex are relatively rich in cholesterol, thus supporting the idea that the adrenal steroid hormones may be derived from cholesterol. The function of this group of hormones relates to regulation of carbohydrate metabolism and of electrolyte balance—two metabolic processes which are of primary importance to the welfare of the animals.

Waxes. Waxes are related to fats: chemically, they are esters which contain fatty-acid radicals, but the hydrocarbon radical is obtained either from a long-chain or a more complex alcohol instead of from glycerol. Physically, waxes have solubilities similar to those of fats. A typical example of a wax is the ester myricyl palmitate, a component of beeswax.

$$C_{15}H_{31}COO\text{————}C_{30}H_{61}$$

Palmitate radical Myricyl radical

Both plant and animal cells secrete waxes. Bees, of course, are responsible for beeswax; sheep secrete a mixture of waxes, commonly known as lanolin, which is composed of the stearate, oleate, and palmitate esters of cholesterol. The sebaceous glands of the skin of humans also secrete a wax, another ester of cholesterol, which serves to keep the epidermis of the skin soft; and, because of the insolubility of this skin wax in water, as well as in dilute solutions of acids, bases, or salts, it is not easily removed. The acid-fast microorganisms make a waxlike material which contributes to the very effective protection which is peculiar to these organisms.

QUESTIONS

1. Compile a list of 10 commonly occurring fat *mixtures*, classifying them as to plant or animal origin. Indicate in the case of each fat its characteristic physical state. In general, what determines the physical state of a fat?

2. From what substances are fats believed to be synthesized (a) in plant cells, (b) in animal cells? Concerning (a) and (b) what experimental evidence gives reason for the belief in each instance?

3. Are fats nutritionally essential components of the human diet? Explain.

4. Make a general statement as to the solubilities of fats. Compare the following agents as to their suitability for the removal of grease spots, considering efficiency, safety, and economy: carbon tetrachloride, chloroform, ether, ethyl alcohol, gasoline, and water.

5. Why is it desirable to protect the hands from contact with the agents commonly used for dry cleaning in the home? (What agents?)

6. What is the purpose of the ether wash sometimes used in preoperative preparation of the skin?

7. List at least five *individual* fats, giving names, empirical formulas, and semistructural formulas. For one of the selected fats assemble the complete structural formula for its molecule.

8. What is the difference (factual) between a saturated and an unsaturated fat? How, theoretically, is this difference accounted for? Give examples of at least one fat of each variety—with name and formula for each. How is the extent of unsaturation of a fat determined?

9. Why should fats be expected to be subject to hydrolysis? Do such reactions take place readily? Give reason. What, in general, are the products of the hydrolysis of fats? What is the class name given to enzymes which favor such hydrolysis? Assemble word and formula equations for the hydrolysis of a typical fat.

10. What reaction can be expected from the contact of fats with sodium or potassium hydroxide? Assemble word and formula equations for a reaction of this variety.

11. What is the nature of the reaction involved in the hydrogenation of fats? Why are such reactions of economic importance? Assemble word and formula equations for the hydrogenation of olein.

12. What is margarine? How does it compare with butter as a food?

13. Linseed oil is frequently used in paint mixtures. What is the nature of the change involved in the drying of such paints?

14. What is a sterol? Name two which are physiologically important, stating their occurrence and the physiological functioning of each.

15. What is a phospholipid? Where do such compounds occur? Name at least one respect in which they are important physiologically.

16. What is the chemical nature of a wax? Name some common waxes or mixtures with wax components, stating their occurrence.

CHAPTER 28

PROTEINS

Biological importance and sources. Proteins are of special interest because of their outstanding biological importance. They make up a large part of every living organism and participate, in one role or another, in almost all reactions within living cells. The name *protein*, which comes from a Greek word meaning "of first importance," was given in the belief that they were the essential components of protoplasm. Proteins occur in both the cells and the circulating fluids of animals. They contribute to the composition of enzymes and to some of the hormones. They are essential constituents of the complex nucleoproteins composing both genes, which determine the development of the organism, and viruses that invade living cells and produce disease. The secret of antibody production, for protection against infection, is also believed to lie in knowledge of protein chemistry.

Proteins are made within plant cells from carbon dioxide, water, and nitrates; but of how this synthesis is accomplished, or what the intermediate steps may be, little is known. Animals cannot use inorganic compounds to build proteins but must depend on plants for these substances from which they take amino acids for the synthesis of similar proteins of their own specific varieties. Therefore, proteins are indispensable components of the food of all animals.

Constituent elements. All natural proteins contain the elements carbon, hydrogen, oxygen, nitrogen, and sulfur. Many proteins contain phosphorus as well. Other elements are found in certain proteins; for instance, iron is a constituent of hemoglobin, and iodine of thyroglobin.

Molecular weights. Proteins have very high molecular weights. These are computed by various methods which yield somewhat vari-

able results. However, the following are representative findings: lactalbumin, 17,400; human hemoglobin, 63,000; insulin, 40,900; thyroglobin, 628,000; myosin of muscle, 1,000,000.[1] Such findings confirm the belief that protein molecules are large, heavy, complex structures.

Composition of molecules. Some of the generally accepted beliefs concerning the composition of protein molecules are as follows.

1. It is believed that protein molecules are large and relatively heavy, each molecule being composed of a large number of incomplete amino acids in combination with each other. The basis for this belief is the known high molecular weights of proteins and the fact that on reaction with water the end products are many complete amino acids. The number of amino acid linkages differs for different proteins. Some of the values which have been suggested are: egg albumin, 386 amino acids; insulin, 288; human serum albumin, 618; human serum globulin, 1525.[2]

2. Protein molecules are probably very complex. This belief finds support in the facts that proteins are very difficult to hydrolyze without catalytic aid, and that, to date, no protein has been synthesized in the laboratory, despite numerous serious efforts to accomplish this feat.[3]

3. A single protein molecule is believed to contain a variety of different amino acid units, as evidenced by the fact that from 13 to 17 different amino acids have been recovered from the hydrolysis of a single protein. There is also evidence to suggest that individual amino acids are repeated in the molecule after a definite pattern, which varies for different proteins. The structure of insulin, which has been established recently, supports this belief.[3]

4. Within the protein molecule the amino acids are believed to be linked to each other through incomplete amino groups (each deficient in 1 atom of hydrogen) and incomplete carboxyl groups (each deficient in 1 hydroxyl atom group) from adjacent acids. These are known as *peptide linkages.*

5. All natural protein molecules contain some *free carboxyl* groups

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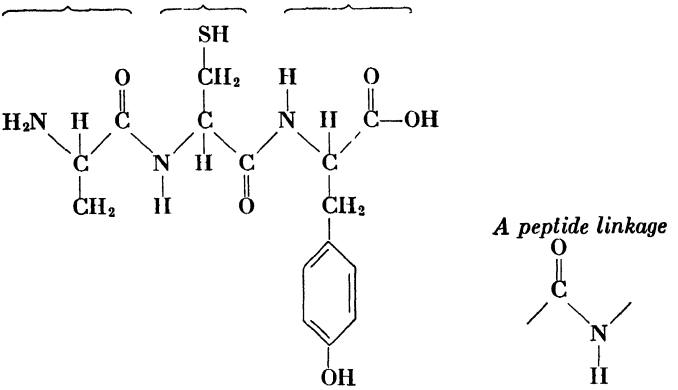
[1] West, Edward S., and Todd, Wilbert T.: *Textbook of Biochemistry*, 2nd ed. The Macmillan Company, New York, 1955, p. 335.

[2] Everett, Mark: *Medical Biochemistry*, 2nd ed. Paul B. Hoeber, Inc., New York, 1946, p. 384.

[3] Linderstrom-Lang, K. U.: "How is Protein Made?," *Scientific American*, 189:100–106, 1953; also Thompson, E. O. P.: "The Insulin Molecule," *Ibid.*, 192:36–41.

through which they react with bases, and some *free amino* groups at which they react with acids (p. 419). Another chemically active group, occurring in most protein molecules, is the *sulfhydryl* group (—SH) provided by the sulfur-containing amino acids (p. 411).

6. Linkages other than those of the amino-carboxyl type probably occur in protein molecules and contribute to their complexity.



The "backbone" of a peptide molecule representing 3 amino acids in combination with each other and 2 typical *peptide* (amino-carboxyl) linkages.

7. The "backbone" of the protein molecule is believed to be provided by the peptide chain. Recent studies of protein structure indicate that, for the most part, these chains are folded or coiled in spiral form with the side chains of the constituent amino acids protruding from the central core. In fibrous proteins the spirals appear to wind around one another very much as cords are twisted together to form a rope.[4]

With keratin, the protein of hair and wool, and the muscle protein, myosin, the fiber can be stretched but returns to its original length on release of tension. The stretching is assumed to result from unfolding of peptide chains.

Many different proteins. More than 40 different amino acids have been reported as products of protein hydrolysis; of these, about 25 are generally accepted as natural constituents of proteins. But with even 25 amino acids as building units, it can readily be seen that numerous combinations of amino acids, hence numerous differ-

[4] Pauling, L.; Corey, R. B.; and Hayward, R.: "The Structure of Protein Molecules," *Scientific American*, 191:51–59, 1954.

ent proteins, should be possible. And actually, a great many different proteins have been discovered. Each species of plant or animal builds proteins peculiar to itself; and several, sometimes many, different proteins are made within the same plant or animal.

Amino acids contributing to proteins. Of the amino acids generally accepted as natural constituents of proteins, the following are selected as representative. (See accompanying table, pp. 410 to 411.) The asterisk indicates indispensable amino acids.

A study of amino acid formulas indicates that certain of these acids, notably arginine, cystine, and lysine, have 2 amino groups in their molecules. Certain others, including glutamic acid and cystine, have 2 carboxyl groups. Inasmuch as 1 amino group and 1 carboxyl group are always involved in the peptide bond which links one amino acid to another, it is probable that the greater number of free amino groups and free carboxyl groups in a protein molecule are provided by the diamino and dicarboxylic amino acid constituents.

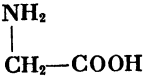
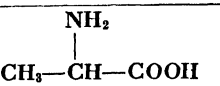
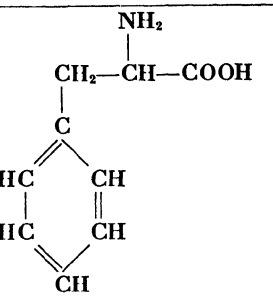
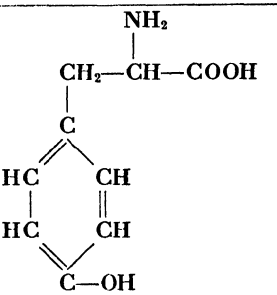
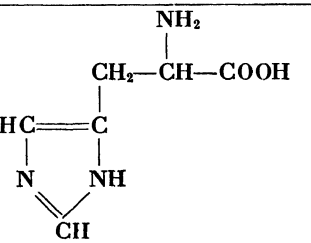
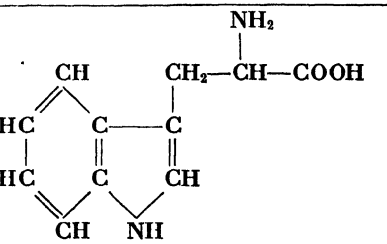
The sulfhydryl group, mentioned earlier as chemically active, is present in cysteine. Reversible oxidation-reduction reactions between cysteine and cystine are believed to occur at this point. This may be of considerable physiological significance in the closing or opening of cross-linkages within protein molecules.

Indispensable amino acids. The amino acids supplied by the proteins of the diet are requisitioned by the cells for the maintenance of tissue proteins; for building new tissue during the growth period; and for production of a variety of special substances such as enzymes, hormones, and creatine. It has been established experimentally that some of the amino acids which are required for these vitally important needs either cannot be synthesized in the animal body or are produced too slowly to meet normal demands for maintenance and growth. Such amino acids must be provided by the food and are known as indispensable amino acids.[5] Much of the experimental work was done with rats, and on this basis the following amino acids are considered as essential.

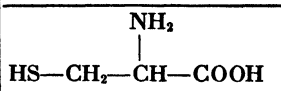
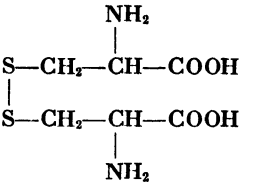
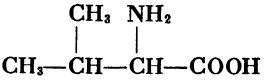
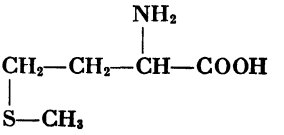
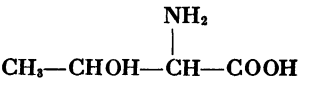
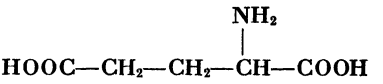
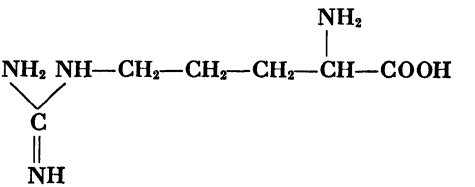
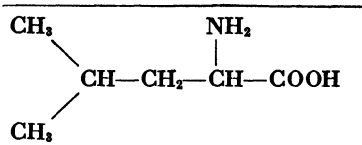
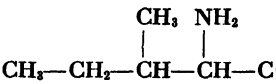
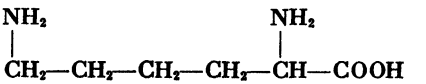
Phenylalanine	Threonine
Histidine	Arginine
Tryptophane	Leucine
Valine	Isoleucine
Methionine	Lysine

[5] Rose, W. C.: "Nutritive Significance of the Amino Acids and Certain Related Compounds," *Science*, **86**:298, 1937.

Representative amino acids

NAME	SEMISTRUCTURAL FORMULA FOR MOLECULE
Glycine (α-amino-acetic acid)	
Alanine (α-amino-propionic acid)	
***Phenylalanine** (α-amino, β-phenyl-propionic acid)	
Tyrosine (α-amino, β-parahydroxy-phenyl-propionic acid)	
Histidine (α-amino, β-imidazole-propionic acid)	
***Tryptophane** (α-amino, β-indole-propionic acid)	

***Representative amino acids** (cont.)*

NAME	SEMISTRUCTURAL FORMULA FOR MOLECULE
Cysteine (α-amino, β-thiopropionic acid)	
Cystine [di(α-amino, β-thiopropionic acid)]	
***Valine** (α-amino, β-methyl, n-butyric acid)	
***Methionine** (α-amino, γ-methylthio, n-butyric acid)	
***Threonine** (α-amino, β-hydroxybutyric acid)	
Glutamic acid (α-amino, β-glutaric acid)	
Arginine (α-amino, δ-guanidino-valeric acid)	
***Leucine** (α-amino, isocaproic acid)	
***Isoleucine** (α-amino, β-methyl-valeric acid)	
***Lysine** (α-ϵ-diamino-caproic acid)	

Although the requirements for growth are more demanding than those for maintenance, it has been demonstrated that the adult rat still needs the full quota of essential amino acids, with the exception of arginine. This amino acid can be made within animal cells but, apparently, not at the rate required to meet the demands for rapid growth in the young animal. Repeated feeding experiments have shown that when *lysine* is removed from the diet the young animal does not grow. When *tryptophane* is removed the animals lose weight and finally die. To some extent certain amino acids not regarded as indispensable can take the place of others which have been shown to be essential. *Tyrosine* can replace about half of the required *phenylalanine*, but without phenylalanine growth ceases. *Cystine* can be substituted in the diet for part of the *methionine*, but cannot replace it entirely.

Human requirements. Knowledge regarding human requirements is more limited but Rose has shown that eight of the amino acids listed as indispensable for the rat are likewise required for man. The exceptions are *histidine* and *arginine*. It is possible that histidine, which can be made in the intestinal tract of man by certain bacteria, may be utilized by the host. The demands of growth may be more exacting than those for maintenance in the adult. It is possible that for the growing child both *histidine* and *arginine* are essential amino acids.[6]

Protein foods vary in relation to providing these food essentials. Milk, eggs, and meat supply the full complement of essential amino acids in proportions that are consistent with human needs. Gelatin contains very little tyrosine or tryptophane. Many of the vegetable proteins are more or less deficient in the amino acids essential for animals. Thus, the proteins of white flour provide the essential amino acids but the proportion of lysine is low. Zein of corn is deficient in lysine and tryptophane. Arachin of peanuts is lacking in methionine and tryptophane. These incomplete proteins, if used alone, would not maintain body weight but it is possible to select combinations of proteins which will supplement each other. In general the American diet includes a sufficiently varied selection of foods to avoid frank deficiencies. However, for growing children and for convalescents, with special demands for tissue building, the full complement of the indispensable amino acids is particularly important, since a deficiency in even one of the essential amino acids becomes a limiting factor in building new tissue.

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[6] White, A.; Handler, P.; Smith, E. L.; Stetten, D.: *Principles of Biochemistry*. McGraw-Hill Book Company, Inc., New York, 1954, p. 1002.

Classification of proteins. So much is still unknown concerning the nature of proteins that, as yet, there is no clear-cut basis for classification. Such classification as has been developed is partly on the basis of certain similarities in chemical behavior and partly on the basis of similar "solubilities," meaning the tendency of proteins to form colloidal solutions in various media. There are, accordingly, three main classes of proteins: simple proteins, conjugated proteins, and derived proteins.

Simple proteins. Simple proteins are those which hydrolyze to make amino acids.[7] There are several varieties of simple proteins of which those of greatest physiological importance are the albumins, globulins, and albuminoids. *Albumins* are coagulated by heat and form colloidal dispersions in water and in dilute salt-and-water solutions. *Globulins* are also coagulated by heat and form colloidal dispersions in dilute salt solutions but not in water alone. *Albuminoids* are decidedly insoluble substances as they do not form colloidal dispersions either with water or with dilute solutions of acids, bases, or salts.

Conjugated proteins. Conjugated proteins are compounds which on hydrolysis make simple proteins and other products.[8] Important members of this group are as follows.

1. *Nucleoproteins* are especially abundant in cell nuclei; on hydrolysis they make simple proteins and nucleic acid (p. 424).

2. *Phosphoproteins* are found in the cytoplasm of cells; they hydrolyze to make simple proteins and phosphorus-containing compounds. Casein of milk and vitellin of eggs are phosphoproteins.

3. *Glycoproteins* hydrolyse to yield simple proteins and carbohydrates. Examples are the mucin of saliva and the gastrointestinal secretions, the proteins of synovial fluid, and the mucoid of tendons, cartilage, and bone. Ovumucoid is also a glycoprotein.

4. *Chromoproteins* are characterized by color. An outstanding example is hemoglobin of the red blood cell, which hydrolyzes to yield a simple protein and hematin—an iron-containing complex. The cytochromes, which occur in all aerobic cells and function in oxidation-reduction reactions, are also iron-containing chromoproteins.

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[7] Recent findings have shown a carbohydrate group to be present in some of the so-called simple proteins.

[8] The nonprotein group that contributes to these complex proteins is referred to as the *prosthetic* group, from the Greek *prosthetos* meaning "to put on."

The flavoproteins known as "yellow respiratory enzymes" likewise belong to this group.

Derived proteins. Derived proteins are products of certain changes in naturally occurring proteins. This group includes:

1. *Proteoses, peptones,* and *peptides* are intermediate products in the hydrolysis of simple proteins.

2. *Proteans* are the insoluble proteins which result from certain enzyme actions on selected proteins of milk and blood. *Calcium paracaseinate* of milk clot, made through the action of rennin in the digestion of casein, the *clot of Junket,* and *fibrin of clotted blood,* made from fibrinogen of blood, are examples.

3. *Coagulated proteins* are insoluble compounds made from the more soluble proteins through various means, such as the action of heat or prolonged contact with alcohol. Familiar examples are coagulated proteins made by heating the "soluble" proteins of egg and meat during cooking; also those of stiffened egg white that result from beating.

SIMPLE PROTEINS

Albumins, globulins, and albuminoids. The *albumins* and *globulins* are widely distributed in plants and animals. They are usually associated, with one or the other in predominance. Albumins predominate in milk and in egg white; both occur in blood, in the intercellular fluids, and within cells. In general, globulins predominate within cells and albumins in the circulating fluids. The terms serum albumin and serum globulin are used frequently when referring to these proteins in blood plasma. *Albuminoids,* also known as scleroproteins, are found in skin, hair, nails, and in the collagen of connective tissue. Gelatin is a product of hydrolysis of albuminoids.

Solubilities and their importance. The fact that *albumins* and *globulins* form colloidal dispersions in dilute salt solutions is of considerable importance physiologically. It is also of interest in cookery.

The blood, lymph, and contents of cells are dilute salt solutions, thus ensuring colloidal dispersion of albumins and globulins. The fact that these proteins are in colloidal rather than in true solution explains why they do not diffuse freely through membranes. Thus, they do not normally pass through the intestinal membrane into

the blood: blood proteins remain within the blood vessels; cell proteins do not escape into the fluid surrounding the cells. Some exceptions to these generalizations must be recognized in that it appears that albumins do diffuse to a slight extent from blood capillaries into the intercellular fluid. It is also considered possible that certain protein allergies may be related to absorption of some protein particles across an abnormally permeable membrane.

In cookery, when it is desirable to have the nutritive materials from the meat cells escape into the surrounding fluids, as in the preparation of soups or stews, the meat is covered with dilute salt solution. This enables the albumins and globulins, along with other components, to escape from ruptured cells and become distributed in the surrounding water.

Physiologically, the fact that *albuminoids* are insoluble in water, as well as in dilute acids, bases, and salts, is of importance because, in this way, the exposed tissue affords protection in the everyday contacts with water and dilute solutions of electrolytes.

CHEMICAL BEHAVIOR OF PROTEINS

Denaturation. Proteins are very sensitive to environmental conditions and readily undergo changes known as denaturation. One of the commonest examples of this is the coagulation that occurs when certain proteins are heated. Similar, although often less evident, changes result from exposure to ultraviolet, x-ray, and gamma radiation, to violent shaking, and to prolonged contact with alcohols, acids, bases, and certain other chemicals. In general, denatured proteins are less soluble than the natural ones, hence the tendency to coagulation; but they are hydrolyzed more readily. Natural proteins which exhibit specific biological functioning, upon being denatured, become inactive. Thus, the enzymes pepsin and trypsin are inactivated by high temperatures; the protein insulin is claimed to be inactivated by contact with alcohol; and proteins which function specifically in immunity reactions lose this ability when denatured. As to the character of these reactions, very little is known; they are believed to involve disorganization of molecule structure with release of some of the inner molecule linkages, notably of sulfhydryl groups (p. 409).

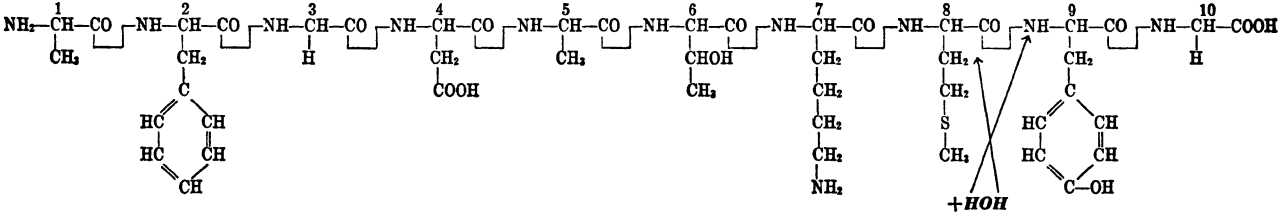
Importance of coagulation of proteins by heat. The *coagulation of proteins* when subjected to heat is of practical interest be-

cause of the part it plays in a variety of concerns. At temperatures of 60° C and above it occurs rapidly. When heat is used as a *means of sterilization*, the destruction of microorganisms is due largely to coagulation of proteins within their cells as a result of the high temperatures provided. This property of proteins is sometimes employed as a means for *testing for their presence in the urine.* Should any considerable quantities of protein be present therein, the urine specimen, when heated, will become cloudy because of the insoluble coagulated proteins made. *In cookery* it is responsible for the coagulated proteins of soft- and hard-cooked eggs. And, in cake-making, the egg proteins, previously distributed in the cake batter through beating, then lifted by hot escaping gases coagulate in the heat of the oven. In this manner the cake is "lightened," and a supporting mesh is provided for the cake mixture. *In cleaning* milk bottles and dishes with clinging egg, or in cleaning clothes or linen soiled with bloodstains or other protein material, this property of proteins is somewhat of a nuisance to the careless or uninformed housekeeper. Such dishes, clothing, or linen should first be rinsed thoroughly with cold water, or better with dilute salt solution, for carrying the proteins away in colloidal solution. If hot water is used first, the proteins coagulate, and the insoluble compounds thus made are very difficult to remove.

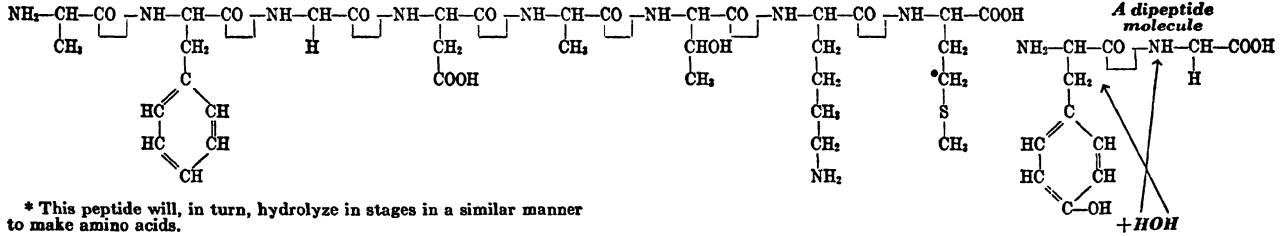
Subject to hydrolysis. Proteins are subject to hydrolysis, the end products being amino acids. These reactions are inappreciable at ordinary temperatures unless a favoring catalyst is provided. Exposure to superheated steam over a period of days, or boiling for several hours in the presence of a favoring catalyst, such as dilute hydrochloric or sulfuric acid, is necessary to produce appreciable results. In cookery, therefore, probably little or no hydrolysis of proteins occurs. In the cells of plants and animals, however, protein hydrolysis does occur even at ordinary temperatures, since various enzymes, called proteases, are provided for speeding up these reactions. The best understood of these reactions, and the best known of the enzymes concerned, are those involved with protein digestion along the alimentary tracts of animals, including humans. The proteolytic enzymes there provided are pepsin in the gastric juice, and trypsin and erepsin[9] found in the digestive juices in the intestines.

[9] Erepsin is not a single enzyme but is a mixture of different enzymes of the peptidase variety.

A diagrammatic representation of the hydrolysis of a hypothetical polypeptide molecule

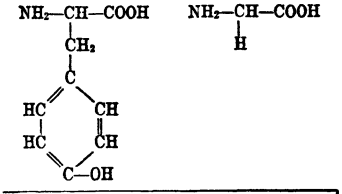


A *peptide molecule* made up of 8 amino acid molecules*



* This peptide will, in turn, hydrolyze in stages in a similar manner to make amino acids.

A dipeptide molecule



Amino acids (end products)

Amino acid constituents of the above particles

Alanine—1, 5
Phenylalanine—2
Glycine—3, 10
Aspartic acid—4
Threonine—6
Lysine—7
Methionine—8
Tyrosine—9

The hydrolysis of proteins in digestive reactions takes place in stages as represented in the following.

$$\text{Proteins} + \text{Water} \xrightarrow{\text{pepsin}} \text{Proteoses} + \text{Peptones}$$

$$\left.\begin{matrix}\text{Proteins}\\ \text{Proteoses}\\ \text{Peptones}\end{matrix}\right\} + \text{Water} \xrightarrow{\text{trypsin}} \text{Peptides}$$

$$\text{Peptides} + \text{Water} \xrightarrow{\text{erepsin}} \text{Amino acids}$$

Presumably, during this process the large protein molecule undergoes a progressive step-by-step hydrolysis to yield successively smaller molecules of protein derivatives with shorter and shorter chains of amino acids; first proteose and peptone molecules, then polypeptide molecules, and finally amino acids.

In hydrolysis reactions water molecules are believed to attack the protein molecule—and its derivatives—at the peptide linkages. The hydrogen atom completes an amino group, while the hydroxyl completes an adjoining carboxyl group, thereby severing the protein molecule at this point. The accompanying diagram (p. 417) suggests the manner of such reactions.

Protein hydrolysates for therapeutic use. The hydrolysis of proteins to amino acids has long been of interest to chemists as one step toward a better understanding of these important compounds. But the preparation of amino acid mixtures for intravenous administration to persons unable to take food by mouth, or needing supplementary protein, was first accomplished in 1937. To perform its function, the protein hydrolysate must provide all of the essential amino acids; hence, it is prepared from the casein of milk (p. 414) or other complete protein. Two methods are in use at present. One is by subjecting casein to prolonged heat with an acid catalyst, the other by use of enzyme catalysts. Each method has certain disadvantages. With acid hydrolysis there is destruction of cystine and tryptophane; the latter, being an indispensable amino acid, must be replaced in the mixture. Hydrolysis of casein with enzyme catalysts is not carried to completion, from 30 to 50 per cent of the resulting mixture being composed of polypeptides; however, this does not preclude the use of the mixture for either oral or intravenous administration. These protein hydrolysates are of great value in the treatment of patients, when an adequate amount of protein cannot be provided through the usual dietary channels.

Proteins are amphoteric. By amphoteric is meant that proteins are in part acids and in part bases (p. 324). ***As acids,*** in an alkaline environment, proteins react with bases to make water and salts. In this way hydroxyl ions are removed, and their concentration in the solution is decreased. The attack, supposedly, takes place at free carboxyl atom groups in the protein molecule, as represented

in the following equation. R in the formula for the protein molecule represents the rest of the molecule.

$$R{-}\underset{\displaystyle NH_2}{\underset{|}{C}}H{-}COOH + Na^+ + OH^- \longrightarrow HOH + R{-}\underset{\displaystyle NH_2}{\underset{|}{C}}H{-}COO^- + Na^+$$

Protein + Sodium hydroxide ⟶ Water + Sodium proteinate

As nitrogen bases, in an acid environment, proteins react with acids, thereby decreasing the hydrogen-ion concentration of the solution concerned. Supposedly, the acids enter into combination with the protein molecules at their free amino groups. Such a reaction takes place readily between a protein and hydrogen chloride.

$$R{-}\underset{\displaystyle NH_2}{\underset{|}{C}}H{-}COOH + H^+ + Cl^- \longrightarrow R{-}\underset{\displaystyle NH_3^+}{\underset{|}{C}}H{-}COOH + Cl^-$$

Protein + Hydrochloric acid ⟶ Protein hydrogen chloride

It is believed that the hydrogen ion becomes bound to the protein molecule to make the hydrogen protein ion as indicated. In this way the concentration of hydrogen ions in a solution is decreased.

Because of their amphoteric nature, proteins of the cells, intercellular fluid, and blood exert an important *buffer effect.* Through these counterreactions they help to maintain the hydrogen- and hydroxyl-ion concentrations in these fluids within the very slightly basic range (*p*H 7.33 to *p*H 7.51) that is necessary for life and health.

Proteins react with salts. Proteins, functioning as acids, react with salts. This behavior is of considerable importance in the transportation of certain metal ions in the blood. Thus, from 30 to 50 per cent of the calcium carried in the blood is in combination with protein, and potassium ions are held in the red blood cells in association with hemoglobin.

Proteins with some salts make insoluble proteinates. When silver nitrate solution is brought into contact with a solution of protein a white, insoluble product, silver proteinate, at once appears. The reaction which takes place may be represented by the following equation.

$$R{-}\underset{\displaystyle NH_2}{\underset{|}{C}}H{-}COOH + AgNO_3 \longrightarrow HNO_3 + R{-}\underset{\displaystyle NH_2}{\underset{|}{C}}H{-}COOAg\downarrow$$

Protein + Silver nitrate ⟶ Nitric acid + Silver proteinate ↓

If, instead of silver nitrate, a solution of mercuric chloride (corrosive sublimate) is used in the same manner, another heavy, white, insoluble substance will appear, this time a mercury salt, namely,

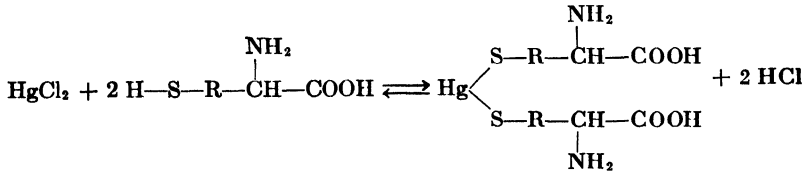
mercuric proteinate. Lead and copper salts likewise form insoluble proteinates.

Salts which react thus with proteins to make insoluble protein salts are more or less caustic, in that when they come in contact with albumins and globulins of cell protoplasm they destroy these proteins, with the resulting death of the cells. This reaction provides the basis for understanding some of the uses which are made of such salts and some of the dangers attendant upon their use.

Uses and dangers. Solutions of certain salts are used *as disinfectants*, notably silver nitrate and mercuric chloride. Their functioning in this capacity lies in their destructive attack, on either the proteins of bacterial cells or on enzymes, likewise protein in nature, which are essential for the vital functions of the organisms. In a similar manner a silver nitrate (lunar caustic) pencil is sometimes used *to destroy* the *excess granular tissue about a wound.*

The very caustic, hence *poisonous*, effect of such salts as mercuric chloride or silver nitrate when taken internally, by accident or with suicidal intent, is due to their reaction with proteins along the alimentary tract. The effect of plenty of egg albumen or milk, *as antidotes* for such poisoning, is obvious, since they provide proteins for the salts to react with instead of those of the tissue cells. The importance of immediate administration of the protein-containing antidote after such a salt is taken is self-evident.

Mercuric salts as disinfectants. It has long been assumed that the disinfectant effect of mercuric salts, notably mercuric chloride, was due, primarily, to the formation of insoluble mercuric proteinates. Recent experimental evidence suggests another mechanism. The mercuric ion, even in dilute solutions, appears to have the specific ability to attack the sulfhydryl groups of proteins and in this way to inactivate enzymes and produce a bacteriostatic effect without necessarily destroying the microorganisms. If the exposure is prolonged the cells die. However, if the exposure is of short duration and favorable conditions are established, the reaction can reverse and enzyme activity be re-established. This throws some doubt on the reliability of mercuric salts as germicides.[10] The following equation suggests the nature of the reaction.

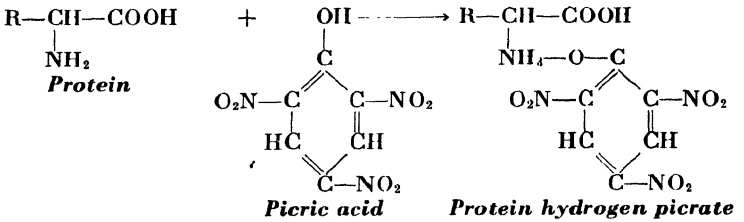


[10] Goodman, L. S., and Gilman, A.: *The Pharmacological Basis of Therapeutics*, 2nd ed. The Macmillan Company, New York, 1955, pp. 1102–1103.

Proteins with some acids to make insoluble products. Certain acids, for instance, picric and tannic acids, react with protein to form insoluble products.

Protein + Picric acid → Protein picrate↓
Protein + Tannic acid → Protein tannate↓

There are several tannic acids, the formulas for which have not been determined satisfactorily. The presumable reaction between molecules of picric acid and protein is represented as follows.



Uses made of such reactions. Both picric and tannic acids are used to some extent *in the treatment of minor burns.* When either acid is painted over the burned area, it comes in contact with proteins of the tissue cells and reacts with them to make insoluble picrates or tannates, as the case may be. A somewhat impervious layer over the injured area is thus provided which excludes air, thereby reducing pain. At the same time the acids have a disinfectant effect because they react with proteins of any bacteria with which they come in contact.

Reagents used in urinalysis. The reagents usually used to detect the presence of albumin in urine are acids that react with proteins to form insoluble compounds. Among the substances employed for this purpose are: *picric acid* (in Esbach's reagent), *nitric acid, trichloroacetic acid,* and *sulfosalicylic acid.*

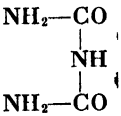
Tungstic acid also belongs to the group of acids which react with protein to form insoluble compounds. This acid is used in analysis of blood to remove protein and thus enable the laboratory worker to identify the electrolytes and other soluble components of blood.

Proteins in reactions to make significant colored compounds. These reactions are used to signify the presence either of amino-carboxyl linkages, or of specific cyclic structures. Frequently, they are called protein tests, a statement which is an error since in every instance there are compounds other than proteins which give similar effects. However, when a positive result is obtained with

any one of these reactions, it is *suggestive* that a protein may be present; and if the material under investigation responds to several of these reactions, the likelihood that a protein is present is increased. But the chief value of these reactions to the chemist lies in the fact that, when applied to compounds *known* to be proteins, positive responses, made evident by the appearance of the colored compounds concerned, signify the presence of definite amino acid constituents.

The biuret reaction. The procedure for obtaining this reaction calls for adding to the dilute protein dispersion under test, first 1 or 2 drops of sodium or potassium hydroxide to provide a basic environment, then a few drops of dilute copper sulfate solution. A complex compound of unknown composition is made which varies in color from blue-violet to red-violet. In general, the blue-violet compound is obtained with proteins, whereas the red-violet compound is more indicative of peptones and peptides. The reaction is reported as being *significant of at least two amino-carboxyl linkages;* hence, it applies to all proteins and their hydrolysis products down to and including, tripeptides. It functions only with proteins in colloidal dispersion, not with insoluble proteins such as albuminoids and coagulated proteins. It is unreliable if colored compounds are present.

Since the biuret reaction is specific for the linkages mentioned, it gives positive response not only with proteins but with all compounds which contain said linkages. Among such compounds is the one called biuret from which the reaction derives its name. The formula for *biuret* is as follows.



Xanthoprotein reaction. When a protein, either soluble or insoluble, comes in contact with nitric acid, a compound, lemon-yellow in color, is made. In an alkaline environment, this color deepens to an orange. It is from xanthoprotein, meaning *yellow protein,* that this reaction derives its name. The yellow stain that appears when nitric acid is spilled on the skin, or on wool or silk, is due to this reaction.

If the protein is in solution in a test tube, and if nitric acid (concentrated) is poured carefully down the side of the tube, the precipi-

tated yellow protein appears in a ring formation, called *Heller's ring*, at the junction of the two liquids. This procedure is frequently used for testing the possible presence of proteins in the urine.

The appearance of xanthoprotein is *indicative of the benzene nucleus*, hence signifies the presence of one (or all) of the three amino acid linkages which contain this nucleus: namely, phenylalanine, tyrosine, and tryptophane. Almost all natural proteins respond to this test.

Compounds other than proteins which contain the benzene ring also make yellow compounds when treated with nitric acid. Picric acid (p. 343) is such a yellow nitrobenzene derivative.

Millon's reaction. The reagent used in Millon's reaction is a mixture of mercuric and mercurous nitrates. When this reagent is mixed with a protein and heated, an insoluble reddish compound of unknown composition is made, *providing the protein contains a tyrosine linkage.* Gelatin does not respond to this test, which is evidence that it contains little or no tyrosine. Peptones and peptides give the red color but not the insoluble material. Millon's reaction is not specific for tyrosine but is given by phenols in general.

Hopkins-Cole or glyoxylic acid reaction. The reagent used in the reaction is glyoxylic acid (formula CHO—COOH), and a positive response to the reaction indicates the *presence of indole* as a constituent of the compound tested. The procedure is as follows. Equal quantities of glyoxylic acid solution and the solution under investigation are mixed in a test tube. Then concentrated sulfuric acid is poured carefully down the side of the tube, held in a slanting position, in such a way that the denser acid does not mingle with the solution but settles as a distinct layer beneath it. If the compound tested contains an indole constituent, a delicate violet ring appears at the junction of the two liquids (Fig. 88). If the compound is a protein, a positive response signifies the presence of the one amino acid which does contain indole—namely, tryptophane. All adequate proteins contain tryptophane; gelatin, which is deficient in this amino acid as well as in tyrosine, does not react with glyoxylic acid

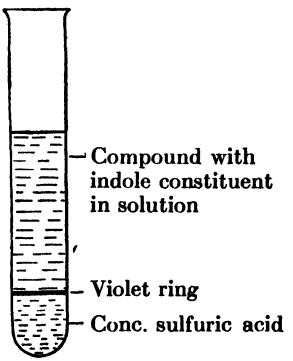
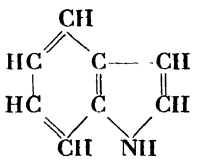
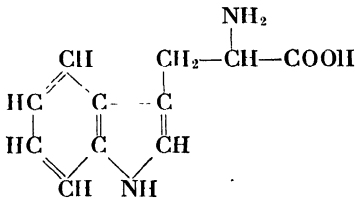


Fig. 88. With Hopkins-Cole reagent.

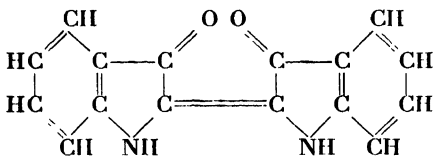
in the manner described. The nature of the reaction is not known, but inasmuch as indigo, which is blue, is known to be oxidized indole, it is conjectured that the glyoxylic acid may oxidize the indole portion of compounds containing it, such as tryptophane, to make other compounds which approximate the blue color of indigo. The following formulas for indole and indigo, also for tryptophane, suggest this relationship.



Indole



Tryptophane



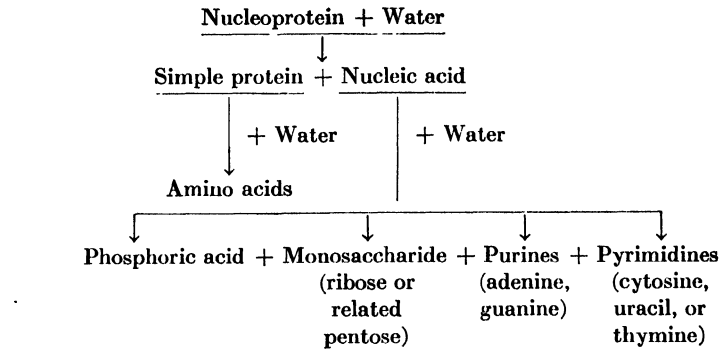
Indigo (*oxidized indole, which is blue*)

Tryptophane oxidized in similar manner presumably results in a compound with a color that is suggestive of that of indigo.

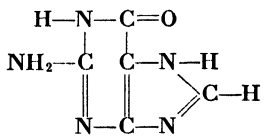
NUCLEOPROTEINS AND RELATED COMPOUNDS

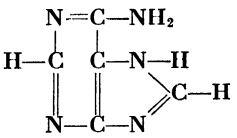
Nucleoproteins. Nucleoproteins are present within the cells of both plants and animals. They have long been recognized as components of the nuclei; they are now known to occur in the cytoplasm as well. They abound in glandular tissues which are rich in nuclear material, notably in liver, spleen, pancreas, thymus, and kidney; they are not abundant in muscle cells. In plants the richest sources of nucleoproteins are germs of grains and yeast cells. They are also components of cells of bacteria and other microorganisms, notably of viruses.

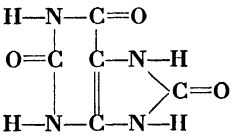
Hydrolysis products. Nucleoproteins are conjugated proteins which on hydrolysis yield simple proteins and nucleic acid. Nucleic acid, in turn, hydrolyzes to yield phosphoric acid, a monosaccharide, purines—usually adenine and guanine, and pyrimidines—cytosine and either uracil or thymine. Both purines and pyrimidines are nitrogenous compounds of the heterocyclic (p. 352) variety.



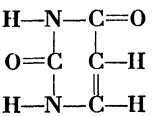
Purines

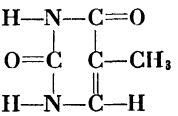

Guanine

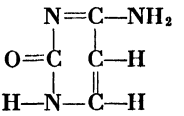

Adenine


Uric acid

Pyrimidines


Uracil


Thymine


Cytosine

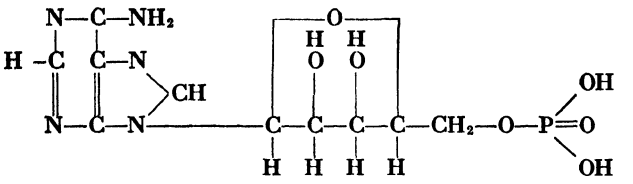
Two varieties of nucleoprotein have been discovered. Formerly it was thought that this represented a distinctive difference between the nucleoproteins of plants and animals. It is now believed that no such distinction can be made, but, rather, that one variety contributes to cell nuclei and the other to the cytoplasm.

Biological interest. Concerning the functioning of nucleoproteins within living cells, very little is yet known with certainty. As essential components of the *chromosomes*, they are believed to function in cell reproduction and the transmission of hereditary traits. The *viruses*, which appear to be essentially nucleoprotein in composition, are of unusual interest because when virus nucleoprotein enters the cells of the host it induces the cell to reproduce virus protein, even at the expense of the natural constituents of the cell.

Purines and *pyrimidines* contribute to substances other than nucleoproteins which function in metabolic reactions. *Adenine*, for in-

stance, forms part of the structure of adenylic acid and the related compounds adenosinediphosphate (ADP) and adenosinetriphosphate (ATP) which function in energy production within living cells (pp. 460 to 464).

Adenylic Acid



Adenine also contributes to coenzyme I, the diphosphopyridine nucleotide (DPN) and to coenzyme II, the triphosphopyridine nucleotide (TPN),[11] which function in oxidation-reduction reactions within cells. (See Chapter 29.)

The vitamin *thiamine* contains a pyrimidine group (p. 353) and this, in turn contributes to the enzyme cocarboxylase, which functions in carbohydrate metabolism (p. 468).

Both plants and animals build their own nucleoproteins. Experimental evidence obtained through use of substances containing the nitrogen isotope, N^{15}, indicates that both purines and pyrimidines are made within animal cells from intermediate products of protein metabolism.[12] One exception appears to be that the animal is dependent on plants for thiamine. The present knowledge of nucleoproteins and their functioning is far from complete, but there is no doubt as to their great importance in cellular metabolism, reproduction, and development.

ENZYMES AND PROTEIN HORMONES

Amino acids provided by the proteins of food contribute to the composition of the enzymes and certain of the hormones which regulate reactions within living cells. Of the more than 20 different enzymes that have been obtained in relatively pure crystalline state,

[11] A nucleotide is a compound composed of a purine or pyrimidine linked with ribose, or a related compound, and a phosphate group.

[12] Schoenheimer, Rudolf: *The Dynamic State of Body Constituents*. Harvard University Press, Cambridge, Mass., 1946, p. 61.

all are protein in nature. Of the protein hormones the best known is *insulin*, secreted by the pancreas. The composition of this hormone has been determined and its constituents include 16 different amino-acid units, also the element zinc. The protein nature of insulin accounts for its destruction in the digestive tract and why it must be administered hypodermically rather than by mouth.

Normally, insulin is secreted in response to metabolic demands. The diabetic has the problem of regulating his insulin supply in relation to food intake and activities. The ordinary insulin, which gives an almost clear solution, following injection is rapidly absorbed and carried to the cells. In an attempt to delay absorption and prolong the action of insulin, the more complex protamine zinc insulin was developed through combination of insulin with a zinc salt and protamine, a simple protein of fish origin. The resulting preparation forms a turbid colloidal solution which is absorbed slowly and gives prolonged action. Other modifications are NPH-50, a stable mixture of active insulin and protamine zinc insulin, and globin zinc insulin in which the protein globin substitutes for protamine. Both of these preparations have a moderately long insulin action.

Thyroglobin, the hormone produced by the thyroid gland, is also a protein. It consists of a globulin in combination with thyroxine, an iodine-containing amino acid (p. 484). The hormone *epinephrine* or *adrenaline*, secreted by the adrenals glands, is believed to be made from tyrosine (p. 484). And, it has recently been reported that ACTH, the adrenocorticotropic hormone secreted by the anterior pituitary gland, is also a protein hormone.

QUESTIONS

1. What factual findings indicate the biological importance of proteins?
2. Many different proteins are known; each species of plant or animal builds its own specific proteins. How is this fact explained theoretically?
3. Assemble a semistructural formula representation for a hypothetical peptide molecule showing: (a) at least five different contributing amino acids, (b) several peptide linkages, (c) two or more free amino atom groups and two or more free carboxyl atom groups, and a sulfhydryl group.
4. What is meant by the term *indispensable amino acids?* List the indispensable amino acids and mention at least two foods which supply *all* of these essential components.
5. What is the source of the commercial protein hydrolysates? Name their essential components.
6. What is meant by a simple protein? A conjugated protein? A derived protein? How do these proteins differ? Name several examples of common proteins belonging to each class.

7. Keeping in mind the "solubilities" of various simple proteins and their behavior on being subjected to high temperatures, explain each of the following:
   a. The disinfectant effect of high temperatures
   b. The best procedure for the removal of egg stains, bloodstains, and mucous secretions from fabrics
   c. How the presence of eggs in the batter affects the leavening of cake or muffins
   d. The procedure for treating meat in the making of soup or stew
   e. The advantage of rinsing blood from syringes before autoclaving them

8. What is meant by the statement that proteins are amphoteric? How does this property enable them to function as "buffers"? Illustrate by means of equations the possible reaction of the protein upon introduction into the solution of an acid; of a base.

9. From the standpoint of the protein involved account for:
   a. Why salts of heavy metals are poisonous. Name several such salts.
   b. The action of white of egg or milk as an antidote for such poisonings. Why is prompt administration essential?
   c. The action of mercuric chloride as a disinfectant
   d. The use of the silver nitrate pencil for destroying excess granular tissue about a wound

10. Egg albumen, when subjected to the following tests, gives positive results with each—biuret, Millon, xanthoprotein, Hopkins-Cole. What information is thereby provided concerning the composition of this protein? Gelatin, when subjected to the same tests, fails to give a positive result with either the Millon or Hopkins-Cole reagent. What information is thereby provided concerning this protein? Of what nutritional significance is this finding as to gelatin?

11. What are nucleoproteins? Where are they located in the body?

12. On the basis of chemical nature account for the facts that: (a) enzymes are inactivated by exposure to high temperatures, and (b) insulin cannot be administered effectively by mouth.

CHAPTER 29

ENZYMES AND THEIR FUNCTIONING

Earlier in our study enzymes were introduced as catalysts that are produced in cells of plants and animals to promote chemical reactions of biological importance (p. 52). Much of the early interest in catalysts centered around yeast fermentation and the digestive reactions. More recently means for exploring the chemical changes within the less accessible cells of tissues reveal that practically all reactions carried on in cells of animals and plants—including microorganisms—are under enzyme control.

A great variety of enzymes can be produced by a single plant or animal, each different enzyme controlling a different reaction. Some function within the cells where they are produced, and these are known as *endo*cellular enzymes. Others are secreted within the cell and released to function outside; these are known as *extra*cellular enzymes. Some understanding of enzymes and their functioning will provide a foundation for understanding the digestive reactions and metabolic processes in general.

Classification of enzymes. There is no very satisfactory basis for classifying enzymes. They are usually classed according to the type of reaction catalyzed and the substrate with which they act. The following types are among those that will be frequently encountered in our continued study.

1. ***Hydrolytic enzymes,*** as the name suggests, favor hydrolysis reactions. Some of these enzymes are already familiar, having been introduced in our earlier study. They include:

a. *Carbohydrate hydrolyzing enzymes:* cellu*lases*, produced by bacteria and molds to function in hydrolysis of celluloses; amy*lases*—

including ptyalin and pancreatic amyl*ase*—which favor hydrolysis of starches; and sucr*ases*, lact*ases*, and malt*ases* for hydrolysis of sucrose, lactose, and maltose, respectively.

b. *Esterases for hydrolysis of esters, including fats:* lip*ases* functioning with fats; cholester*ase* in blood and other tissues for hydrolysis of cholesterol esters; lecithin*ases* in kidney, brain, and intestinal membrane to hydrolyze lecithin; and phosphat*ases* for releasing phosphoric acid from organic phosphates.

c. *Protein hydrolyzing enzymes* which function at peptide bonds. These include pepsin and rennin of the gastric juice; trypsin and chymotrypsin secreted in the pancreas; peptid*ases* produced along the intestinal tract and by bacteria; plant enzymes of which *papain* produced by the papaya plant and used as a "meat tenderizer" is cited as an example.

2. ***Enzymes functioning in oxidation-reduction reactions.*** These include:

a. *Dehydrogenases* which transfer hydrogen atoms from the substrate to a hydrogen receiver, usually some other organic compound. Some of the flavoprotein enzymes, containing the vitamin riboflavin, belong to this group and function in intermediate metabolism of glucose and glycogen (p. 468).

b. *Oxidases* which engage in the transfer of electrons from metabolic intermediates to oxygen, thus preparing for the combination of oxygen with hydrogen to make water—an end product of metabolic reactions.

3. ***Carboxylases*** (or decarboxylases) which effect the removal of carbon dioxide from carboxyl groups—as in the decomposition of histidine to make histamine (p. 491).

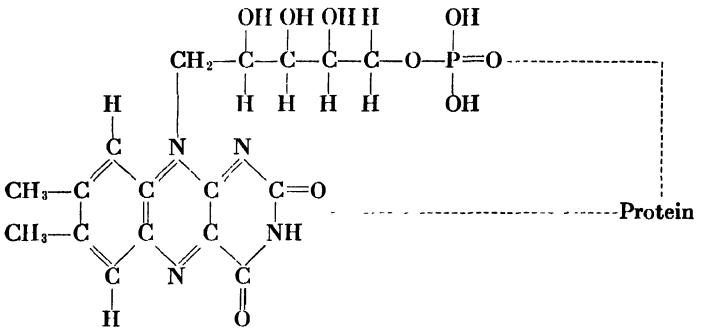
4. ***Transaminases*** functioning in the transfer of amino groups from one organic compound to another; for instance, in building amino acids from carbohydrate intermediates (p. 482).

5. ***Others:*** Many other types of enzymes are known to function in specific reactions. For instance, a hexokin*ase* favors the making of glucose-6-phosphate (p. 460), whereas isomer*ases* and mut*ases* bring about rearrangements of atoms within molecules. In fact the number and variety of different enzymes appear to be endless.

Nature and composition of enzymes. All enzymes studied to date are proteins, either in whole or in part. Some, including trypsin and pepsin, appear to be simple proteins. Others resemble the conjugated proteins in that they are composed of a specific protein with

an associated nonprotein group known as a *coenzyme*. Both the specific enzyme protein and the coenzyme must be present in order for the enzyme to be active.

Some of these ***coenzymes*** are themselves complex in structure; for example, the iron-containing *heme* group occurs in the cytochromes, and in the flavoproteins (yellow enzymes) the coenzyme is riboflavin phosphate. In fact it is noteworthy that a number of the members of the vitamin-B complex have been identified as contributing to coenzymes (p. 434), thus affording a clue as to why these vitamins are nutritionally essential.



Riboflavin phosphate with enzyme protein

Metal ions appear to be essential for the functioning of some enzymes. For instance, zinc is associated with carbonic anhydr*ase* which catalyzes the reversible reaction of carbon dioxide with water to make carbonic acid.

$$H_2O + CO_2 \underset{\longleftarrow}{\xrightarrow{\text{carbonic anhydrase}}} H_2CO_3$$

Copper is required for building hemoglobin although it does not appear in hemoglobin itself; presumably it contributes to an enzyme catalyst. In fact, when metal elements are always present, but in mere traces, their possible enzyme functioning is suggested.

The protein nature of enzymes provides an explanation for their sensitivity to many destructive agents. Thus, all enzymes are inactivated by prolonged heating. Although some enzymes produced by bacteria can withstand temperatures up to 100° C, most enzymes are destroyed at temperatures of from 60 to 80° C. Enzymes are not used up in the course of their catalytic functioning. But, because

of their unstable organic nature, they are readily destroyed; hence, they must be continuously replaced by the cells in order that enzyme activity may be carried on.

Many enzymes are secreted in an inactive form and require the presence of some particular condition or auxiliary substance to produce the active catalysts. For instance, the gastric mucosa secretes an inactive substance known as pepsinogen which is the precursor of the enzyme pepsin. In an acid environment of at least *p*H 5.4, and with a trace of active pepsin already present, the catalyst pepsin is made from inactive pepsinogen. Another example is provided by trypsin. This enzyme is made when trypsinogen,[1] secreted by the pancreas, comes in contact with the enzyme enterokinase, secreted by the intestinal glands; but, strangely enough, for more trypsin to be made some must be already present.

Mode of action. Enzymes, in general, are specific in their action. A given enzyme will function as a catalyst for only a given type of reaction and with a given substrate (reacting substance or substances). For example, pepsin accelerates the hydrolysis of proteins but does not influence the hydrolysis of either fats or carbohydrates; also different enzymes appear to be required for the hydrolysis of the closely related compounds sucrose, lactose, and maltose. One explanation of this selectivity is that a given enzyme will act at only certain linkages in the substrate molecule, and unless these are present no reaction will occur.[2] For example, pepsin and trypsin, although both functioning in the hydrolysis of proteins, are believed to attack different points in the protein molecule.

It is believed that the first step in enzyme functioning involves an actual reaction of the enzyme with the substrate, but that, in the course of a subsequent reaction, the enzyme is remade and once more becomes available for reaction with other portions of the substrate.

(1) Substrate + Enzyme $\longrightarrow$ Activated substrate

(2) Activated substrate + Partner substance $\longrightarrow$ New products + Enzyme

In this manner, a small amount of enzyme can catalyze the reaction

[1] In general, the ending *-ogen* indicates that the substance referred to is the precursor of a closely related but more active compound.

[2] Fruton, J. S.: "Enzymic Hydrolysis and Synthesis of Peptide Bonds" in *Currents of Biochemical Research*, David E. Green, ed., Interscience Publishers, Inc., New York, 1946, pp. 123–27.

of a large quantity of the reacting material. For example, 1 mg of rennin can bring about the clotting of casein in 4.5 liters of milk within 10 minutes; and 1 mg of sucrase can effect the hydrolysis of 200,000 times its weight of sucrose.[3]

Enzyme-catalyzed reactions frequently take place at temperatures much lower than those required for the same reaction without the enzyme, or even with an inorganic catalyst. It is thought, therefore, the enzyme may act to decrease the quantity of energy required to initiate the reaction.

Factors affecting the speed of enzyme action. 1. *Temperature.* As with most chemical reactions, there is increase in the speed of enzyme action with increase in temperature. At 0° C enzyme activity is slow or inappreciable, but as the temperature of the substrate is raised the action of the enzyme becomes more pronounced, until a temperature is reached at which the accelerating action is offset by destruction of the enzyme. The environment most favorable for action of the digestive enzymes is between 40° and 50° C.

2. *Hydrogen-ion concentration.* Enzymes are sensitive to changes in hydrogen-ion concentration and, for most enzymes, the conditions which are optimum for their catalytic activity occur within rather narrow ranges. For pepsin this range is from *p*H 1.8 to 2.2; for ptyalin from *p*H 5.6 to 6.6; for trypsin about *p*H 7.5 to 8.3.[4] Extreme variation in hydrogen-ion concentration often results in destruction of the enzyme. Further reference will be made to the relation of hydrogen-ion concentration and enzyme activity as this study progresses.

3. *Concentration relations.* The establishment of good surface of contact between the enzyme and the reacting material is also important. In general, the speed of enzymatic reactions is roughly proportional to the concentration of the enzyme. However, if the substrate is too dilute, the full catalytic function of the enzyme may not be called into action. On the other hand, if the substrate is in excess, the enzyme may become involved in the substrate-enzyme combination and thus not be immediately available for further enzyme activity.

4. *Presence of specific ions.* For some, perhaps all, enzymes, the presence of certain ions is essential for optimum activity. Thus, calcium ions are known to favor the activity of trypsin and sodium

[3] Williams, Roger J.: *Textbook of Biochemistry*, 2nd ed. D. Van Nostrand Company, Inc., New York, 1942, p. 233.

[4] *Ibid*, p. 238.

ions the activity of ptyalin. Enzymes can also be inactivated by contact with certain ions in the solution, notably those of mercury and silver, also fluoride and cyanide ions. The effects of these ions are sometimes, but not always, reversible.

Terminology. The ending *ase* has come to be used to designate enzymes. Frequently, but not always, this ending is used in conjunction with the name of the principal substance involved in the reaction; thus, sucr*ase* is the enzyme which hastens the hydrolysis of sucrose; lip*ases* catalyze the hydrolysis of fats (lipins). Some of the longest-known enzymes, including ptyalin, pepsin, and trypsin, are still referred to by names which do not suggest their function.

VITAMINS CONTRIBUTE TO ENZYMES

As has already been intimated, a number of vitamins have been identified as contributing to various coenzymes. Thus, gradually, some insight is being provided as to the biological functioning of vitamins although, in most cases, the relation between biological functioning of the vitamin and the train of symptoms associated with vitamin deficiency is as yet incomplete. The following members of the B complex have been definitely identified as constituents of enzymes.

1. *Thiamine* diphosphate is the coenzyme for cocarboxylase, an enzyme which catalyzes the decarboxylation of pyruvic acid. This decarboxylation is the first step toward the oxidation of pyruvic acid to carbon dioxide and water (p. 468).

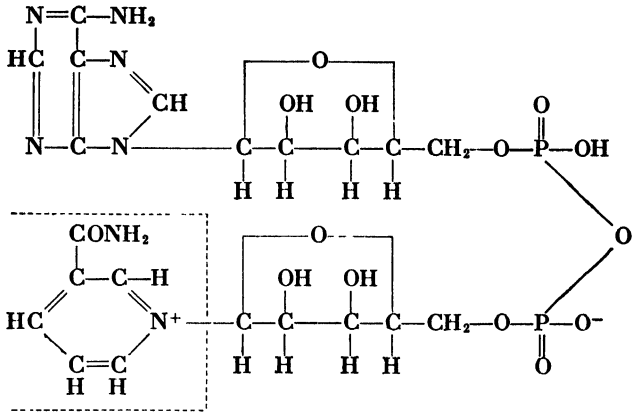
2. *Riboflavin* is a constituent of the flavoprotein enzymes which function as dehydrogenases in certain oxidation-reduction reactions (p. 431).

3. *Nicotinamide* occurs in both the diphosphopyridine nucleotide (DPN) and the related compound triphosphopyridine nucleotide (TPN), also known as coenzyme I and coenzyme II. These compounds contribute to many of the dehydrogenases, including some which function in the oxidation of glucose in muscle cells.

4. *Pyridoxyl phosphate*, derived from pyridoxine vitamin B_6, has been identified as a coenzyme for certain of the transaminases.[5]

5. *Pantothenic acid* is reported to be part of coenzyme A which facilitates the transfer of the acetyl radical from one organic compound to another. As such it is believed to be involved in the inter-

[5] Fruton, J. S., and Simmonds, S.: *General Biochemistry*. John Wiley & Sons, Inc., New York, 1953, p. 667.



Diphosphopyridine nucleotide, showing nicotinamide group

mediate metabolism of both fats and glucose, also to aid in formation of acetyl choline (p. 401).[6]

It is considered probable that other members of the vitamin-B group will be found to have enzyme functions. *Ascorbic acid* also has been mentioned as part of a coenzyme functioning in the metabolism of tyrosine. None of the fat-soluble vitamins has yet been found in enzymes.

QUESTIONS

1. What is an enzyme? A coenzyme?
2. What, in general is the chemical composition of enzymes? What chemical behavior of enzymes in general can be explained by their composition?
3. What is meant by the statement that enzymes are specific in reaction? Illustrate by specific examples.
4. How does the penetration of hydrochloric acid into the food mass in the stomach affect the activity of ptyalin? Of pepsin? What might be expected to be the effect of a large dose of sodium bicarbonate taken by mouth on the activity of pepsin? Explain.
5. How could enzyme activity be checked at a desired stage in laboratory study?
6. Explain each of the following terms: hydrolytic enzyme, esterase, oxidase, dehydrogenase, carboxylase, transaminase. Locate—in other parts of this text—one example of a metabolic reaction typifying each of these types of enzyme function.
7. What relation appears to be characteristic of vitamins of the B complex and enzyme action? Illustrate by reference to typical instances.

[6] *Ibid*, pp. 885–87.

CHAPTER 30

CHEMISTRY OF DIGESTION

The foods of the usual diet contain carbohydrates, fats, proteins, vitamins, salts, and water, all of which contribute to the vitally important metabolic reactions within the cells of the living animal. Of these substances, glucose, vitamins, salts, and water are ready for absorption and use within the body when they enter the alimentary tract. But the larger portion—including most of the carbohydrates, all of the fats, and all of the proteins—must undergo digestive reactions to make other substances which can be absorbed into the blood and lymph and carried to the cells. Still other components of the food mixture are never absorbed but are eliminated directly from the intestinal tract.

What is digestion? Although these digestive reactions are chemical in nature, they are preceded and accompanied by physical processes which greatly facilitate the chemical changes. *Digestion is the sum total of the changes, both physical and chemical, that carbohydrates, fats, and proteins undergo in order to provide absorbable nutrients for transportation to the cells.*

Physical processes of digestion. The physical processes of digestion include (1) motility, which provides for thorough mixing of the contents along the alimentary tract; (2) provision for obtaining various substances in either true or colloidal solution or emulsion; (3) the extensive provision for absorption; and (4) the considerable time that the food mass remains in the alimentary tract, which depends upon the motility of this tract and upon the effectiveness of absorption.

In the mouth, mastication of the food mass breaks it up into smaller particles and mixes it with the saliva. This begins the process of providing for a large area of contact for the food mixture, first with the saliva, later with the

other digestive juices—a condition favorable to the progress of all chemical reactions. At the same time, the food mass is lubricated by mixing with water and slippery mucin, components of saliva, thus making the swallowing process easier. Following the act of swallowing, the food passes along the esophagus to the stomach, its passage being aided by the peristaltic contractions of the esophagus.

In the stomach. Soon after this food mass enters the stomach the strong muscular walls of that organ set up contractions which "churn" the food mass, breaking it up into smaller particles and thoroughly mixing it with the gastric secretion, thereby continuing the process of obtaining a larger surface of contact between the food mass and the digestive secretion. Most of the mechanical action goes on in the pyloric portion of the stomach (Fig. 89), the peristaltic contraction originating about the middle of the organ and traveling toward the pylorus. The fundus region of the stomach is much less active and serves as a reservoir from which portions of the digesting mass are gradually passed on to the more motile regions. From time to time, as digestion progresses, a stimulus is set up which causes the pyloric valve guarding the entrance to the duodenum to open and allow some of the material from the stomach to enter the small intestine. Due in part to the thorough mixing of insoluble substances with water and in part to chemical changes already accomplished, the partially digested mixture leaving the stomach is, for the most part, in a liquid or semiliquid condition. The time required for the passage of a meal through the stomach varies from about 1½ to 4 hours. In general, proteins are retained longest in this location, whereas carbohydrates leave in a shorter time. Fats slow down gastric digestion.

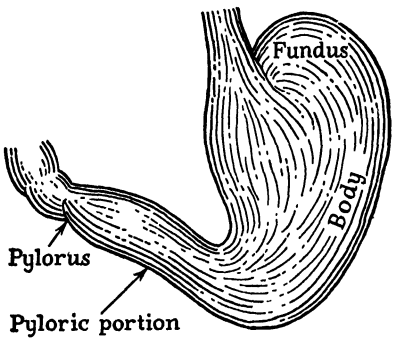


Fig. 89. The stomach. (From Kimber, D. C.; Gray, C. E.; Stackpole, C. E.; and Leavell, L. C.: *Textbook of Anatomy and Physiology*, 13th ed. The Macmillan Company, New York, 1955.)

In the small intestine. In this region the peristaltic and antiperistaltic movement carries the food in a wavelike motion forward and back but nonetheless steadily onward along the digestive tract. Another movement, described as rhythmic segmentation, keeps breaking up the mass into new segments. These two varieties of motion further the process of digestion in a number of ways. (1) There is a continuous mixing of intestinal contents whereby digestive secretions from the pancreas, gallbladder, and intestinal glands are brought in contact with the components of the food mass. (2) Formation of dispersions is favored in the case of substances capable of either true or colloidal solution. (3) The emulsification of fats is promoted. (4) All materials are propelled and distributed along the intestine.

These processes favor the digestive reaction (1) by greatly increasing the surface of contact between the undigested components of the food mass and the digestive juices carrying enzymes and other digestive aids; (2) this movement

of materials promotes absorption of end products of digestion by bringing them in contact with the extensive area of the absorbing membranes; (3) the pressure created by the muscular contractions along the intestine forces blood and lymph, laden with the end products of digestion, out of the capillaries and lacteals of the villi into the larger blood vessels and lymphatics; then the alternate release of this pressure favors an inrush of new blood supplies to pick up new supplies of digestive end products. In this manner absorption is carried forward continuously throughout the small intestine.

The movement along the small intestine is relatively slow, requiring several hours. The time factor is important because it determines how long the components of the food mass will be kept in contact with the digestive secretions and also the opportunity for absorption. Finally, the undigested residue is carried along to the large intestine, from which it is eliminated normally in the course of about 18 more hours.

In the large intestine. The slow movement of the food mass along the large intestine provides for prolonged contact of the undigested residue with various bacteria—normal habitants of this area—thus favoring further digestive attack on certain of the remaining substances. It also permits the reabsorption of a considerable portion of water, helping, thereby, to maintain the fluid balance within the body; as a result, normally, the material that is eliminated at the rectum is in a soft-solid condition.

CHEMICAL DIGESTION

Digestion may be said to begin with the cooking process. At baking and toasting temperatures, very small portions of starch may be hydrolyzed to the dextrin-maltose stage. In baking and broiling, small portions of fats may hydrolyze. Protein connective tissues are softened during cooking procedures, their albuminoid collagen is hydrolyzed to gelatin, and the tissues of the food mass are thereby rendered more pervious to the later penetration of digestive secretions. Other proteins are probably not hydrolyzed in cookery to any extent. Cookery further promotes digestion by rendering the food mass more pleasing to smell, sight, and taste, in this way setting up a reflex stimulation favorable to the secretion of saliva and gastric juice.

By far the greater part of chemical digestion remains to be carried on along the alimentary tract, where nature provides specific enzymes for catalyzing these digestive reactions.

SALIVARY DIGESTION

The saliva. In the mouth the food mass comes in contact with the first of the digestive juices. Saliva is secreted, from substances

obtained from the blood stream, by the parotid, sublingual, and submaxillary glands whose ducts empty into the oral cavity. Its secretion is stimulated both by psychic stimuli, such as pleasing sight, smell, or even thought of food, and by the mechanical stimulus of mastication. From 1000 to 1500 ml of saliva are normally secreted daily, the quantity varying somewhat according to the nature of the food mass and the length of time of mastication. Acids, condiments, and lengthy mastication markedly stimulate secretion; dry and bland foods and brief chewing have only a moderate effect.

The principal components of whole saliva are: water, which makes up over 99 per cent of the whole; *proteins*, chiefly the glycoprotein *mucin*, which accounts for the slippery character, and the enzyme *ptyalin;* inorganic ions, notably sodium, potassium, calcium, chloride, bicarbonate, and the phosphates. The hydrogen-ion concentration is about neutral or slightly acid, varying for different individuals and in relation to meals. One study made on a large number of normal persons found the range to be from *p*H 5.75 to 7.05.[1] This fairly constant range is maintained by buffer reactions which are operating continuously in the saliva. Neither *acids*, from foods or from bacterial action on food particles, nor *bases*, from the use of sodium bicarbonate, basic tooth pastes, or mouthwashes produce more than a slight variation from this reaction. Even then, within a very short time after the entrance of such substances, the reaction of the saliva again becomes normal.[2] The compounds responsible for maintaining this relatively constant hydrogen-ion concentration are carbonates and phosphates that are always present in saliva. Equations for reactions are as follows.

Buffer control of hydrogen-ion-hydroxyl-ion concentration of saliva

One pair of buffers

$$K^+HCO_3^- + H^+ \longrightarrow H_2CO_3 + K^+$$
$$H_2CO_3 + OH^- + K^+ \longrightarrow K^+HCO_3^- + HOH$$

The other pair of buffers

$$K_2{}^+HPO_4{}^- + H^+ \longrightarrow K^+H_2PO_4^- + K^+$$
$$K^+H_2PO_4^- + OH^- + K^+ \longrightarrow K_2{}^+HPO_4{}^- + HOH$$

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[1] Starr, H. E.: "The Determination of the Hydrogen Ion Concentration of Human Saliva," *J. Biol. Chem.*, 54:55, 1922.

[2] This natural control of the hydrogen-ion concentration of saliva within a range which is somewhat more on the acid than basic side of neutral is at variance with the notion which many people have that an acid reaction in the mouth is undesirable and that steps should be taken to bring about an alkaline condition. Such an idea is without scientific justification.

Saliva performs two functions in the digestive processes: it begins chemical reactions involving starches under the catalytic action of ptyalin, and it assists in swallowing because of the lubricating effect of water and the slippery mucin provided.

Reactions involved. The reactions involved in *salivary digestion* are believed to be hydrolytic in nature and to take place in sequence, as represented by the following word equations.

Starches + Water → "Soluble" starch + Maltose
"Soluble" starch + Water → Erythrodextrins + Maltose
Erythrodextrins + Water → Achroödextrins + Maltose

The fate of a single molecule of starch in the process of hydrolysis may be represented by the following series of equations. A hypothetical starch molecule composed of 12 incomplete maltose molecules has been arbitrarily selected for this representation.

$(C_6H_{10}O_5 \cdot C_6H_{10}O_5)_{12}$
Starch
$\downarrow$ + 2 HOH
$(C_6H_{10}O_5 \cdot C_6H_{10}O_5)_{10}$ + 2 $C_6H_{11}O_6 \cdot C_6H_{11}O_5$
Soluble starch — *Maltose*
$\downarrow$ + HOH
$(C_6H_{10}O_5 \cdot C_6H_{10}O_5)_9$ + $C_6H_{11}O_6 \cdot C_6H_{11}O_5$
Erythrodextrin — *Maltose*
$\downarrow$ + HOH
$(C_6H_{10}O_5 \cdot C_6H_{10}O_5)_8$ + $C_6H_{11}O_6 \cdot C_6H_{11}O_5$
Erythrodextrin — *Maltose*
$\downarrow$ + HOH
$(C_6H_{10}O_5 \cdot C_6H_{10}O_5)_7$ + $C_6H_{11}O_6 \cdot C_6H_{11}O_5$
α-Achroödextrin — *Maltose*
$\downarrow$ + HOH
$(C_6H_{10}O_5 \cdot C_6H_{10}O_5)_6$ + $C_6H_{11}O_6 \cdot C_6H_{11}O_5$
β-Achroödextrin — *Maltose*

A limited amount of evidence as to these reactions can be ascertained by the simple means of chewing an unsweetened cracker. The cracker, which is mainly starch, becomes mixed with the saliva and presently a sweet taste becomes evident which is due to the making of a sugar, in this case maltose.

Favoring conditions. The salivas of different individuals have been found to vary markedly as to their starch-digesting ability. But carefully controlled experimental studies have shown that regardless of the source of the saliva, there are certain conditions which favor the functioning of *ptyalin.* These conditions are as follows.

1. Digestion progresses most favorably at a *temperature* somewhat above body temperature; hence, the reactions appear to be favored by warm food. Cold temperatures, such as those of ice water, inhibit but do not destroy the action of ptyalin. It is destroyed quickly at 100° C and more slowly at temperatures as low as 65° C.

2. The *hydrogen-ion concentration* most favorable for the activity of ptyalin is at about *p*H 6.6; but digestion can proceed in a slightly basic environment. Ptyalin is destroyed in environments more acid than about *p*H 3. Salivary digestion of starch continues in the stomach until ptyalin activity is finally stopped by the high concentration of hydrogen ions provided by hydrochloric acid.

3. The functioning of ptyalin *decreases continuously with a rising concentration of the products* of the reactions, namely, dextrins and maltose. This is undoubtedly one of the reasons why salivary digestion is not carried entirely to the maltose stage, there being no provision for the separation of maltose from the digesting mass.

Continued in the stomach. Following the brief mastication period in the mouth, the food mass, more or less well mixed with saliva, enters the stomach. The reactions involved in salivary digestion may meet with their most favorable hydrogen-ion concentration in the fundus where there is relatively little mixing with hydrochloric acid, and they may continue for some time, but with decreasing speed, as products of digestion accumulate.

GASTRIC DIGESTION

It is a comparatively simple matter to secure supplies of saliva for making a firsthand investigation of salivary digestion, but the investigator who wishes to study the processes of gastric digestion is confronted with a much more difficult problem. One means of collecting gastric secretion for such purposes is a stomach tube, but the process is often quite uncomfortable for the subject, and specimens of gastric juice obtained are always already mixed with food particles.

Direct observations of what goes on in the stomach of the human animal is possible only in cases in which, owing to some accident, an opening leading

into the stomach permits firsthand examination. In the case of dogs and other animals such openings are sometimes made purposely, but in either case conditions are not entirely normal. Early workers in the field devised some very original and interesting methods of securing gastric secretions for purposes of experimentation.[3] The first studies of gastric digestion were made about 1822 by Dr. William Beaumont, an Army surgeon stationed on Mackinac Island at the head of Lake Michigan. It happened that he was called to give aid to Alexis St. Martin, a Canadian woodsman, who had received a gunshot wound in the abdomen. This wound healed, leaving a permanent fistula opening into the stomach. Dr. Beaumont, recognizing this opportunity to make firsthand studies of the stomach and the processes of gastric digestion, hired St. Martin to submit to such studies. In spite of his isolation, crude equipment, and an uncooperative subject, Dr. Beaumont did a remarkable piece of work which is regarded as a classic in the field of physiological chemistry. Another classic study which added much to the information concerning gastric digestion was that of Pavlov working with dogs as experimental subjects.

Gastric juice. The digestive secretion of the stomach is known as gastric juice. It is about 99.4 per cent water; it contains hydrochloric acid and other electrolytes, notably sodium ions, potassium ions, and traces of phosphate ions; it contains mucin, a glycoprotein, the enzyme pepsin, and possibly a lipase.[4] A small amount of gastric juice appears to be secreted continuously, but this is greatly augmented during the period of digestion. The stimulation which produces the first increase in flow is of psychic origin—that is, induced by the sight, smell, taste, or even thoughts of food; it is transmitted by impulses which travel along the vagus nerve. There is a further increase in production of gastric juice on the entrance of food into the stomach. This is attributed to the action of a hormone known as *gastrin*,[5] a substance produced in certain glands of the stomach and

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[3] For a summary of early methods used in collecting gastric juice for study, also for a very interesting account of Dr. Beaumont's work in this connection, the student is referred to the account given by Mathews, A. P.: *Physiological Chemistry*. William Wood & Company, Baltimore, 1930, pp. 350–56.

[4] The regurgitation of milk from the stomach of the young infant carries the odor of butyric acid. This means that some hydrolysis of fat has occurred in the stomach, suggesting that a *lipase* may be active at this age, if not later. The proteolytic enzyme *rennin* is usually included among the gastric enzymes. It is found in the stomach of the calf but probably not in humans.

[5] The identity of gastrin has not been established, but it bears a close resemblance to histamine, a derivative of the amino acid histidine (p. 491). The subcutaneous injection of histamine is followed by increased gastric secretion, and this compound has been employed for this purpose both experimentally and clinically.

duodenum and distributed by the blood to the gastric secretory glands which it incites to action.

The secretion of gastric juice is checked by both psychic and chemical means. Fear, worry, and pain tend to reduce gastric secretion, and a meal rich in fat also lessens gastric activity. The latter effect is attributed to the production of a hormone, *enterogastrone*, which appears in the mucous membrane of the duodenum when undigested fat enters this part of the digestive tract.

Hydrochloric acid is secreted by glands located both in the fundus and the central portion of the stomach, in close proximity to the glands which produce the digestive enzymes. This acid appears to be essential for the production of *active pepsin* from inactive pepsinogen. The high concentration of hydrogen ions supplied by this acid also favors continued peptic activity.

Another fortunate but incidental effect of hydrochloric acid in the gastric juice is that the high concentration of hydrogen ions provided thereby is unfavorable to bacterial growth; consequently, many of the bacteria which enter the stomach with the food mass are either inhibited in their growth or actually killed.

Physiologists have long been interested and greatly puzzled as to how this strong acid can be secreted from blood which is basic in reaction, and how it can be made without destroying the cells that produce it. Certainly this acid is present in the stomach and the normal mucosa is not attacked by it, although there is evidence that if the mucosa is injured there can be such an attack. Certainly it is not stored in the cells of the gastric mucosa but appears *to be made immediately before it enters the stomach.* Many theories have been advanced, but the real answer is not yet known. One theory suggests that hydrochloric acid is made in the secreting cells from sodium chloride, brought by the blood, and carbonic acid which either originates in the cells or enters from the blood. The acid is then secreted directly into the stomach while the sodium bicarbonate is absorbed into the blood, as suggested in the following:

H_2CO_3	+	NaCl	⟶	HCl	+	$NaHCO_3$
Made in the cells or from the blood		From the blood		Secreted directly into the stomach		Reabsorbed into the blood

Support for this theory is found in the decrease in plasma chloride and the simultaneous increase in bicarbonate in the blood, the so-called *alkaline tide* which results in excretion of more alkaline urine

following a heavy meal. Furthermore, the enzyme carbonic anhydrase is found in cells where hydrochloric acid is produced. This enzyme functions in the production of carbonic acid from carbon dioxide and water. Continued production of carbonic acid in these cells would be favorable to this reaction.

Gastric digestion of protein. The most important digestive reactions in the stomach involve proteins. Under the catalytic influence of *pepsin* water reacts with protein to make what are referred to as proteoses and peptones.

$$\text{Proteins} + \text{Water} \xrightarrow{\text{Pepsin}} \text{Proteoses} + \text{Peptones}$$

The hydrolytic attack is believed to occur at selected peptide linkages within the protein molecule (Fig. 90).[6]

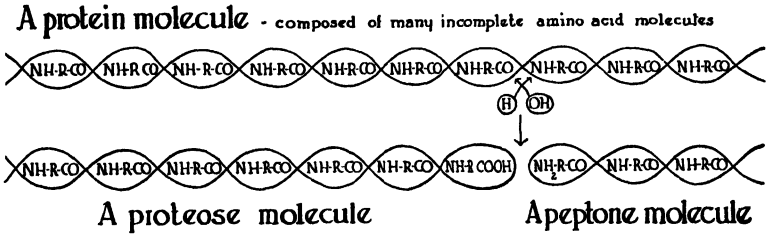


Fig. 90. A diagrammatic representation of a portion of a protein molecule, showing the nature of the hydrolytic attack.

One of the results of the hydrolytic attack is the clotting of the casein of milk which can frequently be observed in the milk-fed animal, including the human. The student may wonder what possible advantage this can be to the young animal. The reason may be that, whereas fluid milk would quickly pass through the stomach to the intestine, the semisolid curds are delayed, thus providing for longer exposure of milk protein to the proteolytic enzymes in the stomach and a more gradual feeding into the intestinal tract.

Favoring conditions. Certain conditions which favor the reactions concerned with the digestion of proteins have already received some attention. (1) The *large surface of contact* between pro-

[6] Pepsin appears to be an endopeptid*ase*, that is, an enzyme that functions somewhere along the protein chain rather than at the terminal linkages. An amino linkage attached to either tyrosine or phenylalanine appears to be selected for attack by pepsin. Fruton, J. S., and Simmonds, S.: *General Biochemistry*, pp. 597–99.

teins and gastric juice is provided for by the considerable quantity of water secreted and by mixing caused by muscular movements of the stomach. (2) The *hydrogen-ion concentration* in which the proteolytic enzymes function is another important factor. The optimum for pepsin activity varies somewhat for different proteins but lies within the comparatively high range of *p*H 1.5 to 2.5. (3) *The time element* of from 1½ to 4 hours that the food mass remains continually in contact with the gastric juice—although in decreasing quantities as portions are passed on to the intestine—is another factor which favors gastric digestion.

Gastric digestion of fats. Whether or not the digestion of fats takes place at all in the stomach has long been a debated question. The strongly acid character of adult digestive juice would seem to be unfavorable to the action of *gastric lipase*, an enzyme which is most active at *p*H 5.0. Since the infant secretes a less acid gastric juice, it is possible that the gastric digestion of fats is more important in the young mammal than for the older individual. It is generally agreed that such digestion is only of fats which are already emulsified, such as those of milk, butter, and egg yolk. The reaction involved is believed to be that of hydrolysis.

$$\underset{\text{Fats (emulsified)}}{} + \underset{\text{Water}}{} \xrightarrow{\text{gastric lipase}} \underset{\text{Fatty acids}}{} + \underset{\text{Glycerol}}{}$$

$$\underset{\text{Glyceryl butyrate}}{C_3H_5(C_3H_7COO)_3} + 3\ HOH \longrightarrow \underset{\text{Butyric acid}}{3\ C_3H_7COOH} + \underset{\text{Glycerol}}{C_3H_5(OH)_3}$$

Gastric digestion of carbohydrates. No enzyme is provided in the gastric juice to catalyze the digestion of carbohydrates. It is probable that the only carbohydrate digestion that takes place in the stomach is the previously mentioned continuation of salivary digestion of starch which is catalyzed by ptyalin in the less acid portions of the gastric food mass.

Gastric digestion continues in the intestine. The semifluid digesting mass, on its entrance into the duodenal part of the intestine, is strongly acid in reaction. However, as it comes in contact with basic secretions, from the glands of the pancreas, liver, and intestine, the hydrogen-ion concentration is decreased. But this is a very gradual process; as a result, it is reasonable to conclude that the peptic hydrolysis of proteins can continue in the more acid regions within the intestine, at decreasing speed with decreasing hydrogen-ion concentration, until the pepsin is destroyed by hydrolysis—a reaction which is catalyzed by trypsin at about *p*H 5.5.

INTESTINAL DIGESTION

The difficulties which the investigator encounters in attempts to obtain information concerning intestinal digestion are even greater than with gastric digestion. Not only the intestine, but two glands, the pancreas and the liver, are involved. Furthermore, the great length of the intestine itself complicates the problem, since digestive phenomena observed in one part of the intestine may differ from those in other parts of this lengthy organ. But despite difficulties, considerable information has been gleaned from such observations and experimental studies as have been possible.

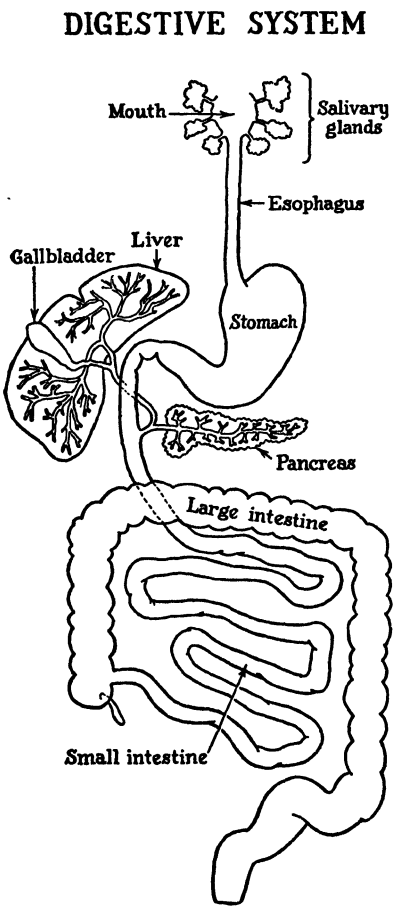


Fig. 91.

The digestive secretions. The partially digested, semifluid material which passes from the pylorus of the stomach to the duodenum is known as *chyme.* The entrance of this acid chyme into the duodenum stimulates the secreting glands of the intestinal mucosa; as the result a fluid, known as *intestinal juice* (or succus entericus), is poured into the intestine. The acid chyme also stimulates the secretion within the intestinal mucosa of a hormone, called *secretin,* which is absorbed by the blood stream, carried to the pancreas, and causes it to secrete *pancreatic juice.* This secretion flows through the pancreatic duct and empties into the duodenum about 5 in. below the pyloric valve. *Bile,* which is made in the liver, likewise enters the duodenum through the common duct which carries both pancreatic juice and bile (Fig. 91).

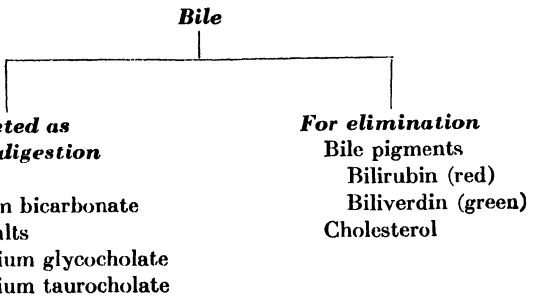
Pancreatic secretion. The pancreatic secretion provides a number of digestive enzymes of which the most important are (1) *trypsin, chymotrypsin,* and *carboxypeptidase,* which function together in the hydrolysis of proteins; (2) *pancreatic lipase* (*steapsin*), which catalyzes the hydrolysis of fats; and (3) *pancreatic amylase* for the hydrolysis of starches and dextrins.

The pancreatic secretion itself contains the inactive trypsinogen and chymotrypsinogen, precursors of the active enzymes. However, when the pancreatic secretion enters the duodenum, trypsinogen comes in contact with *enterokinase*—secreted by the duodenal glands —and active trypsin is made. This, in turn, continues to activate trypsinogen and the production of chymotrypsin. Both of these active enzymes function as catalysts for the hydrolysis of proteins, proteoses, and peptones with the production of peptides. Chymotrypsin favors the clotting of the proteins of milk. Carboxypeptidase is believed to attack only at the end of the protein molecule, near a terminal carboxyl, with the production of amino acids.

Pancreatic amylase is a more powerful catalyst than ptyalin and probably the more essential of the two enzymes.

The intestinal secretion. Secretory glands are distributed throughout the mucosa of the entire length of the small intestine, but they are most concentrated in the duodenum and the upper regions of the intestine. The secretions of these glands provide another group of enzymes: (1) *enterokinase,* which activates trypsinogen to make trypsin; (2) *erepsin,* which is now recognized to be a mixture of polypeptidases, which complete the hydrolysis of peptides to amino acids; (3) *nucleotidases* and *nucleosidases,* which catalyze the hydrolysis of nucleoproteins (p. 425); (4) a *maltase,* a *sucrase,* and a *lactase,* which catalyze the hydrolysis of the disaccharides maltose, sucrose, and lactose, respectively. It is noteworthy that lactase is more abundant in the digestive juice of young children and of the young of animals whose food is largely milk than in the digestive juice of adults, in whose diet milk plays a less important part.

Bile. This secretion is made in the liver and between periods of digestion is stored in the gallbladder. As digestion sets in, bile flows into the duodenum by way of the common duct. Bile contains substances for excretion as well as substances which aid digestion; this is because the liver is an excretory as well as a secretory organ. Bile components vary somewhat in different animals, but the following substances are fairly common to all.



In contrast to all other digestive juices bile contains no enzymes. *Bile salts* function as emulsifying agents for fats. This necessary substitute for solution is of exceeding importance in two ways because (1) it removes fat coatings around bits of carbohydrate and protein, thus rendering these substances available for digestion, and (2) it effects the distribution of fats as fine globules thereby providing a larger area of contact with digestive juices, hence with the fat-digesting enzyme steapsin. *Bile salts* also aid in the absorption of the fatty-acids, end products of fat digestion; moreover, they are essential for the absorption of vitamins D and K, although not for vitamin A. When, owing to some obstruction, bile fails to enter the intestine, the digestion of fats is interfered with (consequently, to a lesser extent, that of carbohydrates and proteins), and fatty material is excreted in the feces.

Substances for elimination. *Cholesterol* (p. 402) is excreted by the liver. The bile salts aid by keeping this difficultly soluble substance in suspension, thus preventing its precipitation in the gallbladder and bile ducts and helping to provide for its transportation to the intestine and its final elimination in the feces. When, for some reason, the concentration of cholesterol becomes abnormally high, precipitation may occur in the gallbladder or bile ducts, giving rise to accretions known as gallstones.

The *bile pigments*, bilirubin and biliverdin, are made from the hemoglobin of worn-out red blood cells and are emptied with the bile into the intestinal tract for elimination; they are responsible to a considerable extent for the characteristic color of feces.

Chemical digestion in the intestine. The food mass (now called the chyme), as it enters the intestine from the stomach, contains proteins, fats, carbohydrates and related compounds.

Protein in nature	***Of fat origin***	***Carbohydrates***
Undigested proteins	Undigested fats	Glucose
Proteoses	Glycerol } in small	Fructose
Peptones	Fatty acids } amounts	Sucrose
Nucleoproteins		Maltose
		Lactose
		Undigested starches
		Dextrins
		Celluloses

Only the small amounts of glycerol, fatty acids, glucose, and fructose which are present are ready for absorption.

Intestinal digestion of proteins. Reactions of the remaining proteins and of proteoses and peptones with water to make peptides are speeded up all along the small intestine through the action of the enzymes trypsin and chymotrypsin. The peptides, in turn, are hydrolyzed to make the digestive end products amino acids; these reactions are catalyzed by the mixture of peptidases known as erepsin.

$$\left.\begin{matrix}\text{Proteins}\\ \text{Proteoses}\\ \text{Peptones}\end{matrix}\right\} + \text{Water} \xrightarrow{\text{trypsin and chymotrypsin}} \text{Peptides}$$

$$\text{Peptides} + \text{Water} \xrightarrow{\text{peptidases (erepsin)}} \text{Amino acids}$$

Hydrolysis appears to take place at specific amino-carboxyl linkages along the protein molecule, depending on the attacking enzyme. These proteolytic enzymes function best in a slightly basic environment. Typical findings are *p*H 8.0 for trypsin; *p*H 7.4 for carboxypeptidase, and *p*H 7.5 to 8.0 for intestinal peptidases.

The nucleoproteins are also hydrolyzed in the intestinal tract, presumably first to protein and nucleic acid. Then the nucleic acid is attacked by a variety of enzymes found in the intestinal secretion.

Intestinal digestion of fats. Save for the very small portions of already emulsified fats which have been hydrolyzed by gastric lipase, fats reach the intestine just as they were on the plate. In the intestine, however, they meet with provision for their emulsification and with the enzyme pancreatic lipase, or steapsin, for speeding up their hydrolysis to make fatty acids and glycerol.

$$\text{Fats} + \text{Water} \xrightarrow{\text{steapsin}} \text{Glycerol} + \text{Fatty acids}$$

For example:

$$\underset{\text{Stearin}}{C_3H_5(C_{17}H_{35}COO)_3} + \underset{\text{Water}}{3\ HOH} \xrightarrow{\text{steapsin}} \underset{\text{Glycerol}}{C_3H_5(OH)_3} + \underset{\text{Stearic acid}}{3\ C_{17}H_{35}COOH}$$

The environment most favorable to the activity of steapsin appears to be about *p*H 8.0.

Intestinal digestion of carbohydrates. In the presence of the enzyme pancreatic amylase starches and dextrins react with water to make maltose. Maltose, sucrose, and lactose, in the presence of the enzymes maltase, sucrase, and lactase, respectively, are hydrolyzed to make glucose, fructose, and galactose. (See page 380 for an equation representing such reactions.) These reactions probably progress most favorably in a hydrogen-ion concentration about neutral or slightly acid, the reported optimum for pancreatic amylase functioning being about *p*H 6.7 to 7.0; for intestinal sucrase *p*H 5.0 to 7.0. The end products of carbohydrate digestion are glucose (predominantly), fructose, and galactose.

Enzymes for digestion of celluloses are not provided in the intestinal secretions of humans; consequently, celluloses do not undergo hydrolysis in the intestine of the human. Save for some attack by bacteria, chiefly in the large intestine, they are eliminated as celluloses in the feces. They do, however, play an important part in digestion in that they provide *bulk* for the intestinal contents, which is one of the peristalsis-promoting factors.

Favoring conditions for completion of digestion. The digestive reactions are practically completed in the small intestine It is in this region only that all of the factors essential for continuance and completion of these reactions are encountered. They are as follows.

1. ***Favoring enzymes.*** Foremost among the essentials for carrying forward the digestive reactions is the aid rendered by the specific enzyme catalysts.

2. ***Favoring hydrogen-ion concentrations for enzyme activity.*** All three of the secretions provided—pancreatic juice, intestinal juice, and bile—are basic in reaction.[7] The component provided by these secretions which is mainly responsible for this basic reaction is *sodium bicarbonate.* Hydroxyl ions are provided as this salt reacts with water. These ions, on coming into contact with hydrogen ions (for the most part provided by hydrochloric acid carried along from the stomach with the food mass), combine with them to make water, thereby decreasing the hydrogen-ion concentration in whatever locations this reaction occurs.

[7] The following values have been reported: pancreatic juice, *p*H 7.5 to 8.0; bile, *p*H 7.5 to 8.5; succus entericus, *p*H 7.1 to 7.6. Everett, Mark: *Medical Biochemistry.* Paul B. Hoeber, Inc., New York, 1946, p. 132.

$$\underbrace{Na^+ + HCO_3^-}_{\text{From pancreas, liver, and intestine}} + HOH \longrightarrow Na^+ + OH^- + H_2CO_3$$

$$\left.\begin{array}{l} H^+ \\ \downarrow \\ H_2O \end{array}\right\} \text{From hydrochloric and other acids in intestinal contents}$$

But the mixing of the intestinal content takes place gradually; hence, this decrease in hydrogen-ion concentration takes place gradually, thus giving rise to considerable variation in *p*H of the content in different parts of the digestive mass. In this way each enzyme stands an excellent chance of meeting somewhere along the intestinal tract with the specific hydrogen-ion concentration that is favorable to its activity in the digestive process.

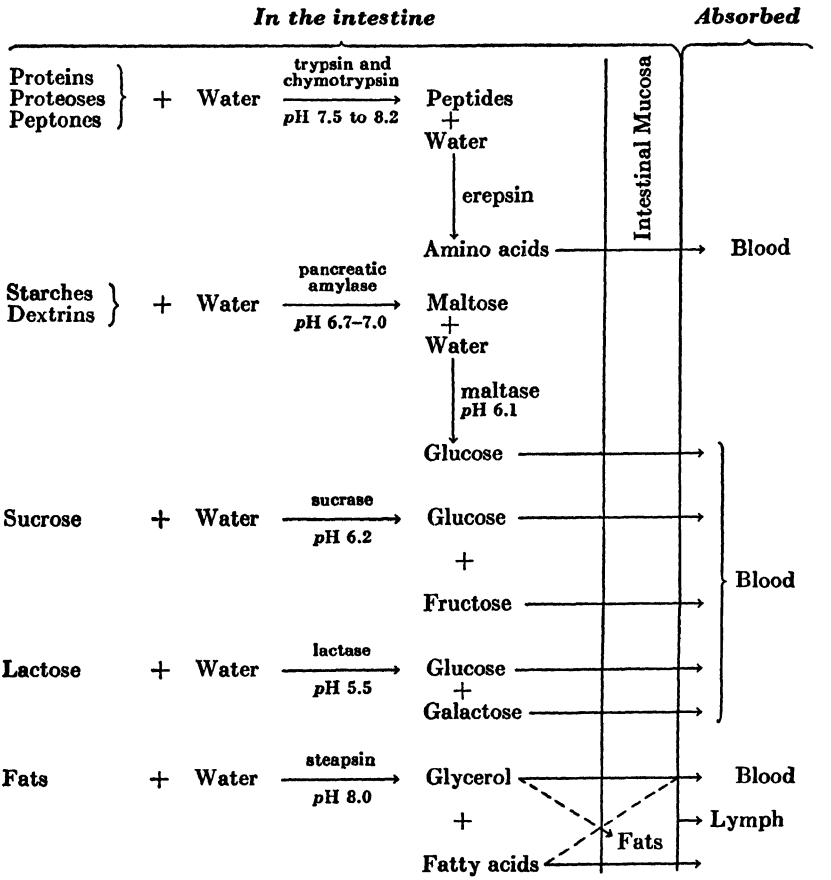
3. ***Large surface of contact.*** Another favoring condition is the remarkable provision of nature for bringing the reacting food substances into large surface of contact with water and enzymes. This is accomplished by means of: (a) the considerable intestinal area, owing to both the length of the intestine and the villi of the mucosa, along which secreting cells continuously pour digestive juices into the food mass; (b) the unceasing mixing accomplished by muscular movements of the intestine; and (c) the spreading out that is obtained as the disaccharides distribute in true solution; the proteins, proteoses, peptones, and peptides in colloidal dispersion; and the fats (through the aid of cholesterol, bile salts, and soluble proteins) form emulsions.

4. ***Time.*** The length of time, normally from 5 to 7 hours, required for the food mass to pass through the small intestine provides an opportunity for long periods of contact between components of the digesting mass, water, and the favoring enzymes.

5. ***Provision for absorption.*** Lastly we come to absorption, the final factor which determines whether or not all of the proteins, fats, and carbohydrates will be digested. It is only upon the removal of the products of reaction that the enzyme can continue to function until hydrolysis is complete. It is *only* in the intestine, where ample provision is made for the removal of end products, that this is possible.

Absorption from intestine. ***Of monosaccharides.*** Glucose, fructose, and galactose, end products of carbohydrate digestion, are absorbed into the capillaries of the villi and carried through the portal tube to the liver. Here they are either used to make glycogen or distributed through the general circulation to the cells. There is some

evidence to suggest that absorption of these monosaccharides is accompanied by phosphorylation (p. 460), perhaps as a means for providing the energy essential for passage through the membrane.



Of fats and sterols. Following a meal rich in fat, phospholipids appear in the intestinal membrane and fats together with some phospholipids are found in a highly emulsified state in the lacteals—the lymph vessels of the intestines. Just how the absorption of fat is brought about, and whether or not all of the fat must be completely hydrolyzed before absorption, is as yet unknown. A number of theories have been advanced to account for these findings but none

of them is completely acceptable or in full agreement with the observed facts.[8]

Bile salts have an active part in facilitating the absorption of fatty acids, also of cholesterol and other sterols. It is claimed that the lipids, which are insoluble in water, form complexes with the bile salts and the resulting compounds can disperse in water and hence be more readily absorbed.

The absorption of the *fat-soluble vitamins*, D, E and K, also of carotenes (precursors of vitamin A) accompanies the absorption of fats. Vitamin-A absorption, though less dependent, is also favored by the absorption of fats.

Of amino acids. Amino acids, the end products of protein digestion, are absorbed into the capillaries of the villi and carried to the liver by way of the portal circulation. It has been assumed that amino acids are the only products of protein digestion that are absorbed under normal conditions, but there is some evidence that polypeptides may be absorbed to some extent and subsequently used by the cells.

Of salts and water. The absorption of soluble salts and of water takes place readily along the intestine. The slow passage of the digesting mass along the *large* intestine is particularly favorable to the absorption of water.

Proportions of compounds absorbed. With normal alimentary functioning surprisingly small portions of carbohydrates, fats, and proteins, and of their hydrolysis products are carried on into the large intestine with the undigested residue. According to Sherman[9] the following figures are approximate averages.

	End products of digestion absorbed	*Undigested portions and end products not absorbed*
Carbohydrates	98%	2%
Fats	95%	5%
Proteins	92%	8%

Action of microorganisms in the large intestine. A surprising amount of bacterial action takes place in the intestine normally, the

[8] For a brief summary of current theories relating to absorption see: Downes, Helen R.: *The Chemistry of Living Cells.* Harper & Brothers, New York, 1955, pp. 331–37.

[9] Sherman, Henry C.: *Chemistry of Food and Nutrition,* 8th ed. The Macmillan Company, New York, 1952, p. 135.

chief location of these activities being in the large intestine. Although the intestinal tract of the newborn infant is practically free from microorganisms, probably within 24 hours they have begun to accumulate and multiply enormously. From then on, during the entire life of the individual, microorganisms are inhabitants of the intestine. Under normal conditions few living microorganisms are present in the food mass as it leaves the stomach, nor are they abundant in the small intestine; but the number and variety found in the large intestine is almost unbelievable. Indeed, more than one fourth of the solid material of the feces is made up of bacteria, living and dead. Many of these organisms are nonpathogenic, but pathogens are found there as well. However, our present concern is less with the varieties of microorganisms present than with some of the chemical changes which food substances may undergo as a result of enzymes produced by these organisms.

On carbohydrates. The carbohydrates which undergo chemical changes caused by bacterial action are for the most part the otherwise indigestible celluloses present in the large intestine. The products that result from these reactions are chiefly gaseous substances and organic acids, some of which are:

Hydrogen Methane Carbon dioxide	not absorbed but eliminated from the intestine
Acetic acid Butyric acid Lactic acid	absorbed and distributed to the cells

When made in normal quantities, these substances produce no ill effects. But if peristalsis is sluggish, the carbohydrates impregnated with bacteria will remain in the large intestine for a longer-than-normal period. In this event the accumulated gases give rise to considerable discomfort, and some of the products in higher-than-normal concentrations are irritating and may cause diarrhea.

On fats. A certain amount of fat hydrolysis takes place in the large intestine to make fatty acids and glycerol, possibly through the agency of microbial enzymes. Other than this, little is known or conjectured in regard to bacterial action on fats or their digestive products.

On amino acids. Any proteins that are present in the large intestine are subject to bacterial attack to make proteoses, peptones, amino acids, hydrogen sulfide, and ammonia. But the most important bacterial actions on substances of protein origin are those which involve amino acids. These acids undergo two varieties of attack: (1) a decarboxylation, meaning the making of carbon dioxide from the carboxyl of the amino acid; (2) a deaminization followed by decarboxylation. The accompanying table, appearing on page 456, represents some of the most important compounds made through such bacterial attacks on the amino acids *tyrosine*, *tryptophane*, and *histidine*.

These substances are in part absorbed and eliminated in the urine, either unchanged or somewhat altered, and in part carried out in the feces. The odor associated with feces is due to the presence of the compounds indole and skatole.

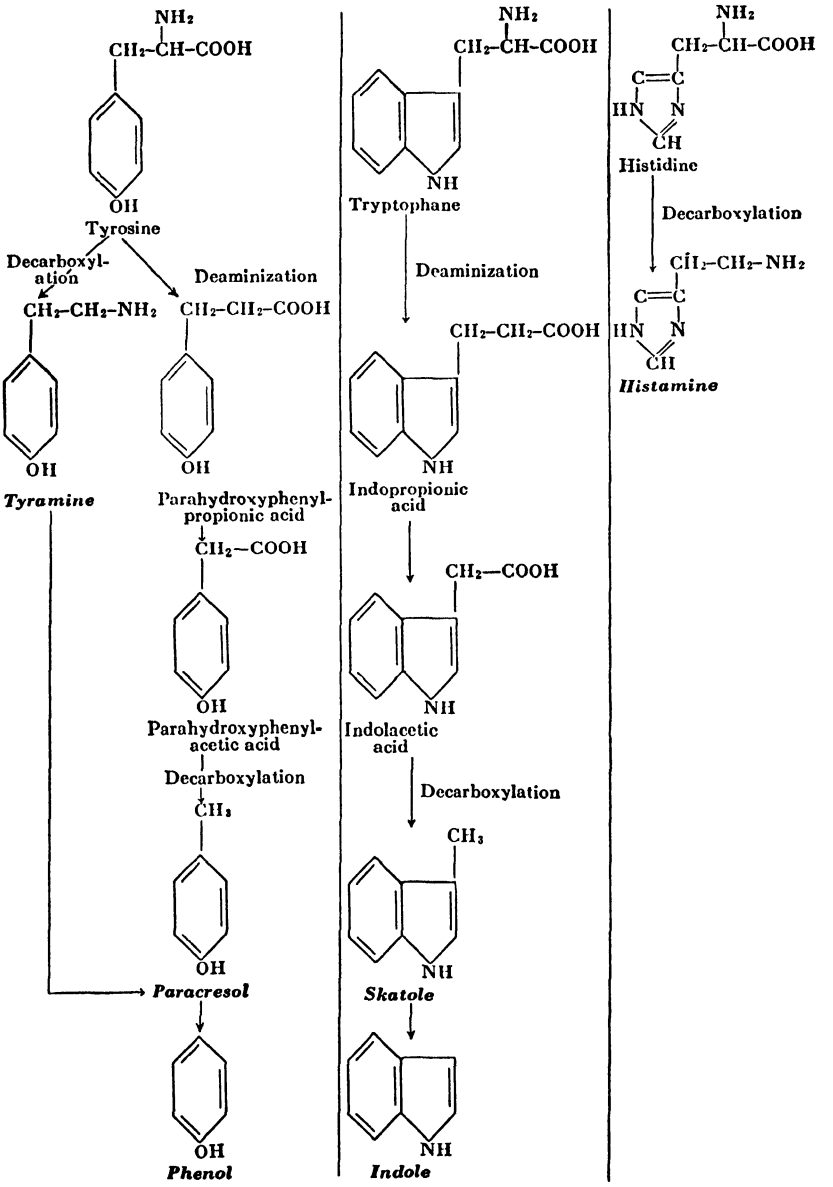
A number of human ills which are associated with constipation—such as headache, drowsiness, insomnia, irritability, skin eruptions, etc.—have for long been attributed to the absorption of some of these substances, especially *indole* and *skatole*, also to a lesser extent *cresol* and *phenol*. But there is no experimental evidence to support these claims; and certain it is that nature provides for the detoxification of these substances in normal quantities through what is called *conjugation*, which involves reaction with sulfuric acid and potassium salts. The end product of this conjugation with indole is indican, which is eliminated in the urine.

Tyramine and *histamine* are very toxic when administered either intravenously or intramuscularly, but when absorbed from the intestine, provision is made by nature for their detoxification; tyramine in the liver and histamine possibly in the intestinal membrane and other tissues.

Vitamin synthesis. Some of the microorganisms inhabiting the intestine, in the course of their life activities, produce certain of the vitamins. For example, *Escherichia coli*, a constant inhabitant of the intestine, produces vitamin K; other microorganisms synthesize various members of the vitamin-B complex, notably biotin, folic acid, and pantothenic acid. The administration of bacteriostatic drugs (such as the sulfanilamides) interferes with this vitamin production, sometimes even to the extent of producing secondary vitamin deficiencies, by inactivating the microorganisms concerned.

Composition of feces. When the processes of digestion, bacterial action, and absorption are complete, any remaining food mass, to-

Bacterial attack on amino acids in the large intestine



gether with certain materials picked up from secretions entering the intestinal tract, are eliminated as feces. In this mass are present:

Water	In variable amounts
Celluloses	Nearly all ingested
Undigested carbohydrates and their digestive products	2%
Undigested fats, fatty acids and glycerol	5%
Undigested proteins and their digestive products	8%
	Approximately, of the quantity taken in from the mass on the plate
Skatole, indole, and other products of bacterial action on amino acids	Largely responsible for the odor of feces
Salts:	
Calcium salts	The greater part of the calcium salts eliminated in the course of metabolism find their exit through the intestine in the feces
Salts of heavy metals	Copper, lead, and iron salts
Bile pigments Bilirubin Biliverdin	Made from hemoglobin of worn-out red blood cells and largely responsible for the color of the feces
Cholesterol	Eliminated through the liver; finds exit in the feces
Various gases Methane Hydrogen Carbon dioxide	From bacterial action on carbohydrates in the large intestine
Hydrogen sulfide	From cystine and methionine by bacterial action
Bacteria—dead and living	Comprise from one quarter to one third of the bulk of the solid matter of feces

QUESTIONS

1. What is digestion? Why is it essential for most components of the food mass to undergo this process? What, if any, components of the food mass can be absorbed without undergoing digestion? Give reason.

2. Explain how the various physical processes along the digestive tract function as aids to the chemical processes of digestion.

3. Why are the digestive reactions classed as hydrolytic in nature? Illustrate, through the use of suitable formula equations for the reactions concerned, hydrolysis of a disaccharide, a starch, a fat, and a tripeptide.

4. What digestive secretions are provided along the alimentary tract? Where is each secreted? What are the major components of each secretion? What, if any, function has each component in relation to the digestive reactions?

5. How are hydrogen-ion concentrations favorable to the functioning of different enzymes provided along the gastrointestinal tract?

6. Prepare a summary chart which will contain the following information regarding the digestive reactions.

   a. Locations along the digestive tract where reactions occur and the average time spent by the food mass in each region
   b. Word equations for the reactions occurring in each region, indicating the functioning enzyme and the *p*H of the environment favorable to the activity of each specific enzyme
   c. The end products of digestion and the path of removal of each product from the digestive tract

7. What provision is made for the emulsification of fats? Give two reasons why emulsification is important for normal digestion.

8. What substances are made in the intestinal tract as the result of bacterial activity? What happens to these substances?

9. What vitamins are produced in the intestinal tract? By what means? Explain how sulfanilamide drugs can cause an avitaminosis in the body.

10. What effect might each of the following conditions have upon the digestive process as a whole: (a) the bolting of food, (b) sluggish peristalsis, (c) hyperactive motility along the intestinal tract, (d) constipation, (e) obstruction of the bile duct, (f) excessive use of sodium bicarbonate or other base-forming compound, especially shortly before meals?

CHAPTER 31

FUNCTION AND FATE OF GLUCOSE FATS, AND PROTEINS IN THE BODY

The scientist who attempts to learn the nature of the reactions which are constantly in progress within living cells and attempts to wrest from nature the secrets of cell functionings encounters great difficulties in his studies. Much of the information acquired must be based upon the study of cells from freshly killed animals, and, no matter how swiftly the work may be done, some changes have already taken place, although just what changes may occur in that brief interval which marks the boundary between life and death are for the most part unknown. Within recent years a number of new methods of study have been developed, including the use of unusual isotopes of common elements for tracing metabolic processes. These have greatly increased the knowledge concerning reactions within living cells, both adding to and correcting previously acquired information. Even so, there remain gaps to be filled; and these gaps the scientist attempts to bridge with the best reasoning guesses which he can devise to fit in with the known facts. But theories with their interpretations of facts frequently must be revised in the light of new discoveries. Consequently, in the study of chemical reactions within living cells, the student enters a field in which there are a few well-established facts, much that is but partially understood, and a great deal that is as yet unknown.

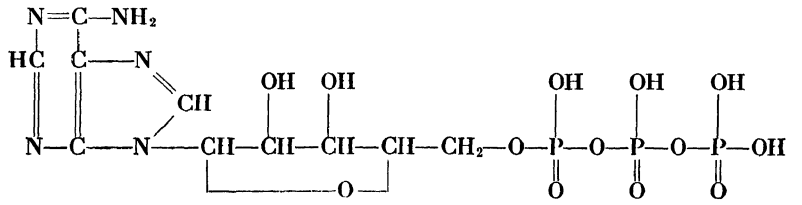
FUNCTION AND FATE OF GLUCOSE

In the liver. When the blood, laden with products of digestion, is brought from the intestine to the liver, part of the glucose, fruc-

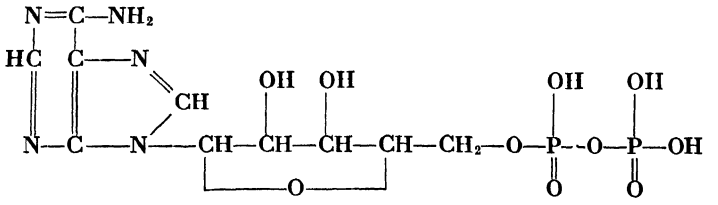
tose, and galactose is removed by the liver cells and used to make glycogen. This is evidenced by the fact that the relative concentration of these sugars in the portal tube, which carries the blood from the intestine to the liver, is considerably higher during the period of absorption than is their concentration in the hepatic vein leaving the liver. This discovery was made by Claude Bernard, a French physiologist, about 1843.

Glycogenesis. Making glycogen from glucose is known as glycogenesis. The first step toward this synthesis, and a process which is regarded as essential for the use of glucose in the cells, is the reaction of glucose with the energy-rich compound *adenosine-triphosphate*[1] to make glucose-6-phosphate. This compound, in turn, forms glucose-1-phosphate, which condenses to make glycogen; the phosphate is released and becomes available for other reactions. Fructose, and presumably galactose, likewise reacts to make a hexose phosphate and subsequently glycogen. The formula $(C_6H_{10}O_5)_n$ used to represent glycogen indicates that an indefinite number of

[1] **The phosphate compounds.** The phosphate compounds, adenosine-*tri*phosphate and adenosine *di*phosphate, are not peculiar to liver cells; they are widely distributed in both plant and animal tissues. They take part in many reactions when energy is required for the work of the cell. Thus, as adenosine-triphosphate reacts with glucose to make glucose-6-phosphate, it releases one of its phosphate linkages, and adenosinediphosphate is made. This reaction is accompanied by a considerable energy product which can be used to further other reactions in the cells. The relation of adenosinetriphosphate to adenosine-diphosphate is indicated by the accompanying formulas.



Adenosinetriphosphate



Adenosinediphosphate

molecules of the monosaccharide contribute to make a glycogen molecule. The various reactions are catalyzed by specific enzymes; these are indicated in the following summary of the reactions.

$$\text{Glucose} + \text{Adenosine-triphosphate} \xrightarrow{\text{hexokinase}} \text{Glucose-6-phosphate} + \text{Adenosine-diphosphate}$$

$$\text{Glucose-6-phosphate} \xrightarrow{\text{phosphoglycomutase}} \text{Glucose-1-phosphate}$$

$$\text{Glucose-1-phosphate} \xrightarrow{\text{phosphorylase}} \text{Glycogen} + \text{Phosphoric acid}$$

Glycogen forms a colloidal dispersion; therefore, it can be held in the cells where it is made. In the liver it becomes a carbohydrate reserve which is built up during the period that follows the absorption of glucose from a carbohydrate meal, thereby preventing an unduly high concentration of glucose in the blood. It is then available, when needed, for replenishing the supply of glucose in the blood.

Glycogenolysis. When glucose is withdrawn from the blood to meet the demands of actively functioning cells throughout the body, reactions set in whereby liver glycogen is used to make glucose. These are essentially the reverse of the reactions by which glycogen was made. But, at the glucose-6-phosphate stage a *phosphatase* enzyme is provided which catalyzes the hydrolysis of this ester; glucose is made and escapes into the blood. The reactions are as follows:

$$\text{Glycogen} + \text{Phosphoric acid} \xrightarrow{\text{Phosphorylase}} \text{Glucose-1-phosphate}$$

$$\text{Glucose-1-phosphate} \xrightarrow{\text{Phosphoglycomutase}} \text{Glucose-6-phosphate}$$

$$\text{Glucose-6-phosphate} + \text{Water} \xrightarrow{\text{Phosphatase}} \text{Glucose} + \text{Phosphoric acid}$$

Metabolism of carbohydrates in the liver

	IN THE LIVER	
From the intestine	GLYCOGEN ↑↓ GLUCOSE-1-PHOSPHATE	To the general circulation
GLUCOSE	+ Adenosine *tri*phosphate ⟶ Adenosine *di*phosphate + GLUCOSE-6-PHOSPHATE + Water → Phosphoric acid	GLUCOSE
FRUCTOSE	+ Adenosine *tri*phosphate ⟶ Adenosine *di*phosphate + FRUCTOSE-6-PHOSPHATE	

Gluconeogenesis. The liver can make glycogen from substances other than the monosaccharides. These include glycerol, lactic acid, and certain amino acids (p. 470). The importance of such a provision for maintaining this carbohydrate reserve, even at the expense of fats and proteins, will become more evident as this study progresses.

The function of liver glycogen. In general, liver glycogen is a somewhat labile reserve of carbohydrate which functions to maintain a relatively constant supply of glucose in the blood for use in active cells. It can be drawn upon almost to exhaustion to supply glucose for transportation to the cells of muscles, nerves, and other tissues engaged in the production of energy.

Glucose in the blood. Glucose is the only sugar present in any considerable amount in the blood leaving the liver, and it is there only for transportation to functioning cells throughout the various tissues and organs. Normally, the glucose content of blood, commonly referred to as blood sugar, is quite constant, varying from 70 to 90 mg per 100 ml of blood. And, although during the period of absorption this content may increase to from 120 to 130 mg per 100 ml of blood, within about two hours after a meal the blood sugar returns to its usual level.

An increase in glucose concentration of the blood above the tolerance of the individual—whether temporary, owing to a high intake of carbohydrate food, or more or less continuous, as in diabetes—results in excretion of glucose by the kidneys, a condition known as glycosuria.

Functioning of glucose within cells of various tissues. Glucose is withdrawn from the blood by the cells of various tissues and organs according to their special needs and functions: (1) for immediate oxidation to provide energy to meet cell needs; (2) for maintaining the glycogen reserves of muscle and other tissues, to be drawn upon as needed for oxidation and the accompanying production of energy; (3) to make fat, another important food reserve; and (4) to be used for making other carbohydrates required for specific purposes, such as lactose, made in the mammary glands during lactation, and probably pentoses, which contribute to the structure of both nucleoproteins and certain enzymes (pp. 431 and 434).

Of these uses for glucose, the one of outstanding importance is its functioning with oxygen for production of energy. Although both fats and amino acids can be used to some extent for energy-producing reactions, there is no doubt that glucose is the preferred and, in some respects, the required substance for these reactions.

Oxidation of glucose for production of energy.[2] At one time it was assumed that in the tissues, as in the calorimeter, the production of energy resulted from direct reaction of oxygen with glucose to make carbon dioxide and water. It is now recognized that the process is more complex, involving a series of reactions with gradual production of energy; moreover, at certain stages of this process, oxygen is not directly involved. But, whatever the oxidative sequence, for each gram of glucose thus used in any cells, 1.06 gm of oxygen are required and 3.75 large calories of energy will be produced when the end-matter products are carbon dioxide and water.

1 gm		1.06 gm					
$C_6H_{12}O_6$	+	$6\ O_2$	⟶	$6\ CO_2$	+	$6\ H_2O$	
↓		↓		↓		↓	
Chemical energy	+	Chemical energy	⟶	Chemical energy	+	Chemical energy	+ 3.75* ***large calories of kinetic energy***, heat, or such other energies as the cells need

* Computed on the basis of 1 mole of glucose, the corresponding energy product is approximately 675 kg-calories.

When the oxidation of glucose takes place in the calorimeter, most of the energy product appears as heat. But, when this oxidation takes place within living cells, much of the energy is used for the work of the cell. This may be as kinetic energy for contraction of muscle; electrical energy for transmission of nerve impulses; energy for the passage of substances across membranes; or chemical energy essential for the synthesis of new substances. In the end these various energies are transformed into heat—which can be dissipated at the surface of the body. Meanwhile the heat will have served to maintain the body temperature at the level characteristic of the living animal.

The oxidation of glucose does not take place in a single step but through a series of intermediate reactions with definite quantities of energy released at intervals. The oxidation in muscle cells has been studied in considerable detail and is presented as representative of the oxidation reactions characteristic of all tissue cells.

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[2] The first study of this important function of oxygen was made by Lavoisier in the latter part of the eighteenth century. He recognized not only the matter products of the reaction, carbon dioxide and water, but also the associated energy products. He did not know where in the body the reactions occur, nor did he have any idea as to the various intermediate stages.

Metabolism of glucose in muscle cells. Part of the glucose which enters the muscle cells is probably requisitioned for immediate oxidation for the production of energy; part is used to make glycogen, the carbohydrate reserve of the cell. In either case, the first reaction is with adenosinetriphosphate to make glucose-6-phosphate. *This process is believed to be essential for any use of glucose within the cell.* For glycogen synthesis the sequence of reactions in muscle cells is believed to be the same as in liver cells (p. 461). However, in muscle cells glucose is not remade but, in response to the demands for energy production in these cells, the reactions proceed from glycogen to glucose-6-phosphate, then through a series of intermediate steps that terminate in the production of either *lactic acid* or *carbon dioxide and water*—depending on the availability of oxygen in the cells. (See chart, p. 466.)

In contrast with conditions within liver cells, muscle glycogen is never completely exhausted—even during prolonged exertion or in starvation. Muscle cells well supplied with glycogen use it freely in reactions for the production of energy; but, as their store of glycogen begins to be depleted, the body institutes measures to conserve this essential substance.

The anaerobic stage of oxidation. It is known that the immediate source of energy for muscle contraction does not involve the oxygen brought to the cells by oxyhemoglobin. Instead, this energy is believed to be obtained through the hydrolysis of certain energy-rich phosphate compounds, notably *adenosinetriphosphate.*[3]

$$\text{Adenosine-triphosphate} + \text{Water} \longrightarrow \text{Adenosine-diphosphate} + \text{Hydrogen phosphate}$$

$$\text{Chemical energy} + \text{Chemical energy} \longrightarrow \text{Chemical energy} + \text{Chemical energy} + \text{12 kg-calories of energy per mole}$$

[3] The functioning of adenosinetriphosphate is emphasized in this discussion. However, this is not the only phosphate compound involved. Creatine phosphate (phosphocreatine) also participates in the process, presumably through remaking adenosinetriphosphate:

$$\text{Adenosine-diphosphate} + \text{Creatine phosphate} \longrightarrow \text{Adenosine-triphosphate} + \text{Creatine}$$

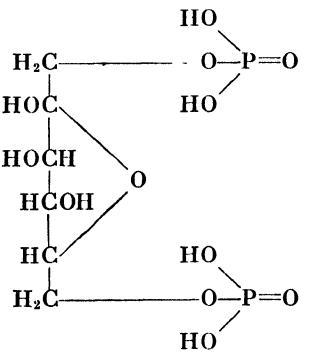
Phosphocreatine is, in turn, resynthesized when energy becomes available through reactions with oxygen. Through these various means phosphate is held in the cells, and the energy-rich phosphates are stored against future demands.

In order to maintain activity within the cells adenosinetriphosphate must continually be resynthesized in the cell. This requires a supply of chemical energy which is provided, largely, through the reaction of glucose intermediates with oxygen during the aerobic stage of the oxidation process (p. 466).

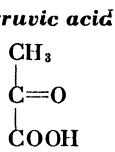
Intermediate steps. When glycogen is drawn upon for production of energy the first step is reaction with phosphate to make glucose-1-phosphate, followed by glucose-6-phosphate then fructose-6-phosphate. This compound then reacts with adenosinetriphosphate to form fructose-diphosphate (formulas appear below). The next step brings a break in the hexose chain, and a series of triose-phosphate compounds are made leading to phosphopyruvic acid (enol form). At the next step *pyruvic acid* is made and the phosphate is released. *Pyruvic acid is an outstanding glucose intermediate.* For completion of oxidation beyond this point, oxygen must enter the reactions; if it is not available, pyruvic acid is reduced to make *lactic acid*, the end product of the anaerobic process. Lactic acid escapes from the cell and enters the blood, from which it can be withdrawn by the liver cells and used to make glycogen. (See chart, p. 467.)

Structural formulas for some of the supposed intermediate products in the glycogen to lactic acid stage of glucose metabolism in muscle cells are:

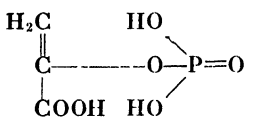
Fructosediphosphate
(Harden-Young ester)



Pyruvic acid



Phosphopyruvic acid
(Enol form)



Lactic acid



The energy product accruing from this series of anaerobic reactions is estimated to supply enough energy for rebuilding 3 or 4 moles of adenosinetriphosphate, from adenosinediphosphate, for each mole of glucose used. This is a relatively small energy yield and it could not sustain prolonged activity within the cell.

With oxygen provided. With an adequate supply of oxygen delivered to the cells, the end products are carbon dioxide and water. The reactions with oxygen, brought by the hemoglobin, begin at the pyruvic acid stage. However, the reaction is not simply between pyruvic acid and oxygen but involves a series of chemical changes whereby carbon dioxide and water appear at different steps in the process with an associated gradual production of energy. The exact series of reactions involved is still uncertain. One of the more generally accepted theories, based on experimental evidence, is outlined in the chart of the *citric acid cycle* that appears on page 468.

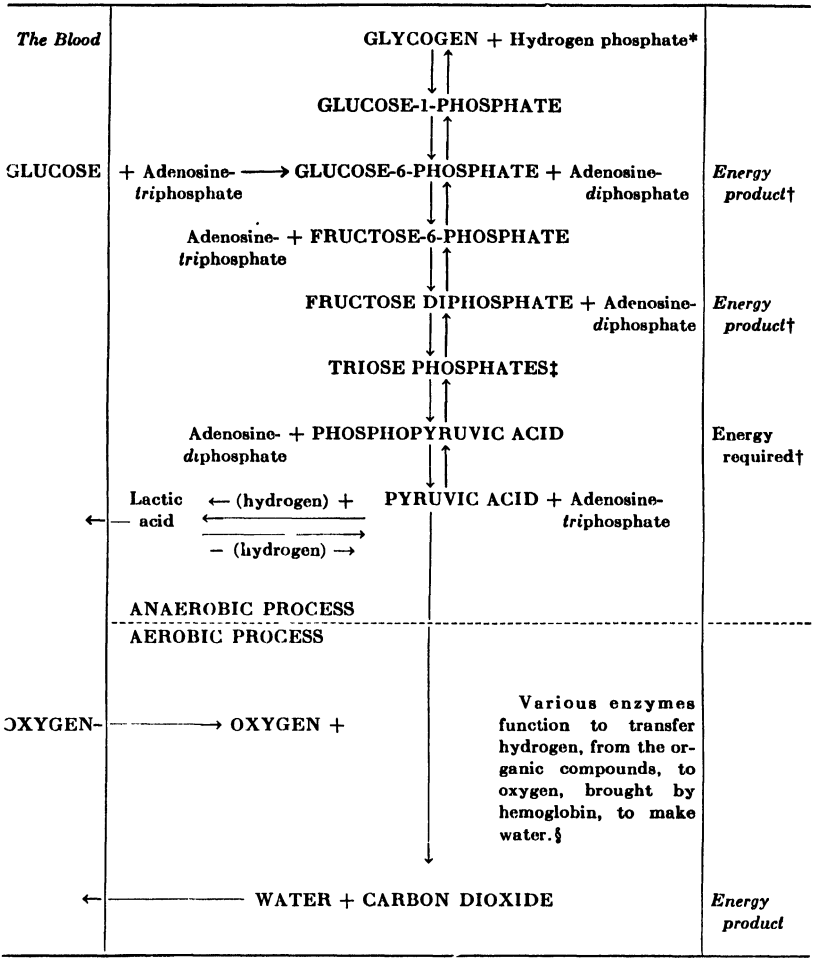
Pyruvic acid is attacked by cocarboxylase, of which thiamine diphosphate is the coenzyme, and carbon dioxide is released. Coenzyme A transfers the acetyl group to the citric acid cycle, and, subsequently, more carbon dioxide is released and hydrogen atoms, removed by dehydrogenases, combine with oxygen atoms to form water.

The greater part of the *energy product* obtained on the oxidation of glucose appears during the oxidation of pyruvic acid to carbon dioxide and water. It is estimated that sufficient energy is provided by this process for the resynthesis of approximately 30 moles of adenosinetriphosphate for each mole of glucose entering the reaction. That means that the energy yield of the aerobic oxidation is from 10 to 14 times as great as from the anaerobic process.

Interrelation of anaerobic and aerobic oxidation. The functional relation of anaerobic and aerobic oxidation reactions within muscle cells has not been established with certainty. It has been suggested that the ability to shift to greater use of anaerobic oxidation, temporarily, when an unusual demand for energy production exceeds the rate at which oxygen can be supplied, may be of advantage to the animal.[4] But the "oxygen debt" thus accumulated must be made up during a resting period, frequently enforced, following such exertion.

[4] Peters, John P., and Van Slyke, Donald D.: *Quantitative Clinical Chemistry*, Vol. I. The Williams & Wilkins Company, Baltimore, 1946, pp. 46–47.

Within muscle cells



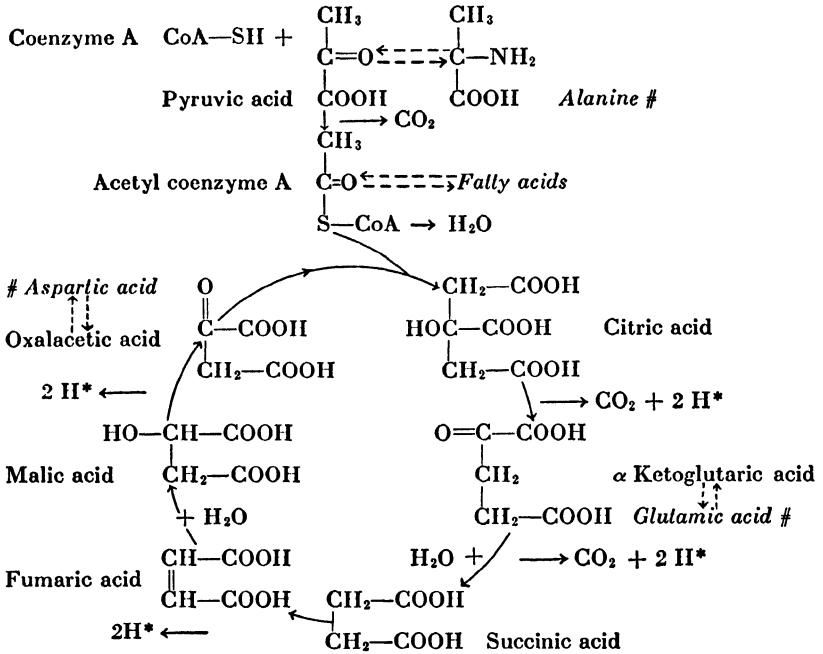
* The phosphate made during this reaction may be used in the cell, either directly or by means of an intermediate reaction with creatine, to remake adenosine*tri*phosphate.

† In order to provide energy during the anaerobic reactions, the energy-rich compound *adenosinetriphosphate* goes out of existence to make *adenosinediphosphate* which contains less chemical energy. But, for remaking adenosinetriphosphate, energy must be supplied. This is believed to be accomplished largely through the reactions in which oxygen becomes involved. (See p. 466.)

‡ A number of triose phosphates, that is, derivatives of sugars with 3 carbon atoms chained together in their molecules, intervene between fructose diphosphate and phosphopyruvic acid.

§ Some details of the aerobic reactions are provided in the *citric acid cycle* on page 468.

Diagrammatic representation of the citric acid cycle indicating the series of reactions in the oxidation of pyruvic acid to carbon dioxide and water. Not all of the details are shown but the following phases of the process are illustrated.



1. Aerobic oxidation of glucose from pyruvic acid to carbon dioxide and water is believed to be carried out through an endless chain of organic compounds which are used, then regenerated, as long as pyruvic acid is provided for continuing the cycle. During the process molecules of *carbon dioxide* are released at intervals under the influence of *carboxylase* enzymes. Hydrogen atoms (H*) are also released by dehydrogenases (p. 430). With the release of hydrogen atoms, electrons are carried by the *cytochrome enzymes* to *cytochrome oxidase* which catalyzes the combination of the hydrogen atoms with oxygen—brought by hemoglobin—to form molecules of water.

2. By means of this series of enzyme-controlled reactions energy is released steadily in small units.

3. At the *acetylcoenzyme A* stage, an interrelation between carbohydrate and fat intermediates is indicated.

4. At the *pyruvic acid* stage, also with *alpha ketoglutaric acid* and *oxalacetic acid*, interrelations with amino acids (#) are possible.

Enzymes and vitamins. As with most reactions that go on within living cells, these oxidations are catalyzed at each step by specific enzymes. Among the enzymes contributing to the oxidative process are some which require vitamins as essential constituents. The initial step in the oxidation of pyruvic acid requires *thiamine* phosphate as part of the decarboxylase enzyme (p. 434).

It follows that a deficiency in this vitamin tends to inhibit the very reactions that are most effective in the production of energy. Coenzyme A, of which *panlothenic acid* is a constituent, also functions at this stage. The dehydrogenases which, together with the cytochrome enzymes, function to remove hydrogen from metabolic intermediates and ultimately to affect the combination of hydrogen with oxygen to form water, include the diphosphopyridine nucleotide (DPN) to which *niacin* contributes (p. 435). They also include the flavoprotein enzymes of which *riboflavin* is a constituent (p. 435). Recognition of the importance of the reactions controlled by these enzymes affords some insight into the physiological importance of these vitamins.

Metabolism of glucose in nerve cells. The cells of the nervous system appear to depend on the oxidation of glucose for the production of energy. Moreover, little glycogen is found in this tissue. This means that nerve cells are very dependent on the glucose supply of blood, and in hypoglycemia the early symptoms of trouble usually come from the nervous system. The intermediate steps in glucose metabolism in nerve cells are similar to those in muscle cells.

The functioning of hormones. The reactions involved in carbohydrate metabolism are influenced by a number of the hormones produced in the various endocrine glands. Of these *insulin*, secreted by the pancreas, appears to be of primary importance. A deficiency in insulin interferes with the synthesis of glycogen and the oxidation of glucose, also with the building of fat from glucose. An explanation for these findings is found in the hypothesis that insulin is essential for the hexokinase reaction for making glucose-6-phosphate,[5] a synthesis which apparently precedes both the building of glycogen and oxidation of glucose. The effect of insulin is considered to be indirect in that it may inhibit the action of one of the *anterior pituitary hormones* which checks the hexokinase reaction and thus the phosphorylation of glucose. The pancreas secretes another hormone known as the *hyperglycemic factor* which stimulates glycogenolysis with the return of glucose to the blood.

Epinephrine, secreted by the medullary portion of the adrenal gland in response to anger, fear, cold, and other types of stress, is also of interest. This hormone stimulates the glycogen to glucose reactions and in this way increases the quantity of sugar carried to the cells of outlying tissues. Epinephrine does not function to sustain

[5] It has been observed that the diabetic animal can oxidize fructose even when it cannot oxidize glucose. This is interpreted as evidence that a different hexokinase enzyme functions to make fructose-6-phosphate from the one which initiates the phosphorylation of glucose.

muscle activity. It seems to be a part of nature's plan to use this hormone to augment the normal supply of glucose to muscle cells when there is an immediate and unusual demand for production of energy. The *adrenocorticotrophic hormone* (ACTH), acting in conjunction with certain *steroid hormones* produced in the cortex of the adrenal gland, stimulates the gluconeogenic reactions, that is, making glycogen from certain amino acids, glycerol, and other noncarbohydrate material. And, controlling the rate of oxidation and energy production throughout the body as a whole is *thyroxine*, which is made in the thyroid gland.

Under normal conditions a remarkable regulation of blood glucose results from this highly coordinated system of hormone controls. Thus, in spite of constantly varying degrees of activity on the part of the animal, the glucose supply to active cells is effectively maintained.

Hypoglycemia. The diabetic who must depend on an external supply of insulin must balance this against the demands for production of energy, as well as against the glucose supplied through the diet. Inadequate insulin results in limited oxidation of glucose at the cells. On the other hand, an excessive dose of insulin can so stimulate glucose oxidation that liver glycogen may be depleted, which results in *hypoglycemia*—a low concentration of blood glucose—and brings about the condition known as insulin shock.

Another type of hypoglycemia which has attracted considerable attention is associated with unusual irritability and fatigue experienced by some individuals in response to emotional or physical stress. The symptoms frequently become evident shortly before regular mealtime and are relieved by food. This type of *functional hypoglycemia* is thought to represent some impairment of hormonal control. Frequently the symptoms are alleviated by a well-selected diet which is relatively low in sugars and carbohydrates in general.[6]

Interrelation of glucose and fat metabolism. That there is a significant relation between oxidation of glucose and fat metabolism has long been recognized. The failure of the cells to oxidize glucose results in increased production of certain products of fat metabolism known as *ketones*. If the condition continues, the systemic condition known as ketosis develops. (See pp. 474 to 476 and pp. 507 to 508.)

Glucose used to make fats. Part of the glucose produced from carbohydrate of the diet is withdrawn from the blood to make fat. This occurs when the glucose concentration of the blood is relatively high, and the immediate needs for production of energy and for gly-

[6] Portis, S. A.: "Life Situations, Emotions, and Hyperinsulinism," *J.A.M.A.*, 142:1281–86, 1950.

cogen storage are being met. Deficiency of insulin appears to interfere with making fat from glucose and its deposit in storage cells.

Glucose used to make lactose. During the latter part of pregnancy and the period of lactation, lactose appears as a component of the milk secreted by the mammary glands. Apparently these cells can make galactose from glucose brought by the blood, since both of these isomeric sugars are constituent units of the disaccharide lactose. Pressure within the gland may force some of the lactose into the blood; when this occurs, lactose appears in the urine. Lactose, like glucose, is a good reducing agent; this fact should be kept in mind when testing urine during pregnancy and the period of lactation.

FUNCTION AND FATE OF FATS

Transportation to the cells. Within a few hours after a fatty meal, the lacteals of the intestinal villi become filled with fat, and the lymph leaving this region acquires a milky appearance—owing to the presence of fat in a high state of emulsification. This lymph is emptied into the thoracic duct, thereby entering the blood just before the latter passes through the heart.

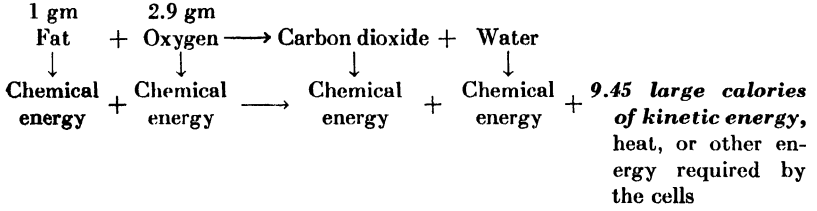
Fatty acids are carried in the blood partly in fats but also as constituents of phospholipids and cholesterol esters. At the fat-storage cells considerable quantities of fat are withdrawn into fat depots (p. 476), likewise at the liver, which is the principal site of intermediate metabolism of fats (p. 474). Cells of other tissues do not appear to use true fats to any great extent but select phospholipids and cholesterol esters, which are essential to cell structure.

Considerable information relating to the fate of fats in the body has been gathered since 1934 when Rudolf Schoenheimer and his associates first introduced the use of deuterium (a heavy isotope of hydrogen) incorporated into the structure of fatty acids which could be fed to animals and used as a means for tracing the reactions which these fatty acids undergo in the cells of the experimental animals.[7]

As cell components. Phospholipids and cholesterol esters, together with proteins, are the major components of cell protoplasm. Phospholipids concentrate at the cell wall where they may play a part in the process of absorption. They are especially abundant in the myelin sheath which serves to insulate nerve fibers.

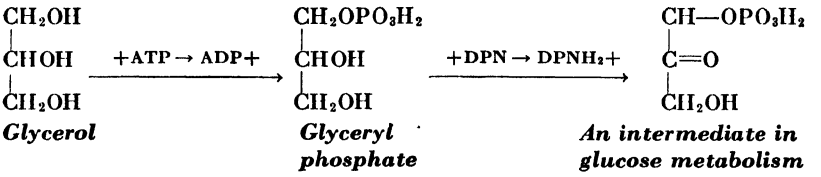
[7] Schoenheimer, Rudolf: *The Dynamic State of Body Constituents.* Harvard University Press, Cambridge, Mass., 1946, Chap. I.

Oxidation for production of energy. That fats are used in reactions with oxygen for production of energy is a well-established fact. These reactions do not take place directly between fats and oxygen but involve a series of intermediate steps. The quantitative involvement and the resulting energy product can be summarized as follows.



As to the exact reactions in intermediate stages in the oxidation of fats, much is yet unknown. However, various experimental studies have afforded a basis for outlining some of the steps that are generally accepted as probable.

Oxidation of glycerol. The glycerol absorbed from the intestine may (1) be carried by the blood directly to the cells; (2) be removed by the liver to make glycogen; or (3) be used for making new fats or phospholipids and, subsequently, following the hydrolysis of these compounds, again become available for reactions within the cells. When glycerol is oxidized for production of energy, it enters the sequence of carbohydrate oxidation at the triose phosphate stage (p. 465). Preceding this there is believed to be a reaction between *glycerol* and *adenosinetriphosphate* to make glyceryl phosphate; then oxidation facilitated by the diphosphopyridine nucleotide (DPN) to make the corresponding ketone. This ketone is an intermediate in glucose metabolism. These reactions may occur as is suggested below:



From this stage the reaction is assumed to continue through the carbohydrate sequence, through pyruvic acid, to make carbon dioxide and water, with the usual release of an energy product.

Oxidation of fatty acids. In relation to the oxidation of fatty acids, the most generally accepted concept is the so-called beta-oxidation theory suggested by Knoop about 1904. This theory assumes that oxidation takes place at the beta carbon of the fatty acid, that is, the second carbon beyond the carboxyl group, with the release of a 2-carbon unit with each succeeding beta-oxidation. In this way the oxidation is believed to proceed from stearic acid to palmitic acid, to myristic acid (with 14 carbon atoms in the chain) and so on.

Studies recently reported by Green and others[8] indicate that before the fatty acid can be oxidized it must, first, be activated through an enzyme-controlled reaction with coenzyme A (p. 434). The energy required to initiate this reaction is supplied by hydrolysis of *adenosinetriphosphate.* The attack at the beta carbon is believed to involve a series of reactions each of which is controlled by a specific enzyme. The 2-carbon compound released as each oxidation is completed is *acetyl coenzyme A*, represented symbolically as $CH_3CO—S—CoA$.

The following summary suggests the steps in the oxidation of a typical fatty acid, according to this theory.

(1) $R—\overset{*}{C}H_2—CH_2—COOH + Enzyme—S—CoA \rightarrow R—\overset{*}{C}H_2—CH_2—CO—S—CoA + Enzyme$

(2) $R—\overset{*}{C}H_2—CH_2—CO—S—CoA \xrightarrow{\text{a dehydrogenase}} R—\overset{*}{C}H{=}CH—CO—S—CoA$

(3) $R—\overset{*}{C}H{=}CH—CO—S—CoA + HOH \xrightarrow{\text{a hydrase}} R—\overset{*}{C}HOH—CH_2—CO—S—CoA$

(4) $R—\overset{*}{C}HOH—CH_2—CO—S—CoA \xrightarrow{\text{a dehydrogenase}} R—\overset{*}{C}O—CH_2—CO—S—CoA$

(5) $R—\overset{*}{C}O—CH_2—CO—S—CoA + HS—CoA \rightarrow R—CO—S—CoA + CH_3CO—S—CoA$

Acetyl coenzyme A

(* Indicates the beta carbon)

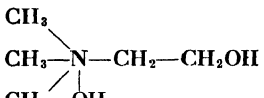
The *acetyl* group, carried by *coenzyme A*, can be oxidized to carbon dioxide and water, entering the aerobic stage of oxidation by combining with oxalacetic acid to form citric acid (p. 468). In this aerobic oxidation the energy product greatly exceeds the energy which was supplied to initiate the reaction. This acetyl compound can be used also in the liver cells for making the ketone *aceloacetic acid*, which

[8] Green, David E.: "The Metabolism of Fats," *Scientific American*, 190:32–36, 1954.

is distributed to muscle and other tissues for oxidation. It can be used for the synthesis of *cholesterol* and presumably the steroid hormones, also for making *acetylcholine* which functions in transmission of nerve impulses.

Making of phospholipids. In the liver, phospholipids are made for distribution to other tissues. These compounds contain a high proportion of the unsaturated fatty acids which are either selected from those brought in the blood to the liver or are prepared in liver cells. The nutritional demand for the highly unsaturated linoleic, linolenic, and arachidonic acids (p. 392) probably exists because they are required for making phospholipids. For certain of these lipids *choline* is also required. A deficiency of choline in the diet results in accumulation of fat in the liver and diminished production of phospholipids.

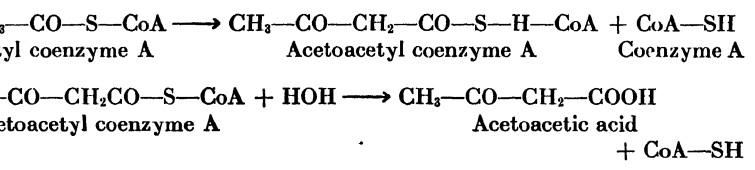
Choline is provided by such foods as egg yolk, meat—especially liver and muscle—legumes, and the germ of cereal grains. It is regarded as a member of the vitamin-B complex.



Choline

Choline contributes not only to the composition of phospholipins but also to the ester acetylcholine, a compound which functions in the transmission of nerve impulses.

Making of ketones. The liver is the chief site of the production of "ketones"—acetoacetic acid, β-hydroxybutyric acid, and acetone. These compounds are made from fatty acids brought to the liver and oxidized to the *acetyl coenzyme A* stage. The production of acetoacetic acid is believed to involve the condensation of two acetyl coenzyme A molecules with the subsequent release of the coenzyme.[9]

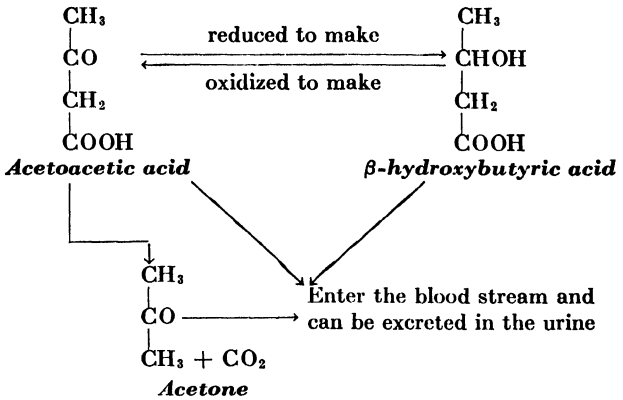


Acetyl coenzyme A — Acetoacetyl coenzyme A — Coenzyme A

Acetoacetyl coenzyme A — Acetoacetic acid

The fact that β-hydroxybutyric acid and acetone are found in association with acetoacetic acid is not difficult to explain when their chemical relations are recognized.

[9] West, Edward S., and Todd, Wilbert R.: *Textbook of Biochemistry*, 2nd ed. The Macmillan Company, New York, 1955, p. 915.



These "ketones" are not oxidized in the liver cells but are distributed to muscles and other tissues where they can be oxidized for the production of energy. Acetoacetic acid appears to enter the aerobic oxidation cycle through reaction with oxalacetic acid, which is provided by the oxidation of glucose (p. 468). Thus, oxidation of the ketones is interrelated with, and to some extent dependent on, the continued oxidation of glucose in the cell.

Ketosis. Making ketones is a normal metabolic process. But, the accumulation of these substances in the blood in concentrations such that they are excreted in the urine has long been recognized as indicative of some interference with carbohydrate metabolism. The resulting systemic disturbance is known as *ketosis.*

Ketosis occurs when the store of liver glycogen is so depleted that the body begins to mobilize its resources, drawing upon fats and even amino acids from its own tissues, for the production of energy and maintenance of glycogen supplies. The increased oxidation of fat in the liver accelerates the production of acetoacetic acid and the related compounds. When these are supplied to the blood faster than they can be used by the peripheral tissues they accumulate in the blood (ketonemia) and are excreted in the urine (ketonuria).

The conditions with which ketosis is especially associated are *diabetes*, in which the insulin deficiency both limits the oxidation of glucose in the cells and interferes with the storage of glycogen, and in acute *starvation*, with exhaustion of liver glycogen.[10] Ketosis can also be produced from a diet which

[10] In conditions characterized by prolonged vomiting, as in some toxemias and in the vomiting of pregnancy, ketosis frequently develops as a result of the inability of the individual to retain food taken by mouth. Peters, John P., and Van Slyke, Donald D.: *Quantitative Clinical Chemistry*, Vol. I, p. 536.

is excessively high in fat and deficient in carbohydrate. Infants and young adults are more susceptible to this disturbance than are adults, perhaps because the active and growing animal uses its glycogen stores more prodigally.

Ketosis is accompanied by a disturbance in the acid-base equilibrium of the body in the direction of an increase in the hydrogen-ion concentration of blood and lymph, a condition known as acidosis. The entrance of acetoacetic acid and β-hydroxybutyric acid brings about reactions with the sodium bicarbonate buffer salt which increase the concentration of carbonic acid in the blood and the escape of carbon dioxide at the lungs.

Acetoacetic acid	+	Sodium bicarbonate	⟶	Sodium acetoacetate	+	Carbonic acid

$$CH_3\text{–}CO\text{–}CH_2\text{–}COOH + NaHCO_3 \rightarrow \underset{\text{For excretion by the kidneys}}{CH_3\text{–}CO\text{–}CH_2\text{–}COONa} + \underset{\text{At the lungs}}{H_2CO_3 \rightarrow H_2O + CO_2\uparrow}$$

At the same time there is increased elimination of sodium, also of acetoacetate and β-hydroxybutyric acid ions, by the kidneys together with an accompanying increase in the excretion of water. Moreover, excretion of ketones also deprives the body of substances which would otherwise be available for energy-producing reactions. (See pp. 507 to 509 for further discussion of ketosis.)

In ketosis, the treatment and nursing care of the individual are directed toward the re-establishment of glucose oxidation in the cells and of glycogen reserves in the liver, as well as the restoration of the fluid and salts. In starvation the administration of carbohydrate checks the excessive production of ketones. In the diabetic the treatment usually calls for both insulin and carbohydrate, the former to enable the cells to oxidize glucose, and the latter to re-establish the store of liver glycogen.[11]

The fats of the storage cells. Deposits of stored fat are widely distributed throughout the body. They are particularly abundant in the subcutaneous tissue, in the omentum and mesentery protecting the intestine, and around the heart and kidneys where they function in supporting the organs.

Of the fats absorbed from the intestinal membrane, considerable portions are removed from the blood by the fat storage cells. Much of the stored fat is made from glucose; also some, but not all, amino acids can be used to make glucose, and this in turn to make fat.

[11] "Lesser degrees of ketosis are encountered continuously or at intervals in diabetes. . . . The glycogen stores are always in a precarious state. At one moment temporary deficiency of insulin may retard the oxidation of sugar; at the next, undue muscular exertion or slightly excessive insulin action may exhaust the scanty stores of glycogen in the liver. In either case ketosis will occur." *Ibid.*, p. 513.

Fat made from glucose. That fat can be made from glucose has long been recognized; but in what tissues this transformation takes place is still uncertain. Probably the liver takes an active part in the process, and the finding of glycogen deposits in fat storage cells suggests that these cells also may participate in the synthesis of glucose to glycogen to fat. Considering the similarity in their composition, it would appear to be relatively simple for nature to make glycerol from glucose, probably through triose intermediates of glucose metabolism.

As to how the fatty acids are made from glucose intermediates there is much uncertainty. Experimental evidence strongly suggests that they are built up from 2-carbon units, presumably with the decarboxylation of pyruvic acid as the first step, then the condensation of the 2-carbon intermediates to make butyric acid. Both coenzyme A and the dipyridine nucleotide (DPN) are believed to function in this process and in the continued acetylation whereby fatty acids with longer carbon chains are built up.

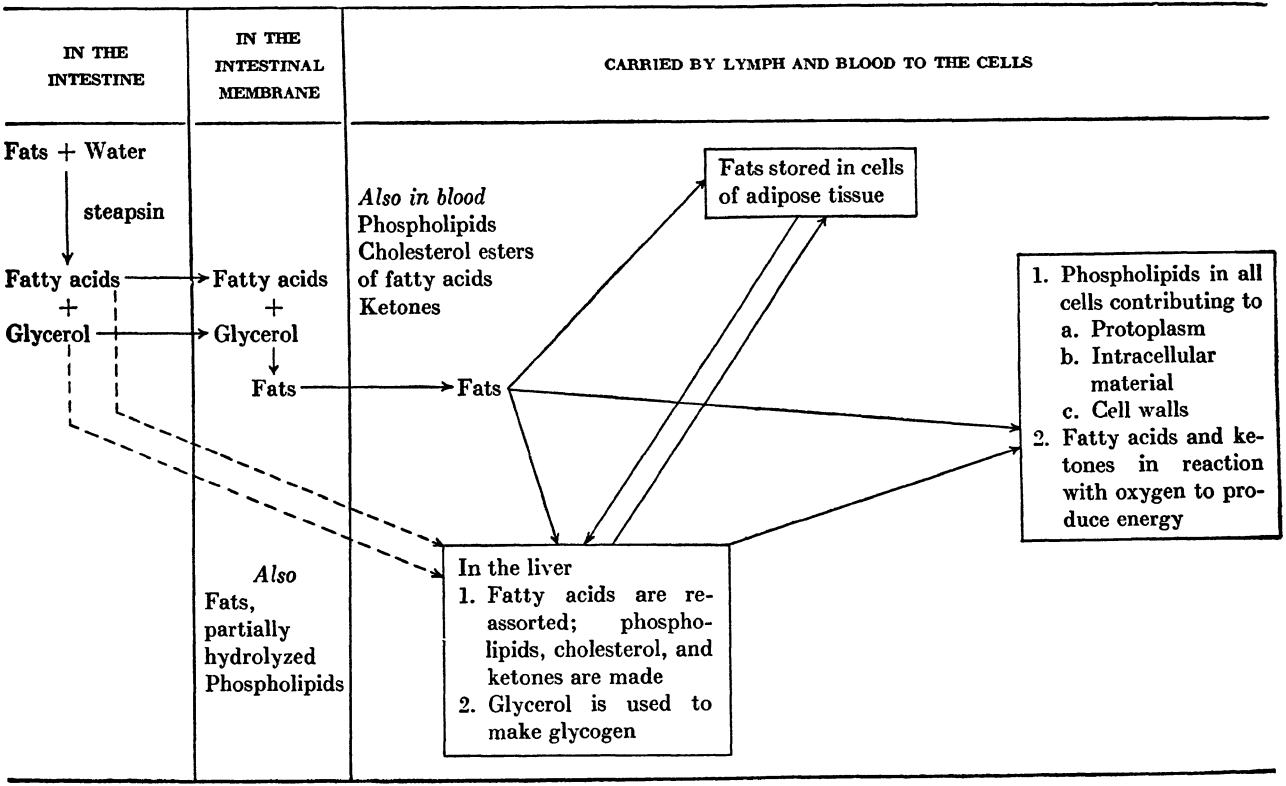
Character of storage fat. The mixture of fats and fatlike substances, which is characteristic of fat in storage cells, differs from that in other tissues in that the *true fats*, largely of the saturated variety, predominate over phospholipids. It is also noteworthy that animals of any given species, when fed on an ordinary mixed diet, deposit a fat in their storage cells which is peculiar to the species. This is probably, in part, the result of a selection by these cells from the fats brought by the blood. But there is also evidence of reactions in liver cells, and in fat storage cells themselves, whereby a different assortment of fatty acids for synthesis of fats can be produced.[12] In general, the following types of transformation appear to be possible.

Saturated acids	Stearic acid $\rightleftharpoons$	Palmitic acid $\longrightarrow$	Short-chain fatty acids
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	
Unsaturated acids	Oleic acid	Palmitoleic acid	

Functions of storage fat. Storage fat, if not in excessive amount, is an important asset to the animal. (1) It is one of the provisions whereby the animal is able to maintain a fairly constant temperature. This is because fats are poor conductors of heat; hence, the fat layer which underlies the skin provides insulation and thereby prevents a too rapid radiation of heat from the body surface. (2) The fatty layers which normally surround certain vital organs, such as

[12] Schoenheimer, Rudolf: *The Dynamic State of Body Constituents*, pp. 15, 21.

Diagrammatic summary of the fate of fats in the body



the kidneys, provide support for these organs and protection from injury. (3) But the primary function of storage fat would seem to be that of ensuring a continual food supply upon which the cells of muscles and other tissues can draw, as required, for the production of energy.

Fat depots should not be thought of as "dead-storage" tissues. There is an active metabolism in these cells. Fats and phospholipids are continually leaving the storage cells for distribution to the liver and other tissues; fats and phospholipids of dietary origin are withdrawn from the blood for storage. In fact, in the course of a single day, the turnover of material in these cells may be quite rapid. Schoenheimer, working with rats, found that there had been a 44 per cent replacement of storage fat within a period of 4 days, without any evident change in weight of the animal.[13] In starvation, when the dietary food supply is inadequate, although the stored fat is never completely exhausted, the accumulation is depleted by the demands of the liver and other tissues. When the caloric intake of the diet is balanced by the demands for production of energy, the quantity of fat within these cells remains remarkably constant.

FUNCTION AND FATE OF AMINO ACIDS

The various amino acids, end products of protein digestion, are absorbed into the portal circulation and carried, by way of the liver, to the general circulation for distribution to the tissues. They appear to be utilized promptly by the tissue cells because, although directly following absorption there is a temporary increase in the concentration of amino acids in the liver, they do not accumulate to any marked degree in either blood or other tissues. Moreover, within a few hours after a meal rich in protein, the normal, well-nourished adult eliminates urea, the outstanding end product of protein metabolism, in a quantity that closely parallels the protein intake.

A dynamic protein metabolism. This rather fixed relation between protein intake and urea output led to a belief that, aside from the protein required to supply amino acids for building new tissues during the growth period and following tissue injury, a limited amount of protein was required for the replacement of worn-out

[13] Schoenheimer, Rudolf: *The Dynamic State of Body Constituents*, pp. 11–12.

tissues. This well-established concept was challenged and significantly modified when, about 1937, Schoenheimer and his associates reported the results of studies in which known quantities of certain of the amino acids, containing unusual isotopes of nitrogen (N^{15}) or of hydrogen (H^2), were included in the food of experimental animals. The fates of these "tagged" amino acids could then be traced within the animal body through the identification of the unusual isotopic elements in substances found in tissues or in excretions. By this means it was discovered that only a small proportion of the amino acids included in the food could be accounted for immediately in excretions. Instead, on sacrificing the animals, the unusual isotopes were located in compounds widely distributed throughout body tissues. Some of the amino acids had been incorporated directly into proteins of the cell structure; some had contributed to the synthesis of other amino acids; and some had been used to make compounds other than proteins.[14] These findings are regarded as significant because they indicate that, throughout the entire life of the animal, an active process of exchange is carried on continually between the proteins of all tissues and the amino acids provided by the proteins of the food. The fact that the well-nourished adult excretes urea in proportion to the protein intake simply indicates that the process of exchange is so regulated that an equilibrium is maintained between the amino acids obtained from food and the amino acids being destroyed in the body.

Functions of amino acids. Amino acids have a unique place in metabolism. They have long been recognized as essential for maintenance of tissue and for growth. They are also required for the synthesis of a variety of essential compounds including enzymes, certain hormones, bile salts, and creatine. They contribute to the highly specialized proteins, known as antibodies, which guard against infectious organisms or the introduction of other foreign proteins. They can be deaminized, and the resulting organic acids can be used to provide partners for oxygen in the production of energy.

For maintenance and building of tissue. The body is dependent on the amino acids of the food for the specific units which are required for tissue building. Apparently, amino-carboxyl linkages in tissue proteins can open both to release amino acids to the blood and, again, to incorporate into the cell protein amino acids brought

[14] Schoenheimer, Rudolf: *The Dynamic State of Body Constituents*, Chap. II.

by the circulation. Even when there is no detectable change in body weight, this interchange of amino acids appears to be continually in operation. For growth and during pregnancy—also for recovery from tissue injury, debilitating illness, or chronic malnutrition—the amino acid intake must exceed the destruction of amino acids, as indicated by excretion of urea and related compounds. This is accepted as evidence that, at such times, amino acids are being retained for construction of new tissue. But, when the diet is deficient in relation to either protein or total caloric requirements, loss of weight may occur, and the building of new tissue is either slowed down or brought to a standstill.

In order to maintain the tissues and organs throughout the body in a good state of nutrition, the normal adult uses from 0.5 to 0.7 gm of protein daily per kilogram of weight. However, because there is a certain inevitable waste of amino acids (p. 485), the nutritionist recommends that the diet should actually provide a daily minimum of 1 gm of protein of good quality (p. 412) per kilogram of body weight. The growing child, the pregnant woman, and the convalescent need a somewhat larger allowance.

Indispensable amino acids. As mentioned previously (p. 42), there are 8 amino acids which are regarded as *indispensable* from the dietary standpoint, for maintenance and building of tissue. These are not the only amino acids required for cell structure and other necessary functions. Nevertheless, with these essential amino acids provided in adequate quantities, the cells appear to be able to make all other amino acids which they require. But, *if even one* of the indispensable amino acids is either lacking or deficient in quantity—although the food may be adequate in all other respects—the building of tissues is thereby limited. Even the essential amino acids, if not used immediately, are deaminized, and the resulting organic acids become available for oxidation and the production of energy. It becomes apparent, therefore, that quality as well as quantity should be considered in choosing the proteins of the diet; for, unless the essential amino acids are all provided and in the right proportions, there will be considerable waste so far as building of tissue protein is concerned.[15] (See also pp. 409 to 412.)

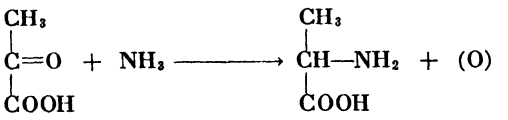
The successful use of *protein hydrolysates* and *amino acid mixtures* gives further evidence that only a selected group of amino acids are actually required

[15] Cannon, Paul R.: *Some Pathologic Consequences of Protein and Amino Acid Deficiencies.* Charles C Thomas, Springfield, Ill., 1948, pp. 4–22.

for tissue building. But, though the feeding of these mixtures serves as an invaluable means for supplying the needs of patients who are unable to take sufficient food by mouth, the fact remains that neither protein hydrolysates nor mixtures of amino acids provide any more completely for tissue needs than does high-quality protein food supplied in the usual manner.

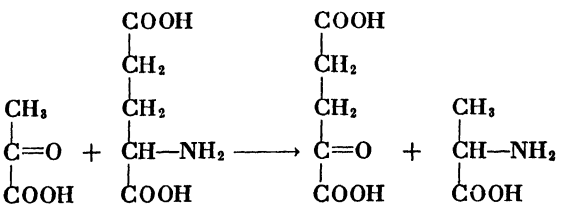
Amino acids made within cells. Some of the amino acids required for cell functioning can be made within the cells, either from related amino acids or from some of the metabolic intermediates of glucose or fat metabolism. *Glycine* and *alanine*, both required amino acids, can be made within the body. The origin of glycine is as yet undetermined. Alanine can be made from pyruvic acid, a glucose intermediate, the synthesis involving either a reaction of pyruvic acid with ammonia, or a *transamination*—that is, the transfer to pyruvic acid of an amino group from some other amino acid. The following equations suggest such possibilities.

a. By reaction with ammonia (possible sequence)



Pyruvic acid + Ammonia ⟶ Alanine + Oxygen element

b. By transamination (more probable sequence)



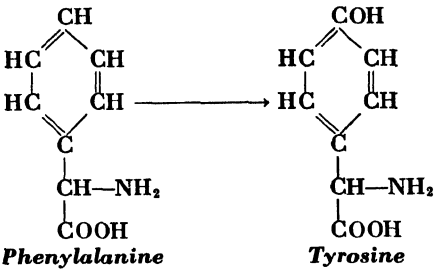
Pyruvic acid + Glutamic acid ⟶ Ketoglutaric acid + Alanine

The dicarboxylic acids, such as glutamic acid, are especially active in the transamination reactions. And enzymes, known as *transaminases*, are widely distributed in the cells of muscle, liver, and blood plasma, where such reactions occur. Pyridoxal phosphate, a derivative of the vitamin pyridoxine, B_6, is a constituent of the transaminase enzymes.

In some instances one amino acid can serve as the precursor of another amino acid. Thus, tyrosine can be made from phenylalanine, cystine from methionine, and ornithine can undergo reactions to

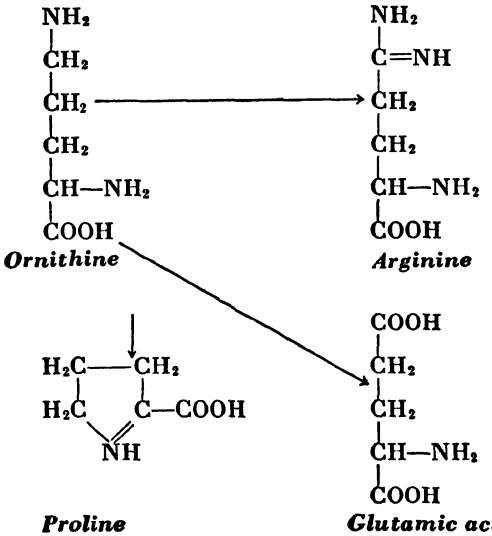
make three different amino acids: arginine, proline, and glutamic acid. The accompanying formulas suggest some of these possibilities.

a. Tyrosine made from phenylalanine



Phenylalanine *Tyrosine*

b. Arginine, proline, and glutamic acid made from ornithine[16]



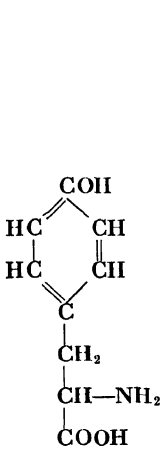
Ornithine *Arginine*

Proline *Glutamic acid*

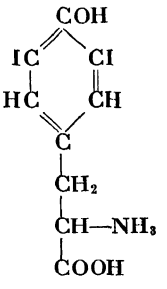
Amino acids for making other essential compounds. Certain amino acids are requisitioned for making essential substances of highly specialized nature and function. These include enzymes, such as pepsin and trypsin, and certain hormones, such as insulin, thyroxine, and epinephrine. For making *insulin*, the islands of Langerhans in the pancreas select a number of amino acids, includ-

[16] Ornithine containing the hydrogen isotope, deuterium, was fed to mice and deuterium was recovered in all three amino acids—arginine, proline, and glutamic acid. Schoenheimer, Rudolf: *The Dynamic State of Body Constituents*, p. 42.

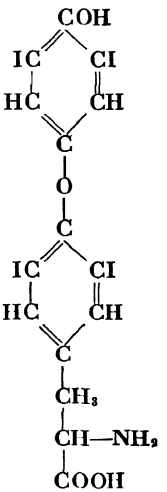
ing glutamic acid, tyrosine, cystine, arginine, leucine, and lycine.[17] Tyrosine is the parent substance for both *thyroxine*, the active principle of the thyroid gland, and its precursor, *diiodotyrosine*.



Tyrosine



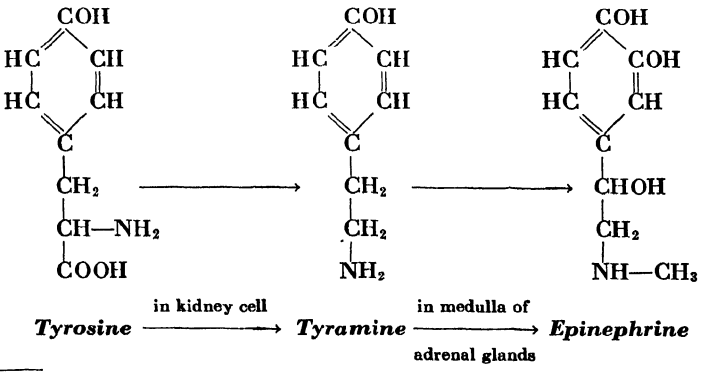
Diiodotyrosine



Thyroxine

The hormone *epinephrine* is also regarded as a tyrosine derivative. It is made in the medullary portion of the adrenal glands, probably from tyramine brought to this gland from the kidneys where it is made from the amino acid tyrosine.

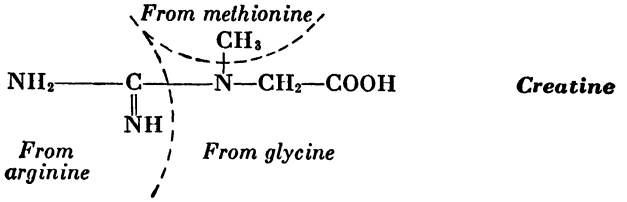
Tyrosine is also claimed to be necessary for making melanin, the dark pigment which gives color to hair, eyes, and skin.



Tyrosine ⟶ ***Tyramine*** ⟶ ***Epinephrine***

[17] Thompson, E. O. P.: "The Insulin Molecule," *Scientific American*, 189:36–41, 1955.

Arginine, *glycine*, and *methionine* all contribute to the making of *creatine*, a compound which functions in muscle cells for making phosphocreatine, an energy-rich compound which is involved in glucose metabolism (p. 464).

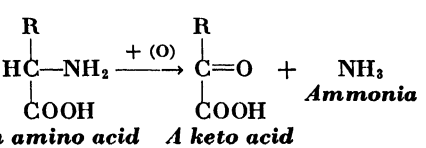


Comparison of the formula for creatine with those of glycine and arginine (pp. 410 to 411) readily shows which portion of the molecule is derived from each of these amino acids. Only the methyl group comes from methionine; however, this illustrates what is, perhaps, the primary metabolic function of methionine—to provide methyl groups for the synthesis of other compounds. Methionine also contributes to the building of choline by supplying methyl radicals.

Amino acids oxidized for production of energy. Although this is not their primary function, amino acids are oxidized in the cells for production of energy. The matter products of such reactions are carbon dioxide, water, and nitrogen compounds of which urea is the most important. It is calculated that for each gram of protein so used, an energy product of approximately 4.35 large calories results.

1 gm (av.) Protein	+	1.23 gm (av.) Oxygen	→	Carbon dioxide	+	Water	+	Urea	
↓		↓		↓		↓		↓	
Chemical energy	+	Chemical energy	→	Chemical energy	+	Chemical energy	+	Chemical energy	+ ***4.35 large calories kinetic energy*** or other energies needed by the cells

Intermediate metabolism of amino acids. Amino acids provided by the diet but not used immediately for making protein, together with those released from proteins of various tissues, shortly undergo oxidation and deaminization to make ammonia and keto acids, perhaps after the manner suggested in the following equation.

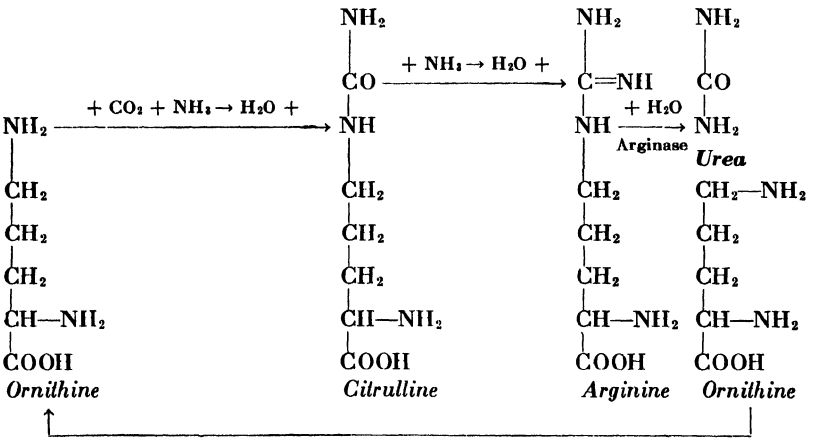


From this stage the ammonia and the organic acids follow separate pathways in metabolism.

Fate of ammonia. The deaminization of amino acids is believed to be carried on chiefly in the liver where the ammonia is used in the production of urea. The kidneys can also deaminize amino acids with the production of ammonium salts for excretion in the urine (p. 515).

The making of urea. It has long been known that the formation of urea ($NH_2—CO—NH_2$), the principal nitrogenous end product of protein metabolism, takes place in the liver. There is still considerable uncertainty as to some of the intermediate reactions in the process. In 1932, Krebs and Henseleit proposed a theory which is supported by considerable experimental evidence. The sequence of reactions which they suggested follows.

Fate of ammonia—Krebs urea cycle



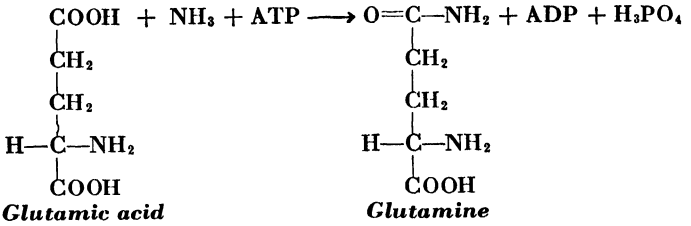
More recent work with isotopic tracers supports this concept but also indicates that the process is actually more complex than the above representation suggests.

It is probable that the synthesis of citrulline from ornithine involves a series of reactions with the active participation of a glutamic acid derivative. Also the formation of arginine from citrulline requires the presence of aspartic acid. The energy required for the synthesis of urea is supplied by reactions with adenosinetriphosphate.[18]

[18] Downes, Helen R.: *The Chemistry of Living Cells.* Harper & Brothers, New York, 1955, pp. 368–73.

Urea is very soluble in water; therefore, the body encounters no difficulty in carrying it away in the blood to the kidneys and to the skin, where it is eliminated.

The functioning of glutamine. Glutamic acid and its derivative *glutamine* also function in the disposal of ammonia. Glutamine is found in many tissues and in the blood in considerable quantities. It has been suggested that it serves as a means for storing amino nitrogen for tissue metabolism. Glutamine is made in various cells, including the liver and kidney, from ammonia and glutamic acid, as suggested in the following equation.



In the kidney cells glutamine can be hydrolyzed to make glutamic acid and *ammonia*—with the elimination of ammonium salts in the urine (p. 516).

Fate of the keto-organic acids. The keto-organic acids resulting from deaminization of amino acids do not all follow the same metabolic pathway. Those derived from *alanine*, *aspartic acid*, and *glutamic acid* can enter the citric acid cycle (p. 468) and are probably oxidized in the cells where they are made. At the liver others, including those made from *serine*, *threonine*, *cysteine*, *arginine*, *histidine*, and *proline*, can be used to make glucose. The keto-organic acids derived from *phenylalanine*, *tyrosine*, and *leucine* can be used to make acetoacetic acid. For some, the details of oxidation are uncertain. But, whatever the pathway, the end products are carbon dioxide and water.

Sulfur-containing amino acids. The sulfur-containing amino acids, methionine, cystine, and cysteine, yield not only carbon dioxide, water, and urea on oxidation but also sulfuric acid. The sulfate radical appears in the urine as inorganic sulfate and also in organic compounds—including those formed by conjugation with phenols absorbed from the intestinal tract (p. 456).

Protein reserves and repair of tissue. In contrast with nature's provision for storage of fats and glycogen, there appears to be no specific storage of protein. Nevertheless, the well-nourished body seems to have protein reserves from which it draws to meet the de-

mands for essential substances, either when the protein of the diet is inadequate, or when blood proteins have been lost—as in hemorrhage. Under these circumstances proteins are withdrawn, apparently, from the tissues themselves. Certain organs—the liver, intestinal mucosa, and kidneys readily give up protein when the protein level of the diet is reduced. Muscles also release protein, but less readily.

The well-nourished body maintains the proteins of the blood and of the fluids surrounding the cells at a level that is consistent with good nutrition within the cells. Prolonged malnutrition, whether of dietary origin or the result of persistent loss of protein (as with the escape of albumin in urine in nephritis) can result in hypoproteinemia, that is, a lowering of the concentration of protein in the blood. When this condition exists, all tissues suffer, wound healing is delayed, and the body is less able to combat infection.

Following severe tissue damage, also accompanying the loss of protein through hemorrhage, blood proteins are regenerated largely from the liver. Globulins, including those essential for the clotting of blood, are replaced rapidly; albumins more slowly. It has been observed, also, that directly following severe tissue damage, as in burns, fractures, surgery, and infections, the body appears to raid its own tissues for amino acids—even though what appears to be an adequate diet is provided. For this reason, measures—either dietary or through the use of protein hydrolysates or blood plasma—are frequently resorted to in treatment of these conditions in order to ensure adequate protein supplies for the tissues and, thus, to promote healing.

Antibodies and immune reactions. The protective mechanism whereby the body resists the invasion of microorganisms and other foreign material is a highly specific form of protein metabolism. When microorganisms gain entrance to the body they provide *antigens*, usually proteins or polysaccharides, which stimulate the production of antibodies. These antibodies react with the antigens, thereby contributing to their destruction. Antibodies are highly specific and, in general, function only against the antigen which stimulated their production.

For example, the *exotoxins* secreted by certain microorganisms act as *antigens*. They are believed to be proteins of low molecular weight which escape from the cells of the organism and circulate throughout the body of the host damaging sensitive tissue cells. The antibodies produced in response to this tissue injury are known as *antitoxins*. They function by combining with the toxin to inactivate it.

Antibodies are proteins, apparently modifications of the gamma globulins normally present in the blood plasma. They can, it is believed, originate in the cells of various tissues, notably the liver, spleen, bone marrow, and probably the lymph nodes. From these tissues they escape into the blood and presently can be located in both circulating fluids and tissue cells.[19] Once antibody formation has begun, it increases gradually, then slowly declines. An antigen frequently stimulates many times its own equivalent weight of antibody, thus leaving a reserve supply in the tissues to resist future invasions of the same type. These antibodies which the animal makes within its own cells are treated as normal tissue proteins in that they are maintained, as are all tissue proteins, through exchange reactions with the amino acids of food origin. The *active immunity* thus produced can continue for an indefinite period of time—sometimes for weeks or even years. However, when the body is inoculated with antibodies which originated in the cells of some other animal, a *passive immunity* of short duration results.[20] This can be accounted for because these antibodies are themselves foreign proteins; although they can function against the invading organism, they are not maintained through exchange of amino acids but, instead, provoke the production of antagonistic substances which shortly effect their destruction. Fully 50 per cent of injected antibodies can disappear within 2 days following their introduction into the body.[21] A lack of resistance to infection has long been associated with conditions of malnutrition; and it is a noteworthy observation that antibody production, hence the development of immunity, takes place more readily in the healthy individual whose tissues are well provided with protein reserves.[22]

Antibody production is not limited to the response of the body to infection. Other foreign materials—such as injected serum, pollens, and sometimes food proteins, as well as certain drugs—can stimulate antibody formation. As a

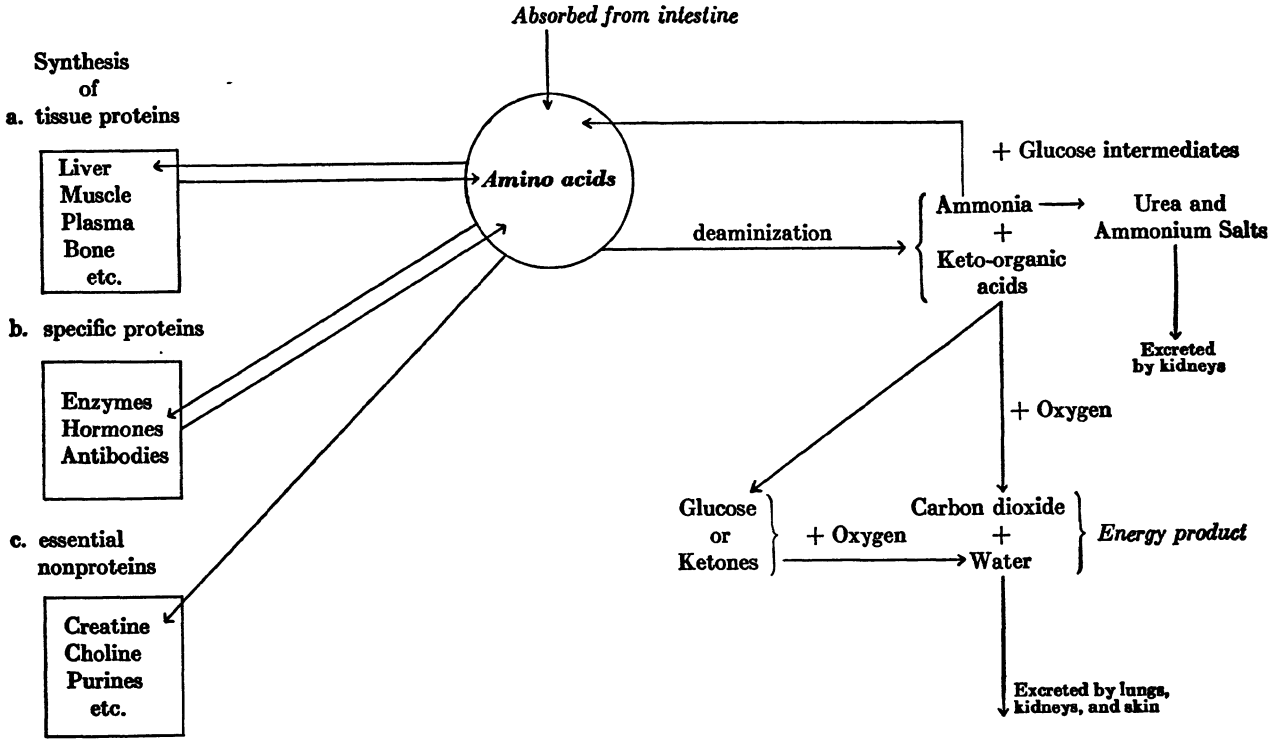
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[19] Boyd, Wm.: *Fundamentals of Immunology*, 2nd ed. Interscience Publishing Company, New York, 1947, pp. 57–60.

[20] The passive immunity of the infant, provided by antibodies made in the cells of the mother, is usually more lasting than when antibodies are supplied from some other source.

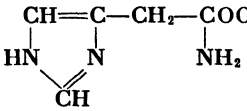
[21] Everett, Mark: *Medical Biochemistry*. Paul B. Hoeber, Inc., New York, 1946, p. 484.

[22] Cannon, Paul R.: *Some Pathologic Consequences of Protein and Amino Acid Deficiencies*, pp. 8–12.

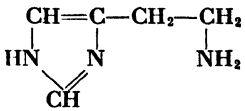

Absorbed from intestine
Synthesis of
a. tissue proteins
Liver
Muscle
Plasma
Bone
etc.
Amino acids
+ Glucose intermediates
deaminization
Ammonia
+
Keto-organic acids
Urea and Ammonium Salts
Excreted by kidneys
b. specific proteins
Enzymes
Hormones
Antibodies
+ Oxygen
c. essential nonproteins
Creatine
Choline
Purines
etc.
Glucose or Ketones
+ Oxygen
Carbon dioxide + Water
Energy product
Excreted by lungs, kidneys, and skin

result the individual becomes sensitive to the subsequent introduction of even minute quantities of the offending antigen. As with active immunity, this hypersensitive condition can continue for weeks and even years, giving rise to a variety of tissue responses known as allergies. One theory suggests that, following the reaction of antigen with antibody, a toxic substance is released in the tissues and is responsible for the allergic response—the hay fever, or hives, or other symptoms of disturbance. This substance has been identified by some investigators as either histamine or a histamine-like compound. The precursor of histamine is believed to be the amino acid histidine.

Histidine



Histamine



Concerning the chemistry involved in antigen and antibody reactions, much remains to be discovered. It does not appear that the specific character of antibodies can be attributed to any selected amino acid units, but rather is the result of specific arrangements of amino acids within protein molecules, each antibody molecule having its own peculiar structural configuration.

Summary of functions and fate of amino acids. (See chart, p. 490.)

QUESTIONS

1. List important functions of the liver in relation to the metabolism of (a) glucose, (b) fats, (c) amino acids. Where possible, illustrate by reference to specific reactions.

2. What is the normal concentration of glucose in the blood? What conditions operating at the liver and at the outlying tissues function to maintain this normal range? How are these normal conditions disturbed in insulin deficiency?

3. What is the major function of glucose in the cells? Trace its fate from absorption, through the liver, to complete oxidation in the muscle cells. Identify important intermediates.

4. Compare the efficiency of (a) anaerobic oxidation and (b) aerobic oxidation in the production of energy within the cell. What is the source of the energy for muscle contraction? How is the involvement of oxygen brought by the blood related to the production of energy in the cells?

5. Compare the nerve cell with the muscle cell as to nature's provision for the production of energy. How does this explain why early symptoms of hypoglycemia come from the nervous system? What are these early symptoms?

6. What vitamins have been identified as contributing to the metabolism of glucose and fats? In what capacities? Explain why a diet adequate in

thiamine favors good appetite, good muscle tone, and a general sense of well-being.

7. Trace the possible fates of a molecule of fat from its absorption into the lacteals to its complete oxidation and elimination. Where possible show equations for metabolic reactions.

8. What are the sources of storage fat? Under what normal conditions can fat stores be built up? What are their functions in the body?

9. What are the so-called ketones made in the liver? Assemble their structural formulas and show how they are interrelated. What is their normal function? What is ketosis? Its probable origin? How is it brought under control?

10. A normal child hurries out to play without breakfast, plays vigorously for most of the morning, then becomes fatigued and irritable. Rest and food soon restore him to normal. What metabolic adjustments going on in his body could account for this observed behavior?

11. What are the unique functions of protein in the metabolic processes? How does the body use amino acids not required for these specific purposes? What are some of the disadvantages of a protein-deficient body?

12. How does recent knowledge relating to antibodies and their production support the observation that well-nourished individuals, in general, have greater resistance to infection than do malnourished persons? Account for the fact that passive immunity is of short duration and, in general, active immunity is more lasting.

CHAPTER 32

THE BLOOD AND ITS FUNCTIONS

The blood has been referred to as a medium of transportation for various substances throughout the body. It carries oxygen from the lungs to the cells and returns from the cells laden with carbon dioxide. It receives nutrients from the intestinal tract, carries them to organs and tissues, and picks up products of metabolism; some to be distributed to other tissues for use, some destined for elimination. But the blood has functions other than transportation; some are essentially physical in nature, others involve chemical reactions. Before considering the specific functions of blood let us look at its composition.

COMPONENTS OF BLOOD

General composition. The blood makes up about $\frac{1}{12}$ of the weight of the human body. It consists of a fluid portion known as *plasma* and suspended in this plasma are the blood cells: *erythrocytes*, or red blood cells, *leucocytes*, or white blood cells, and *platelets*. The principal components of blood are listed below. Small quantities of other substances also appear more or less regularly.

Components of blood.

A. **Cells**—about 45 per cent of the total volume
   1. Erythrocytes, or red blood cells—4,500,000 to 5,000,000 per 100 cu mm of blood
   2. Leucocytes, or white blood cells—about 6000 per 1 cu mm of blood

3. Platelets, or thrombocytes—about 250,000 per 1 cu mm of blood

B. **Plasma**—about 55 per cent of the total volume
   1. Water—about 91 per cent by volume of the plasma
   2. Substances in colloidal dispersion, hence not subject to diffusion across membranes
      a. Proteins—fibrinogen, albumins, and globulins
      b. Lipids—fats, phospholipids, cholesterol, and cholesterol esters of fatty acids
      c. Certain enzymes and hormones
   3. Substances in true solution, hence subject to diffusion across membranes
      a. Glucose, amino acids, vitamins
      b. Certain hormones
      c. Urea, creatine, creatinine, etc.
      d. Electrolytes—notably sodium, potassium, calcium, magnesium, chloride, bicarbonate, and hydrogen phosphate ions; also molecules of carbonic acid, lactic acid, pyruvic acid, and other weak acids
      e. Gases—oxygen and carbon dioxide

The erythrocytes. Erythrocytes are known as the red blood cells because they harbor the red chromoprotein, hemoglobin. They appear to have no nuclei. They have a very delicate membrane composed of lipids and proteins which encloses the hemoglobin and a variety of enzymes, one of which is *carbonic anhydrase* (p. 431). These cells contain practically the same assortment of electrolytes as are found in the plasma except that potassium ions, rather than sodium ions, and magnesium ions, rather than calcium ions, predominate. Osmotic pressure within the cells is the same as in plasma.

The unique function of the erythrocytes lies in the ability of hemoglobin to carry oxygen and release it to the active cells. They also aid in the transportation of carbon dioxide.

Hemoglobin is a conjugated protein composed of the iron-containing group known as heme and a protein—a globin. The structural relationship is suggested in the accompanying diagram.



In acid medium the protein is denatured and the iron-containing groups are released as hemin (see p. 354), which forms distinctive crystals that are easily identified under the microscope. This provides a laboratory method for identifying blood.

The *iron* within the blood hemoglobin accounts for about 70 per cent of the iron in the body. The rest is found in myoglobin, a related compound in muscle cells, in ferritin stores in liver, spleen, and bone marrow, and contributing to various enzymes concerned with oxidation reactions, notably the catalases, cytochromes, and cytochrome oxidase (p. 468). Experimental studies made with isotopes of iron indicate that very little of this element is excreted. When erythrocytes are destroyed, the iron is conserved and either used for building new cells or stored as ferritin--an iron protein complex. The chief loss of iron from the body is through hemorrhage, either from a slow but continued loss or from more massive hemorrhage. The quota of iron in the diet, as recommended by the Nutritional Research Council, is 12 mg daily for the healthy adult with an increase to 15 mg during pregnancy when the unborn infant is gathering its store of iron.

Absorption of iron. Absorption of iron from the intestinal tract is favored by the acid environment provided by hydrochloric acid. An acid environment results in soluble ferrous salts whereas in alkaline environment insoluble iron compounds are made, hence, excreted in the feces. The ferrous ions enter the intestinal membrane and combine with protein in the cells of the intestinal mucosa, forming a compound known as *ferritin.* In response to demand, ferrous ions are released to the plasma and carried, in combination with plasma protein, to the bone marrow where the red blood cells are made or to the liver and spleen where ferritin is stored. There is considerable interest in the factors which determine the extent of iron absorption. Whipple has shown that the anemic animal absorbs more iron than the normal animal and suggests that this may be in relation to its ferritin stores. Other studies indicate that deficiency in the vitamin pyridoxine limits absorption of iron. Still other studies suggest that a low-protein diet may be a limiting factor.[1]

The problem of anemia, characterized by hemoglobin deficiency, is not entirely a matter of the adequacy of iron supplies. In certain types of anemia, such as those encountered during pregnancy and in pernicious anemia, deficiencies in pteroylglutamic acid ("folic acid") and in vitamin B_{12} are involved, and erythrocytes do not mature properly. The functioning of these vitamins is only partly understood. Copper salts must also be present for building hemoglobin, presumably as part of an enzyme system.

[1] Davis, G. K., and Loosli, J. K.: "Mineral Metabolism (Animal)," *Annual Review of Biochemistry*, Vol. 23. Annual Reviews Inc., Stanford, Calif., pp. 465–66, 1954.

The leucocytes. The leucocytes, or white blood cells, are part of the body's provision for protecting against infection. They are nucleated cells which contain proteins, lipids, enzymes, and other substances characteristic of cells in general. They exhibit ameboid movement which enables them to squeeze between the cells of capillaries--in response to tissue damage—and engulf microorganisms and cell debris. This movement to the injured tissues is believed to be in response to chemical changes in the injured area. The phenomenon is known as *chemotaxis.*

The leucocytes are a varied group. Some of the cells are granular in character and are richly equipped with enzymes which enable the cells to digest ingested material. These cells are believed to originate in the bone marrow. Other cells lacking these granules are known as lymphocytes. These are thought to be made in the lymph nodes; they carry antibodies, presumably gamma globulins.[2]

Platelets. Concerning the origin of the platelets, or thrombocytes, little is known for certain. They function in the control of bleeding by entering into the formation of thrombin. They also release a substance which brings about contraction of blood vessels, thus helping to control hemorrhage.[3]

Blood plasma and its components. Next to water, the most abundant components of plasma are the proteins: fibrinogen, albumins, and globulins.[4]

Fibrinogen. Fibrinogen is unique among the proteins in that it can undergo enzyme-controlled reaction to make the insoluble substance fibrin and thereby bring about the clotting of blood. The removal of fibrin from plasma leaves what is known as blood serum, a fluid which does not clot. Normally blood carries about 0.2 gm to 0.3 gm of fibrinogen per milliliter of plasma. The importance of this protein to the animal is indicated by the speed with which it is replaced following hemorrhage, thus re-establishing the clotting mechanism. The liver cells are responsible for making fibrinogen.

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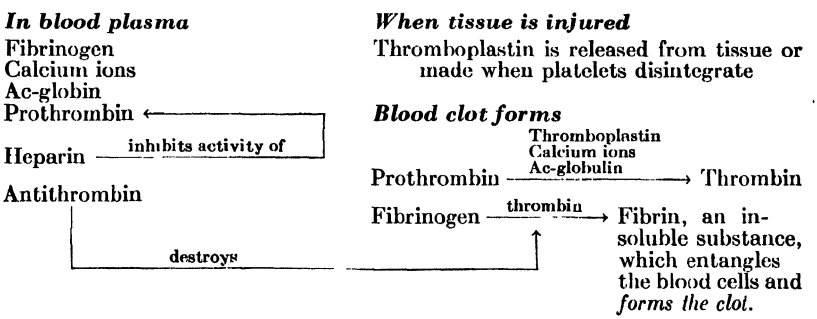
[2] West, Edward S., and Todd, Wilbert R.: *Textbook of Biochemistry*, 2nd ed. The Macmillan Company, New York, 1955, p. 531.

[3] Hawk, Philip B.; Oser, Bernard L.; and Summerson, Wm. H.: *Practical Physiological Chemistry*, 13th ed. The Blakiston Company, Inc., New York, 1954, p. 479.

[4] Actually these terms designate protein groups. About 70 different proteins have been recognized as the components of the plasma protein groups. "Conference on Cellular Elements and Plasma Proteins in Blood," *J.A.M.A.*, 157:80, 1954.

The clotting of blood. Injury to tissue with the escape of blood from the body is a serious threat to the life of the animal. Nature has provided that, in response to tissue injury, blood will coagulate and form a clot, thus checking blood loss. In spite of a great deal of competent study of the problem, many of the details of this process are yet unknown.

It is generally accepted that fibrinogen, calcium ions, and prothrombin, all of which are present in plasma, are essential for the clotting process; also that prothrombin must be activated to make thrombin before coagulation can take place. A fourth essential is thromboplastin, which is found in cells of muscle, lung, brain, and other tissues. This substance must be released at the site of injury or produced in the plasma in response to the disintegration of platelets. The two main steps in the process are: (1) activation of prothrombin to make thrombin and (2) the reaction of fibrinogen to make fibrin, with thrombin serving as the enzyme catalyst. These processes are further accelerated by the presence in plasma of minute amounts of a protein known as Ac-globin. This compound is activated by a small amount of thrombin, and it, in turn, hastens the prothrombin to thrombin reaction.



In blood, at all times, there are small quantities of certain substances which function to check the formation of clots. One of these is a heparin-protein complex which inhibits the activity of prothrombin. Antithrombin, a component of serum albumin, inactivates the enzyme thrombin shortly after it is made. Deficiency in vitamin K also interferes with the clotting of blood, because this substance is essential for making prothrombin in the liver. Exactly how vitamin K functions in this synthesis is not known.

Because calcium ions are essential for the clotting process, they are usually removed from the blood that is to be administered by indirect transfusion, a treatment in which it is important that the blood should not be capable of clotting. This removal is accomplished by mixing sodium citrate with the blood taken from the donor; the calcium is thereby precipitated in relatively insoluble calcium citrate.

$$3\ Ca^{++} + 2\ Na_3C_6H_5O_7 \longrightarrow \downarrow Ca_3(C_6H_5O_7)_2 + 6\ Na^+$$

Albumins and globulins. Albumins and globulins are found in both plasma and cells. In the plasma the albumins normally predominate over the globulins; in the cells globulins are more abundant. A shift in the relation of these two proteins in the plasma sometimes occurs in disease and is of diagnostic value to the physician.

The albumins are more homogeneous than the globulins. They are also of lower molecular weight and therefore more easily dispersed in solution. The *globulins* are variable in composition and have been separated into subgroups known as alpha (α), beta (β), and gamma (γ) globulins, respectively. The *gamma globulins* have attracted special attention because this group can carry antibodies which protect against certain diseases, notably measles, mumps, influenza, scarlet fever, typhoid, and poliomyelitis. Albumins appear to be made in the liver. There is less certainty as to where globulins are produced.

The plasma proteins have an important control over the fluid balance between the blood and the interstitial fluids. Because of their colloidal character, these proteins do not normally diffuse through membranes whereas the soluble components—glucose and electrolytes—do diffuse and equalize their pressure on either side of the membrane. The protein content of the interstitial fluids is lower than in the capillaries. This difference in concentration on either side of the semipermeable membrane creates a difference in pressure which favors the flow of water from the interstitial spaces into the capillaries. At the arterial end of the capillary, the pressure of the heart transmitted along the arteries gives a blood pressure which exceeds the *colloidal* or *oncotic* pressure.[5] This favors the passage of water from the capillaries to the surrounding fluid. At the venous end of the capillaries the blood pressure is less than the colloidal pressure, and this favors the return of water to the capillaries.

[5] The term *oncotic* pressure is sometimes used with relation to colloidal pressure to distinguish it from osmotic pressure which is attributed to electrolytes and other substances in true solution.

Usually these opposing forces are so balanced that fluid does not accumulate in the interstitial spaces. But, if the protein level of plasma is lowered, as sometimes occurs in chronic malnutrition when capillary membranes become permeable to albumin, as in severe burns, or at the kidneys with persistent loss of albumin, this balance is disturbed and water collects in the tissues, giving rise to edema. Because of the relative abundance of the *albumins* and because of their relatively low molecular weight (sometimes approximating that of particles in true solution), most of the colloidal pressure effect is related to these proteins.

Other functions of plasma proteins. The nutritive value of the plasma proteins has been well demonstrated. When injected into the blood of a fasting individual, they are used by body cells to meet the demands for protein. It is believed that they constitute a labile source of protein from which cells can draw to meet their needs.

The plasma proteins also contribute to the buffer action of the blood. Although less active than the electrolytes, their abundance gives them considerable effect. This function is shared with electrolytes and will be considered later (p. 506).

Nonprotein nitrogen compounds. Various nitrogen compounds other than protein are found in the plasma. These include amino acids, urea, creatine, creatinine, uric acid, and other substances of protein origin. The concentration of these substances in blood provides pertinent information as to metabolic reactions within cells. This is what is measured when a nonprotein nitrogen (NPN) test is made.

ELECTROLYTES AND THEIR FUNCTIONS

The electrolytes which circulate in the blood (with the exception of the proteins, which function as weak acids, and protein salts) form true solutions in water. Consequently they can pass through capillary and cell membranes and enter the interstitial fluids and the cells. Their relative distribution, under normal conditions, is represented diagrammatically in the accompanying chart (Fig. 92).

One striking difference in the electrolyte pattern lies in the high proportion of sodium ions in the circulating fluids and the high proportion of potassium ions in the cells. Although these two ions are closely related chemically, and in many situations are interchangeable in function, physiologically each has some unique functions for which the other cannot substitute.

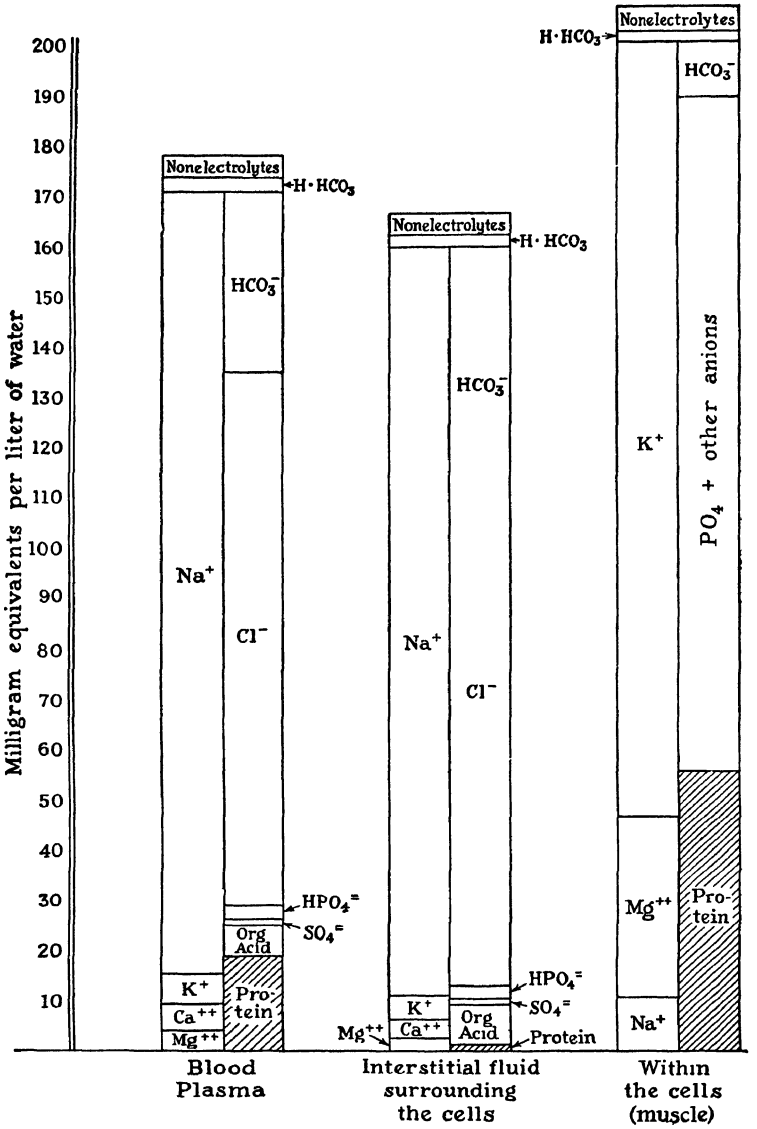


Fig. 92. Chart illustrating relative concentration of electrolytes in blood plasma, interstitial fluid, and within muscle cells. (Modified, by permission of the publishers, from James Lawder Gamble, *Chemical Anatomy, Physiology and Pathology of Extracellular Fluid: A Lecture Syllabus*. Cambridge, Mass.: Harvard University Press, Copyright, 1942, 1947, 1954, by The President and Fellows of Harvard College.)

Specific functions of certain ions. *Osmotic pressure.* The total electrolyte concentration in blood plasma, interstitial fluids, and cells provides for osmotic pressure relations between these communicating fluids. However, the *sodium ions* appear to have a unique function in this relation. It has been observed experimentally that ingestion of large quantities of sodium chloride, without compensating quantities of water, results in increased accumulation of sodium ions and water in the interstitial spaces, thus causing edema. Conversely, restriction of sodium in the food, as in the low-sodium diets, is followed by excretion of water, and this water will be withdrawn from the interstitial spaces. *Potassium ions* function in the cells to maintain normal osmotic pressure and, for this function, neither sodium ions from the plasma nor potassium ions from the cells are interchangeable—save to a very limited degree.

Response of muscle and nerve cells. The response to stimulation of muscle and nerve cells is influenced by the relative concentrations of sodium, potassium, calcium, and magnesium ions and also by the hydrogen ion–hydroxyl ion relationship. In general, the relation may be expressed as follows:

$$\frac{[Na^+] + [K^+] + [OH^-]}{[Ca^{++}] + [Mg^{++}] + [H^+]} \cdot \frac{\text{Increased irritability of tissues}}{\text{Decreased irritability of tissues}}$$

Evidence of this effect is seen in the condition known as tetany which is associated with low calcium concentrations in the blood. This condition is characterized by increased excitability and muscle twitching. Increased irritability of nerve and muscle cells is also experienced in extreme alkalosis, characterized by increased concentration of hydroxyl ions. It is noteworthy that magnesium ions have been used intravenously to produce anesthesia. A deficit of potassium ions in the plasma is claimed to be associated with weakness and sometimes paralysis in skeletal, cardiac, and smooth muscle.[6] However, the picture is not always as simple as appears here. Frequently the concentration relationship between these ions is of more significance than the concentration of any one particular ion. Thus, the relative concentration of calcium and potassium ions is regarded as important in controlling the response of the heart muscle.[7]

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[6] Martin, Helen E., and others: "Etiology and Treatment of Serum Potassium Defects," *J.A.M.A.*, 147:25, 1951.

[7] Mason, M. F.; Harrison, T. R.; and Thorn, G. T.: "Changes in Electrolyte Composition," *Internal Medicine.* The Blakiston Company, New York, 1954, p. 401.

The level of potassium ions in serum is maintained in a relatively constant low level by continual excretion at the kidneys. These ions enter the body with the foods. Since they are components of cells, they are abundant in fruits and fruit juices escaping from ruptured cells and also in meats and meat broths. If not needed by the body cells, they are not allowed to accumulate in the plasma. It is also significant that when new cells are being made, there is a continual demand for potassium ions and they are withdrawn from the blood for this use; they are returned to the extracellular fluids when cells are destroyed. Potassium ions enter the cells, along with phosphates, when glucose is being used to make glycogen. This demand sometimes becomes a matter of concern in the treatment of diabetic acidosis, because when insulin is supplied there is a prompt re-establishment of glucose metabolism in the cells. To offset the possibility that there could be a sudden depletion of potassium ions, with resulting paralysis of muscles, these ions may be provided intravenously. Or if fluid can be taken by mouth, as orange juice and broth, the needed ions are usually supplied in this way.

Calcium ions in relation to bone cells. About 90 per cent of the calcium in the body is located in the bone cells, and the calcium level of blood plasma is relatively low (see chart, p. 500). Nevertheless, calcium ions have important functions in the body; hence, a continuous supply is required for use in the cells. As has been mentioned previously, they are essential for clotting of blood, and they play an indispensable part in the control of muscle and nerve cell response. They also influence permeability of cell membranes; they function in certain enzyme systems; and their contribution to the building of the insoluble structure of bones and teeth, during periods of growth or repair of these tissues, has long been established. The importance of the continuous interchange of calcium ions between the bone cells and the plasma has been recognized more recently. This is a self-regulating mechanism whereby the calcium level of blood is maintained within the normal range.

Study of the crystalline structure of bone indicates a relatively insoluble calcium complex that can be represented by the formula $3\ Ca_3(PO_4)_2 \cdot Ca(OH)_2$. But between these crystals there appears to be a somewhat more labile deposit of calcium ions, and sometimes magnesium ions, associated with carbonate and citrate ions. This more soluble portion makes up only a small part of the bone structure. Recent studies suggest that exchange of calcium (and magne-

sium) ions between this portion of bone and the blood is rapid and a major factor in maintaining the normal calcium-ion level of blood. But, when the calcium level becomes abnormally low, the parathyroid hormone is stimulated and the calcium level of plasma is restored at the expense of dissolution of the more stable crystalline structure of bone.[8] The greater part of the calcium carried in the blood is not diffusible, being in combination with protein.

Although during the period of active development of bone the concentration of both *calcium ions* and *phosphate ions* may be comparatively high in the plasma, in general a reciprocal relation exists between these ions; as the calcium level is increased, the phosphate level decreases and vice versa. Vitamin D plays an active part in mobilizing these ions for deposit in bones and teeth. It favors absorption of calcium ions from the intestinal tract and the reabsorption of phosphate ions at the kidney.

Nutritionally, an adequate supply of calcium in the food is essential for building cells and the healthy development of bones and teeth. The carelessly selected diet frequently does not meet this demand. The best sources of calcium are milk and milk products and the green-leafed vegetables. The recommended daily quota, based on scientific studies, is for 1 gm of calcium per day for the normal adult with an increase to 1.5 gm during pregnancy and up to 2.0 gm during the period of lactation. The needs of children vary with age but, in general, are understandably higher than those for adults.[9]

Anions in the blood. *Chloride* ions are the most abundant of the negatively charged ions. They are associated with sodium ions in the maintenance of osmotic pressure relations across membranes (p. 501). They are interchangeable to some extent with the *bicarbonate* ions, and function in this relation at the red blood cells (p. 510) and at the kidneys (p. 515) in regulating the hydrogen-ion concentration of blood. They are withdrawn from the blood for the manufacture of hydrochloric acid in the stomach but reabsorbed along the intestine.

Phosphates occur in blood both in organic compounds and as the mono and dihydrogen phosphate ions. These ions participate in buffer reactions in blood plasma and cells (p. 506).

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[8] McLean, Franklin G.: "Bone," *Scientific American*, 192:84–91, 1955.

[9] Experimental studies relating to calcium and phosphorus needs and values at all ages are to be found in Sherman, H. C., *Chemistry of Food and Nutrition*, 8th ed. The Macmillan Company, New York, 1952, Chap. 14.

Iodides enter the blood from the food, or from iodide medications. They are either promptly absorbed by the thyroid gland for the production of thyroxine or eliminated at the kidney. The rate of uptake of iodine from the blood and the extent of excretion at the kidneys are both important when radioactive iodine is used for study of thyroid activity or for treatment of thyroid disease (p. 139). Protein-bound iodine is also found in blood, and the concentration of this component is regarded as indicative of the activity of the thyroid gland.

THE ELECTROLYTE BALANCE IN BLOOD AND EXTRACELLULAR FLUIDS

A remarkable balance is maintained at all times within the healthy body between the various electrolytes in the circulating blood, the extracellular fluids, and the functioning cells. This is strikingly illustrated in the relative constancy of the hydrogen ion–hydroxyl ion concentration relationship in the blood, which is maintained within a very narrow range in spite of frequent absorption into the blood of variable quantities of acids and salts from the intestine, the entrance of strong and weak acids from the cells, and the continuous presence of certain salts which react with water to provide alkaline solutions (p. 249). Many interrelated factors contribute to the constancy of electrolyte concentrations, notably, (1) buffer reactions in cells and extracellular fluids, (2) the oxygen–carbon dioxide exchange at the tissue cells and the lungs, and (3) the controlled elimination of ions at the kidneys.

Hydrogen-ion concentration of blood. The normal hydrogen ion–hydroxyl ion relationship in blood is between *p*H 7.33 and *p*H 7.51, slightly on the basic side of neutral. Even in disease, the variations in the living animal are only between *p*H 7.0 in extreme acidosis and *p*H 7.8 in alkalosis. In active tissue cells somewhat greater variations have been reported than in the circulating fluids—from the reaction in blood to about *p*H 5.6.[10]

Buffers and their functioning. The blood, lymph, interstitial fluids, and the cells throughout the body are all provided with efficient buffer systems—weak acids and the accompanying sodium or

[10] Rous, Peyton: "The Relative Reaction of Living Mammalian Tissues," *Science*, 60:363, 1924.

Some of the sources of acids and bases, hence of hydrogen ions and hydroxyl ions, in the blood and lymph

	In blood and lymph		*From cells*	
From food mass of the average diet and *absorbed from the intestine*, such acids as:		Carbonic acid (weak but in large quantities) ←	Carbon dioxide + Water	From the metabolism of carbohydrates, fats, and proteins
		Lactic acid ←		
→ Acetic acid	All weak	Phosphoric acid (weak) ←		From metabolism of proteins
→ Lactic acid				
→ Citric acid				
→ Fatty acids		Sulfuric acid (strong but in small quantities) ←		
From fruits and other foods, salts such as:				
Potassium tartrate + Water →	Tartaric acid (weak) + Potassium hydroxide (strong)			
Potassium citrate + Water →	Citric acid (weak) + Potassium hydroxide (strong)			
Sodium bicarbonate + Water →	Carbonic acid (weak) + Sodium hydroxide (strong)			
	Hydrochloric acid (strong but in small quantities)			

potassium salts (p. 505)—which prevent excessive accumulation of either hydrogen or hydroxyl ions. In general the same buffer substances prevail throughout with sodium salts predominating in the extracellular fluids and the potassium salts in the cells.

The buffer systems of the blood include the carbonic acid–bicarbonate system, the phosphate system composed of both the dihydrogen phosphate and monohydrogen phosphate salts, and the proteins—with the protein functioning as a weak acid in the presence of sodium or potassium proteinate salts. In the red blood cells, both oxyhemoglobin and reduced hemoglobin function as acids in a protein buffer capacity.

Buffer pairs in blood plasma	
Carbonic acid	H_2CO_3
Sodium bicarbonate	$Na^+HCO_3^-$
Sodium dihydrogen phosphate*	$Na^+H_2PO_4^-$
Sodium monohydrogen phosphate	$Na_2^+HPO_4^{--}$
Hydrogen proteinate	
Sodium proteinate	

Buffers in red blood cells	
Carbonic acid	H_2CO_3
Potassium bicarbonate	$K^+HCO_3^-$
Potassium dihydrogen phosphate	$K^+H_2PO_4^-$
Potassium monohydrogen phosphate	$K_2^+HPO_4^{--}$
Oxyhemoglobin and its Potassium salt	$HHbO_2$† / $K^+HbO_2^-$
Hemoglobin and its Potassium salt	HHb / K^+Hb^-

* **Note.** In the phosphate buffer system, the dihydrogen phosphate ion functions as an acid, one of the hydrogen atoms being readily ionizable under conditions existing in the body.

† Hb is the customary abbreviation for hemoglobin: HHb represents hemoglobin as an acid; K^+Hb^- represents the potassium salt of hemoglobin.

The following equations represent reactions through which these buffer systems function to prevent undue increase in concentration of either hydrogen ions or hydroxyl ions.

In the blood plasma: (Similar reactions occur with potassium salts in the cells.)

Carbonate buffers

$$Na^+HCO_3^- + H^+ \longrightarrow H_2CO_3 + Na^+$$
$$H_2CO_3 + OH^- + Na^+ \longrightarrow Na^+HCO_3^- + H_2O$$

Phosphate buffers

$$Na_2^+HPO_4^{--} + H^+ \longrightarrow Na^+H_2PO_4^- + Na^+$$
$$Na^+H_2PO_4^- + OH^- + Na^+ \longrightarrow Na_2^+HPO_4^{--} + H_2O$$

Protein buffers

$$\text{Sodium proteinate} + H^+ \longrightarrow \text{Hydrogen proteinate} + Na^+$$

$$\text{Hydrogen proteinate} + OH^- + Na^+ \longrightarrow \text{Sodium proteinate} + H_2O$$

The *carbonate* buffers are most abundant in the plasma. To buffer effectively at *p*H 7.4 the relative concentrations of carbonic acid to bicarbonate salt must be in a ratio of about 1 to 20, that is:

$$H_2CO_3 : Na^+HCO_3^- \text{ as } 1:20$$

The effectiveness of this buffer system is maintained, therefore, by the continuous decomposition of carbonic acid at the lungs with the escape of carbon dioxide. The phosphate system is never in high concentration in plasma, being maintained at this low level through the elimination of phosphate salts at the kidney. The plasma proteins are important largely because of their abundance. In the red blood cells the hemoglobin buffer systems are very efficient in controlling the hydrogen-ion concentration.

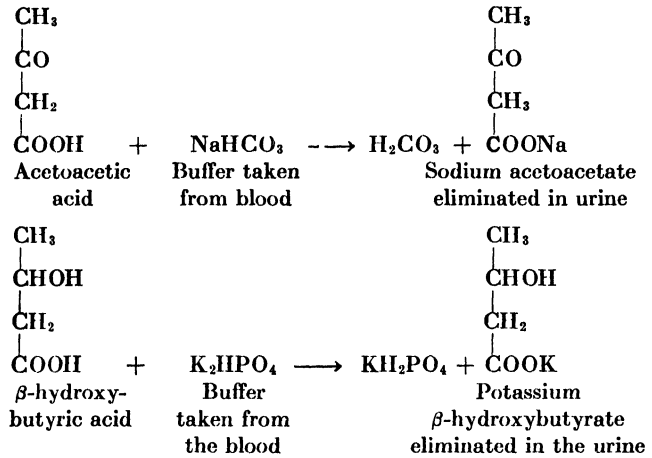
Throughout the body these reactions are in continuous operation. Hydrogen ions entering with the food or as products of metabolic reactions, and hydroxyl ions derived from the hydrolysis of salts or provided by medications are handled, for the most part, very effectively.

Disturbances of acid-base relationships. Marked variation from the normal hydrogen-ion concentration of blood indicates serious disturbance in the acid-base equilibrium. Regardless of their origin, such disturbances soon become systemic in extent.

Acidosis. When the hydrogen-ion concentration of blood increases beyond the normal range the condition is known as *acidosis.* This condition may develop as the result of a respiratory disturbance which prevents the normal escape of carbon dioxide at the lungs. It sometimes results from a serious loss of sodium and potassium salts, as in the severe diarrhea of children, with consequent depletion of the salts of the buffer systems. But, a more frequent cause is metabolic disturbances with excessive production of the "ketones," *acetoacetic acid* (diacetic acid) and *β-hydroxy butyric acid,* as in acute starvation or in diabetic acidosis.

The necessity for transportation of large quantities of acids in the blood makes excessive demands upon the salts of the buffer systems, notably the bicarbonate salts, as the hydrogen-ion concentration is decreased by reactions such as the following:

Removal of acid-controlling buffers during acidosis



The salts thus made are carried to the kidneys where they are excreted, with the result that the concentration of sodium ions of the plasma and interstitial fluids may drop below normal levels, and the accompanying elimination of water may result in severe dehydration. In acidosis, the respirations change in character to favor the elimination of more carbon dioxide, thus relieving the blood of carbonic acid. Return to normal breathing is evidence that the acid-base disturbance is being successfully adjusted.

The term *alkali reserve* is frequently used in discussion of acidosis. This refers to the sodium and potassium salts available, at the time, for buffer action in the blood plasma. Measurement of the sodium bicarbonate concentration in a sample of blood provides a means for judging the extent to which these buffer salts have been depleted through reaction with acids and excretion of sodium (and potassium) salts at the kidneys.

Alkalosis. Decrease in hydrogen-ion concentration below the normal range means a corresponding increase in hydroxyl-ion concentration; this is known as *alkalosis.* Such a condition is most frequently the result of the excessive ingestion of base-forming salts, such as sodium bicarbonate. Or, in adults, it can be produced by excessive vomiting and the consequent loss of hydrochloric acid in the gastric secretion. It may also be induced by a respiratory disturbance which operates to cause an excessive loss of carbon dioxide at the lungs. The condition of *alkalosis* makes excessive demands on the weak acids of the buffer systems but is usually compensated for

by (1) increased elimination of sodium bicarbonate at the kidneys and (2) a change in respiration which favors retention of carbon dioxide in the blood.

The exchange of oxygen and carbon dioxide, and the associated functioning of electrolytes. The exchange of oxygen and carbon dioxide at the active cells and at the lungs is of vital importance to the animal. The hemoglobin within the red blood cells is chiefly responsible for the transportation of oxygen, but the electrolytes function in reactions *at the tissue cells* to provide for (1) the decomposition of oxyhemoglobin with the release of oxygen, and (2) the transportation of carbon dioxide in the blood. *At the lungs*, these reactions are reversed to provide for (1) release of carbon dioxide from combination, and (2) the capture of oxygen by hemoglobin for transportation to the cells.

At the cells. *What happens to carbon dioxide.* As oxygen is used for metabolic reactions within cells, carbon dioxide is made continuously. This results in a higher concentration of carbon dioxide in the cells than in the surrounding interstitial fluid and the blood, and, consequently, a continuous diffusion of carbon dioxide from the tissue cells to the surrounding fluid and across the capillary walls into the blood. (See Fig. 93 on p. 510.)

In the plasma. Some of the carbon dioxide remains in solution in the plasma. Here it engages in a slow reaction with water to make carbonic acid which, in turn, reacts with the salts of the protein and hydrogen phosphate buffer systems and forms sodium bicarbonate.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
$$H_2CO_3 + Na^+ \text{ Proteinate}^- \longrightarrow H \text{ Proteinate} + Na^+HCO_3^-$$
$$H_2CO_3 + 2\ Na^+ + HPO_4^{--} \longrightarrow Na^+H_2PO_4^- + Na^+HCO_3^-$$

In the red blood cells. But the greater part of the carbon dioxide leaves the plasma and enters the red blood cells. Here it encounters oxyhemoglobin and reacts with it to form carbamino hemoglobin,[11] at the same time releasing oxygen for use in the active cells.

$$CO_2 + HHbO_2 \longrightarrow \underset{\text{Carbamino hemoglobin}}{HHbCO_2} + O_2$$

[11] The combination of carbon dioxide with hemoglobin is believed to take place at the amino group of the hemoglobin molecule; hence, it is frequently represented as follows:

$$HHbNH_2 + CO_2 \longrightarrow HHbNHCOOH$$

This accounts for about 20 per cent of the carbon dioxide carried in the red blood cells. The rest reacts with water to make carbonic acid, a reaction which is rapid because of the presence of a favoring enzyme called *carbonic anhydrase.* Within these cells the carbonic acid is buffered very effectively through reaction with the salts of both the protein (hemoglobin) and the hydrogen phosphate buffers.

$$CO_2 + H_2O \xrightarrow{\text{carbonic anhydrase}} H_2CO_3$$
$$H_2CO_3 + K^+Hb^- \longrightarrow HHb + K^+HCO_3^-$$

Through these reactions in plasma and within red blood cells the blood is able to dispose of large quantities of carbon dioxide, made by reactions in cells throughout the body, without causing a marked increase in the hydrogen-ion concentration.

The chloride shift. As the concentration of bicarbonate ions increases within the red blood cells, there is a movement of these ions out of the cells into the plasma. This is compensated for by a shift of chloride ions from plasma into the red blood cells (Fig. 93). This shift maintains the balance of positive and negative ions in plasma and cells.

Conditions favoring release of oxygen from oxyhemoglobin. In spite of the buffer reactions, the entrance of carbon dioxide into the red

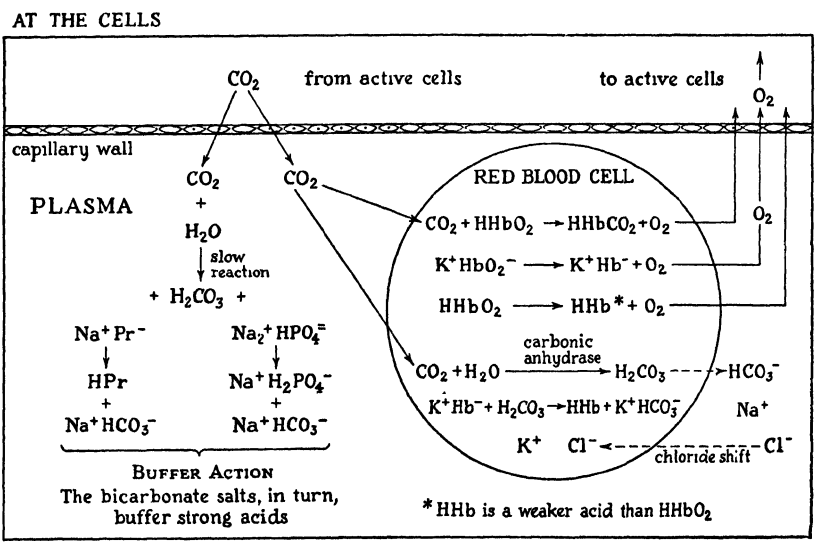


Fig. 93. The oxygen–carbon dioxide exchange at the cells.

blood cells increases the hydrogen-ion concentration over that of arterial blood. Moreover the shift of chloride ions from plasma to blood cells increases the hydrogen-ion concentration in this area. These conditions favor the decomposition of oxyhemoglobin and the release of oxygen to the active tissue cells because oxyhemoglobin becomes more unstable as the acidity of the medium increases.

$$HHbO_2 \longrightarrow HHb + O_2$$

Reduced hemoglobin is a weaker acid than oxyhemoglobin; hence, hydrogen ions will be taken up during this reaction to form molecules of this weak acid.

It is estimated that, as the blood passes through the active tissues, from one-quarter to one-third of the oxyhemoglobin is reduced and thus becomes available at the lungs for remaking oxyhemoglobin.

At the lungs. The concentration of *carbon dioxide* in the blood which reaches the lungs is greater than that in the air entering the alveoli; consequently, there is an unceasing escape of carbon dioxide from the blood to the outside air. At the same time, the concentration of oxygen entering the lungs is greater than that within the blood stream; accordingly, there is a continuous passing of *oxygen* from the air into the blood. Here it meets hemoglobin returned from the active cells and combines with it to make oxyhemoglobin (Fig. 94).

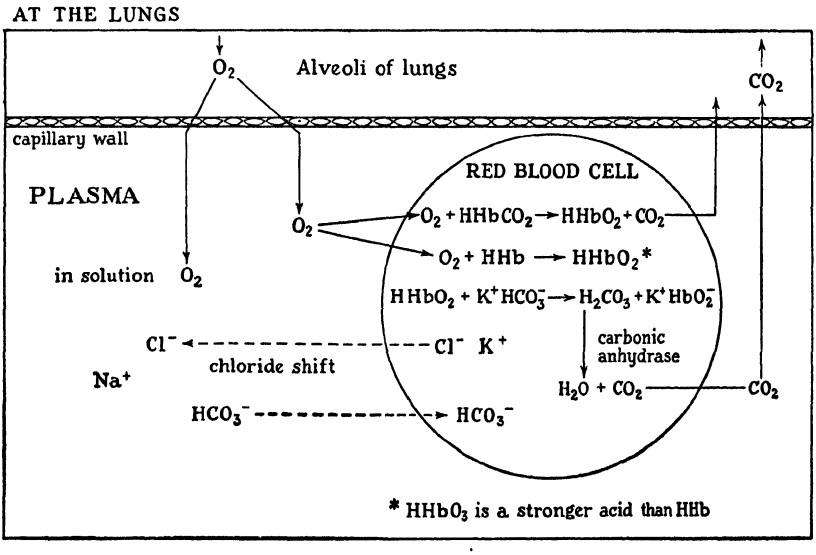


Fig. 94. The oxygen–carbon dioxide exchange at the lungs.

Oxyhemoglobin is a stronger acid than hemoglobin; this condition favors its reaction with potassium bicarbonate in the red blood cells to make more carbonic acid. Then, because of the escape of carbon dioxide, more carbonic acid decomposes to make carbon dioxide and water. Moreover, the enzyme *carbonic anhydrase*, within the red blood cells, now catalyzes the reaction in the reverse direction from that at the tissue cells.

$$HHbO_2 + KHCO_3 \rightleftharpoons KHbO_2 + H_2CO_3$$

$$H_2CO_3 \xrightarrow{\text{Carbonic anhydrase (catalyst)}} H_2O + CO_2 \xrightarrow{\text{removed at lungs}}$$

The entrance of oxygen also favors reaction with carbamino hemoglobin to release carbon dioxide and form more oxyhemoglobin.

$$O_2 + HHbCO_2 \longrightarrow HHb + CO_2 \longrightarrow \text{Escapes into the air}$$

The chloride shift. As the carbonic acid *within the red blood cells* decomposes and carbon dioxide is removed from the system, bicarbonate ions from the plasma are drawn into the blood cells to make more carbonic acid. At the same time chloride ions migrate from the red blood cells to the blood plasma (Fig. 94), thus maintaining the electrolyte balance in the fluid surrounding the cells. A slightly lower hydrogen-ion concentration is produced within the blood cells, as a result of removal of chloride ions, and this is favorable to the combination of oxygen with hemoglobin to make oxyhemoglobin.

The speed of the reactions at the lungs is such that, under normal conditions, the blood leaving the lungs carries about 96 per cent of the hemoglobin as oxyhemoglobin.

Some substances interfere with oxygen transportation. Certain substances act as poisons by interfering with the transportation of oxygen to the cells. One of these is *carbon monoxide* which combines with oxygen to make carbon monoxide hemoglobin (also known as carboxyhemoglobin). This combination prevents hemoglobin from combining with oxygen.

$$CO + HHb \longrightarrow HHbCO$$

This compound is very stable, and the combination is not easily reversed. However, a high concentration of oxygen favors release of carbon dioxide and it can then escape at the lungs.

$$\text{Oxygen in high concentration} \quad O_2 + HbCO \longrightarrow HbO_2 + CO \uparrow \quad \text{Carbon monoxide is exhaled at the lungs}$$

Certain substances combine with hemoglobin to form *methemoglobin.* This is a compound in which the ferrous iron of hemoglobin has been oxidized to make ferric iron. Methemoglobin cannot carry oxygen. Among the compounds capable of this reaction are: chlorates, nitrites, benzene, aniline, and a number of aniline derivatives including the sulfanilamide drugs.

THE FUNCTION OF THE KIDNEYS

The function of the kidneys is to maintain the components of blood in concentrations consistent with normal physiological activities through controlled elimination of water and soluble substances carried in the blood. This involves elimination of certain substances, notably various end products of protein metabolism; selective elimination of electrolytes with retention of those needed to control normal osmotic conditions at membranes and a relatively constant hydrogen-ion concentration in blood, lymph, and interstitial fluids.

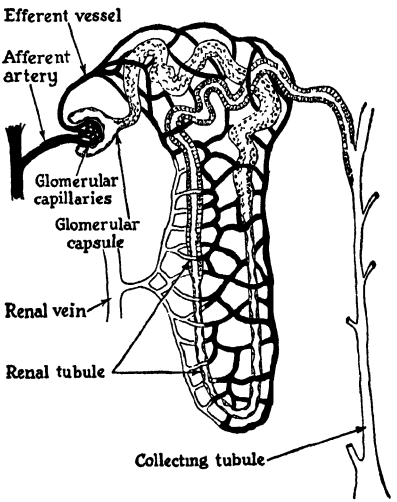


Fig. 95. Diagram of kidney unit. The *glomerular capsule*—where water, salts, urea, and other components of the blood plasma enter by filtration from glomerular capillaries. The *renal tubule*—where changes in the relative concentrations of various salts take place as the reabsorption of components that are needed by the blood occurs. The *collecting tubule*—through which urine finds exit from the kidney unit.

How the kidney functions. As the blood passes through the kidneys, the pressure within the glomerular capsule (Fig. 95) is such that water passes through carrying with it soluble components of plasma, including glucose and electrolytes. The colloidal material—including the lipids and protein—remains in the blood. The filtrate enters the uriniferous tubules and here there are cells which function in the reabsorption of the greater part of the water, also practically all of the amino acids, glucose, ascorbic acid, and electrolytes—in such concentrations as to restore normal physiological relations.

Controlling conditions. The process of reabsorption cannot be explained on the basis of concentration relationships alone. For

example, all of the glucose is absorbed unless it exceeds the "threshold" level for the individual, which for most people is about 140 to 160 mg per 100 ml of blood. Energy for this absorption is believed to be supplied through reactions with adenosinetriphosphate.

The absorption of water and of electrolytes is controlled by certain hormones. When electrolyte concentration is high, whether due to loss of fluids or to excessive intake of salts, if water is not supplied, the posterior pituitary hormone increases its secretion of the antidiuretic hormone. This favors reabsorption of more water and excretion of a scanty, concentrated urine. When electrolyte concentration in plasma is low, more water is allowed to escape at the tubules. The adrenal cortex secretes a hormone, or hormones (desoxycorticosterone), which functions in the reabsorption of salts and regulates the balance of sodium and potassium ions in blood and interstitial fluids. These are some of the means whereby the osmotic conditions are controlled.

To maintain normal hydrogen-ion concentration. The concentrations of the various ions to be reabsorbed into the blood, or excreted in the urine, are adjusted by the kidney cells to maintain the hydrogen-ion concentration of blood within a normal range.

The chief mechanism. One means whereby this adjustment is effected is through reversible reactions involving the buffer salts. Both disodium hydrogen phosphate (Na_2HPO_4) and sodium dihydrogen phosphate (NaH_2PO_4) are brought to the kidneys in the blood and both are excreted in the urine.[12] But whereas *in the blood* the disodium hydrogen phosphate predominates, *in the urine*—under normal conditions of metabolism and on an ordinary mixed diet—the concentration relationship is reversed and sodium dihydrogen phosphate predominates. Consequently, *whereas the reaction of the blood is maintained slightly on the basic side, that of urine is usually more acid than the blood from which it is secreted.*[13]

In the blood brought to the kidneys (about *p*H 7.4)	In the urine as excreted (commonly about *p*H 6.0)
$Na_2HPO_4 : NaH_2PO_4 :: 4 : 1$	$Na_2HPO_4 : NaH_2PO_4 :: 1 : 9$

[12] Although both sodium and potassium salts are present in the blood, the sodium salts are greatly in predominance; hence, to avoid confusion, the discussion is, in the main, in terms of the sodium salts

[13] Disodium hydrogen phosphate on hydrolysis results in a solution which is basic in reaction, whereas sodium dihydrogen phosphate results in a solution which is acid in reaction.

This difference in the *normal* relative concentrations between these buffer salts in the blood and urine is brought about by reactions and accompanying reabsorptions at the cells of the renal tubules, as represented in the following.

$$Na_2HPO_4 + H_2CO_3 \rightleftharpoons NaH_2PO_4 + NaHCO_3$$

Brought to the kidney cells by the blood	A more acid salt, which is excreted by the kidneys	Reabsorbed by the blood, thereby maintaining a relatively high concentration of this base-producing buffer in the blood[14]

When greater than normal demands are made on the acid-controlling buffers, whether through the entrance of large quantities of certain acids in foods or as metabolic products (p. 505), nature favors the conservation of those ions which buffer acids. Thus, more dihydrogen phosphate ions and chloride ions are allowed to escape in the urine while the monohydrogen phosphate ions and hydrogen carbonate ions are retained. This results in a more acid urine.

On the other hand, when the hydrogen-ion concentration of blood falls to lower levels—as may occur when hydrochloric acid is being secreted in the stomach, or with the intake of food or medication which provides large amounts of potassium or sodium salts of weak acids—more of the monohydrogen phosphate ions and hydrogen carbonate ions escape in the urine while dihydrogen phosphate ions and chloride ions are retained. A less acid urine results.

Another control mechanism. Another regulatory mechanism which operates at the kidneys is the formation of ammonia accompanied by the elimination of ammonium ions and conservation of sodium and potassium ions.

Base-making salts returned to blood

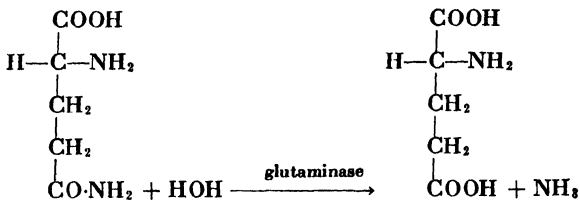
Made in kidneys — Brought by blood

$$\begin{array}{l} 2\,NH_3 + 2\,H_2CO_3 + Na_2SO_4 \longrightarrow (NH_4)_2SO_4 \mid + 2\,NaHCO_3 \\ NH_3 + H_2CO_3 + NaCl \longrightarrow NH_4Cl \mid + NaHCO_3 \end{array}$$

Excreted in urine

[14] The enzyme *carbonic anhydrase* is found in the cells of the renal tubules and probably is involved in the reactions favoring reabsorption of sodium bicarbonate in this location.

The ammonia, which appears in the kidney cells in response to increased demands for eliminating acids, is believed to be made by hydrolysis of *glutamine*, a product of protein metabolism. The kidney cells carry the enzyme *glutaminase* which is believed to catalyze this reaction (p. 487).



Glutamine + Water ⟶ Glutamic acid + Ammonia

But, when the concentration of sodium and potassium salts in the blood is in excess of body needs, the production of ammonia is halted and sodium and potassium salts, even sodium bicarbonate, appear in the urine in greater quantities.

By means of these varied mechanisms the reaction of urine, although most commonly about *p*H 6, varies considerably from time to time. The reported limits are about *p*H 4.6 to *p*H 8.2.

Elimination of salts and excretion of water. Elimination of salts, and other soluble materials, demands an accompanying excretion of water. This is illustrated in the diuretic effect of excessive use of sodium chloride as a condiment. The thirst which accompanies a large intake of salt is a physiological demand on the part of the cells for more water so that the excess of salt may be eliminated from the blood and extracellular fluids. Similarly an excess of water without accompanying salt will have a diuretic effect, with the excretion of urine in which the salts may be unusually low.

The normal kidney does a truly remarkable piece of work in adjusting fluid and electrolyte balance. It should be evident that, especially in illness, unusual fluctuations in the quantities of urine excreted from day to day is of very real significance.

The usual components of urine. About 1 to 1½ liters of urine are usually excreted daily. From 90 to 95 per cent of this fluid is water. Other components can be expected to vary somewhat in quantity according to intake and metabolic activities. The following are among the substances normally expected to be present:

1. *Products of protein metabolism:* Urea, ammonia, creatinine and traces of creatine, uric acid, amino acids.

2. *Electrolytes:*

Inorganic salts

Sodium, Potassium, Ammonium } with { chloride, dihydrogen phosphate, monohydrogen phosphate, sulfate } in predominance
{ hydrogen carbonate (in urine of more basic reaction)

Calcium, Magnesium, Iron } salts in traces, being eliminated chiefly in the feces

Organic salts { urates (always present); oxalates, citrates, lactates } in larger amounts when the urine is more basic

Weak acids, such as citric acid, oxalic acid, lactic acid

3. *Others:* Ascorbic acid, thiamine, organic sulfates, indican, glucose (sometimes in traces), ketones (sometimes in traces).

QUESTIONS

1. What cells are found in blood? Briefly summarize the principal functions of each.
2. What varieties of protein are associated with blood? Briefly state the specific functions of each.
3. Where is the element iron found in the body? With what physiological functions is it associated? About how much iron is needed daily?
4. The blood and lymph are highly buffered solutions capable of maintaining a relatively constant hydrogen-ion concentration.
   a. What is meant by the expression "buffered solutions"? Name three pairs of buffer substances found in these fluids.
   b. Mention two acids which normally enter the blood as metabolic end products. Indicate by means of equations the manner of reaction on the part of functioning buffers with each of these acids.
   c. Cite one source from which a base enters the blood. Indicate by the use of equations the resulting reactions with one functioning buffer.
   d. What is the reported normal *p*H range within the blood and lymph that is consistent with health?
   e. How does the removal of carbon dioxide at the lungs affect the hydrogen-ion concentration of the blood and lymph?
5. Follow the processes involved in the transportation of oxygen from the air sacs of the lungs to the actively functioning cells, indicating:

a. The conditions at the lungs that favor its entrance into the blood stream
b. The reactions involved in providing for its combination with hemoglobin
c. The conditions at the cells that favor the decomposition of oxyhemoglobin and the entrance of oxygen to the functioning cells

6. Follow the processes involved in the passage of carbon dioxide from the cells where it is made to its escape at the lungs, indicating:

a. The conditions at the cells favorable to the entrance of carbon dioxide into the blood
b. Nature's provisions for its transportation in the circulating fluids, indicating reactions concerned
c. Reactions at the lungs that result in the remaking of carbon dioxide and conditions there encountered which favor its escape to the air

7. What salts are commonly excreted by the kidneys? Which of these salts are mainly absorbed directly from the food mass? Which are made in the processes of metabolism?

8. What two mechanisms operate at the kidneys to maintain the normal concentration of buffer salts in the blood? As a result, what salts would you expect to be eliminated in larger than usual quantities (a) in acidosis, (b) in alkalosis?

9. Review the entire chapter and list conditions mentioned as functioning to maintain normal fluid and electrolyte concentrations within the blood.

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